Investigation of a Hydrometallurgical Process Route to Recover Metals from Waste Printed Circuit Boards

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ABSTRACT

The loss of valuable materials such as base and precious metals is increasing due to the increase in waste electronic and electric waste (WEEE). Most of these metals in WEEE are on the printed circuit boards (PCBs). This study aims to compare different pre-treatment methods to recycle copper from PCBs using a hydrometallurgical process. In order to obtain a uniform/consistent sample across all the tests done, similar custom-made PCBs with 55.45% wt copper were used to compare different parameters. Pre-treating the PCBs is the first stage of the process and it is done to liberate metals which are then dissolved in subsequent leaching stages. Eight different pre-treatment methods were explored. The pre-treated PCBs were then leached under similar conditions in a diagnostic leach test in order to get an indication of the effectiveness of the pre-treatment. Copper recoveries corresponding to each of the pre-treatment methods were compared. In addition to recovery, other factors such as time taken for copper recovery, material losses incurred, practicability, environmental impact, health and safety were used to compare the pre-treatment methods. A score was given for each factor and the average was used to choose the optimal pre-treatment method. A method where the PCBs were cut into 1.5 cm x 2 cm pieces and then soaked in 2 M NaOH at 40 °C for 24 hours had the highest average score. This pre-treatment method was then used to prepare PCBs that were used for test work done with the aim to optimise copper leaching. The influence of total ammonia concentration, liquid to solid ratio and choice of ammonium salt used in the buffer system, were investigated in the copper leaching optimisation stage of this thesis. Using ammonium carbonate resulted in lower recoveries compared to ammonium sulphate in the diagnostic leach test. Increasing the ammonia concentration to 7M did not have a significant effect on the copper recovery. Decreasing the liquid to solid ratio from 20ml/g to 10ml/g resulted in a slower rate of recovery. The optimal leaching conditions were found to be; 750 ml mixture of 4 M NH_3, 2 M $(NH_4)_2SO_4$, 100ppm $CuSO_4$ at 25 °C and 500 rpm using the optimal pre-treatment method for the PCBs.

COMPREHENSIVE SUMMARY

Due to technological advancement, there has been an accelerating growth of electric and electronic waste (WEEE). WEEE is being dumped in landfills or getting incinerated which in turn causes land and air pollution thereby damaging the environment. Furthermore, WEEE contains toxic substances such as lead and mercury which are a threat to human health. Therefore, there is need to reduce the amount of WEEE that is disposed. In 2018, an estimate of 49.8 million tonnes of e-waste was produced and this is expected to increase by 5% per annum. Besides the toxic substances, WEEE contains other valuable materials such as base and precious metals. PCBs make up 3% of WEEE and they contain the highest concentration of the metal compared to other parts of WEEE. PCBs contain around 30% copper. The aim of this study is to investigate the process of recovering the copper from PCBs. Recycling copper for secondary use aligns with the sustainability developments goals and it is crucial for the development of a circular economy.

The main objectives of this study are to characterise a particular custom-made PCB, compare different pre-treatment methods and optimise some leaching parameters. In order to know the structure of the PCB, the manufacturing process and blueprint were investigated. In addition to that, the PCB was analysed using QEMSCAN and 3D X-ray Computed Tomography Scans to know the metal distribution. Samples of the PCB were also leached in aqua regia and elemental analysis was done on the leachate. They contain 55.45% copper by mass and about 0.11% gold. The PCBs have 4 layers of metal which are mostly copper. There are two inner layers where about 69% of the copper sits and there is 29% copper on the outer layers and the remainder is electroplated on the walls of the holes that connect the layers (connectors). The copper on the outer layers is covered by thin layers of nickel, gold and an ink mask whilst the inner copper layers form a laminate with the Fibreglass resin (FR4).

Eight methods were tested to make the copper more accessible to the lixiviant. The eight methods are in the following table.

Number	Method
1	Cut into 5 cm x 5 cm pieces
2	Cut into 5 cm x 5 cm pieces + NaOH treatment
3	Cut into 5 cm x 5 cm pieces + NaOH Treatment & Drilled
4	Cut into 2 cm x 1.5 cm pieces + NaOH treatment
5	Shredded
6	Shredded then Pulverised
7	Cut into 5 cm x 5 cm pieces + Burnt in an Open Flame
8	Cut into 5 cm x 5 cm pieces + Burnt in a Furnace

The NaOH treatment involves soaking PCBs in 2 M NaOH at 40 °C for 24 hours to remove the top ink mask. The methods were compared by leaching the PCBs in the same conditions and comparing recovery and other factors associated with the method. The diagnostic leach test conditions are in the following table.

Parameter	Condition
25% Ammonia Solution (Merk) Concentration	4 M
Ammonium Sulphate (Merk) Concentration	2 M
Copper Sulphate (Merk) Concentration	~100 ppm
Temperature	25 °C
pH	8 - 11
Agitation	500 rpm
Volume	1000 ml
Liquid: Solid Ratio	1000 ml per PCB (~50g)
Time	120 hrs+

Below is a table that shows the copper recovery achieved for each method.

Method	1	2	3	4	5	6	7	8
Recovery of Cu (%)	11.43	23.23	26.29	49.34	36.86	25.36	44.44	69.22

The highest recovery was achieved using the PCBs that were cut into 5 cm x 5 cm pieces and burnt in a furnace. In addition to recovery, the factors that were also compared were material losses associated with the pre-treatment method, time taken for maximum recovery, practicability, environmental impact, health and safety. Scores were given based on the results for each category and the method with the best average score was reported as the optimal method. The method with the highest average is method 2 where the PCBs were cut into 2 cm x 1.5 cm pieces and treated in NaOH. This method was then used to test a number of leaching parameters.

Firstly, leaching was done with a different ammonium salt thus ammonium carbonate instead of ammonium sulphate. The conditions for the ammonium carbonate system were also changed. The parameters that were varied are the ammonia concentration and the liquid to solid ratio (LTSR). The concentrations used were 4 M, 5.5 M and 7 M. For the liquid to solid ratio, instead of using 1000 ml for every PCB (50g), 750 ml and 500 ml were also tried.

The results show that increasing the concentration does not have a pronounced effect on the recovery, but it generally decreases the recovery of the copper slightly by less than 3%. Furthermore, decreasing the liquid volume did not have a significant effect on the recovery but it did have an effect on the time it takes for maximum recovery. The system with the 500ml was the slowest and had a little less copper dissolved in solution.

Most of the copper that was leached out was the copper on the outer layers, but the inner copper layers remained inaccessible to the solvent. The inner copper layers have a strong bond with the FR4 which forms a protective layer against the lixiviant. A pre-treatment method that delaminates the PCBs, that has low energy consumption and has minimal emission of toxic gases ought to be developed. The PCBs used in this study were unpopulated and there is need to explore metal recovery from populated printed circuit boards.

GLOSSARY

Term	Definition
Base Metals	Metals such as aluminium, copper, lead, nickel, tin, titanium and zinc
Bio-Leaching	The use of micro-organisms to extract metals from a solid
Chemical Leaching	The use of chemicals to extract metals from a solid
EEE	Electric and Electronic Equipment
E-waste	Electronic Waste
FR4	NEMA grade designation for glass-reinforced epoxy laminate material
Gerber	Software used to design printed circuit boards
Incineration	Combustion of Organic Material
Leaching	Extraction of substances from a solid by dissolving in liquid
Lixiviant	Chemical used to leach metals from an ore/host material such as PCBs
PCB	Printed Circuit Board
PCBs	Printed Circuit Boards
Photoresist	Silver halide sheets that are used to print designs on copper to make PCBs
Populated PCB	PCB with components soldered onto the surface
Precious Metals	Rare metals such as gold, silver and other platinum group metals (PGMs)
Precipitation	The formation of a solid from a solution
Pyrometallurgy	Extraction and Purification of metals using furnaces
Unpopulated PCB	PCB without solders
WEEE	Waste Electrical and Electronic Equipment
XCT	X-ray Computed Tomography

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1. INTRODUCTION

Background

Electronic and electric equipment is any equipment that is dependent on either electric current or an electromagnetic field to work. These include television sets, mobile phones and computers to mention a few. When they reach their end of life, they hardly have any secondary uses and usually end up in landfills or get incinerated (Tuncuk et al, 2012). A total of 41.8 million tonnes of waste electronic and electric equipment (WEEE) was reported for the year 2014. A third of that came from the US and China alone. It is estimated that in 2018, about 49.8 million tonnes of WEEE will be produced worldwide (Cui & Anderson, 2016). This is expected to increase by 3-5% per annum (Drechse, 2006). The rapid increase is due to economic growth, technological innovation and market expansion (Tuncuk et al, 2012). According to Xu et al (2016) the increase in electronic waste volumes poses an ecological threat and there is need to mitigate that.

Most WEEE contains chemicals like mercury, cadmium, chromium, and ozone-depleting chlorofluorocarbons that are hazardous to the environment and people's health. However, WEEE also contains large quantities of valuable metals such as gold, platinum, silver and copper which may total to a value of US$52 billion (Xu et al, 2016). It can be used as a secondary source of base and precious metals due to its high metal content (Tuncuk et al, 2012). Recycling WEEE will consequentially reduce the quantities of waste thereby alleviating the health and environmental challenges such as pollution that are associated with dumping or incinerating. Recycling processes may also cause environmental impacts and act as a source of human health hazards, but this mostly happens during semi-formal WEEE recycling operations in developing countries.

WEEE has many components that contain organic and inorganic material and these vary depending on the manufacturer, type and age of equipment (Tuncuk et al, 2012). Of particular interest are Printed Circuit Boards (PCBs) which make up about 3 wt % of the WEEE (Robinson 2009; Cui & Anderson 2016). This is because they are the richest in base and precious metals (Cui & Anderson, 2016). PCBs are typically composed of 63 wt. % metals, 24 wt. % ceramics and 13 wt. % polymers (Batnasan et al, 2018).

Of the metals in a PCB, copper contributes an average of 30 wt. % of the board (Jadhav & Hocheng 2015; Bari et al 2009). In comparison with mineral ores, the average copper ore grade for China is 0.8% wt. % (Xu et al 2016). This shows that the PCBs are a richer source of copper than the traditional mineral ores (Cui & Anderson 2016). Additionally, the grade of the traditional ores is declining, it is reported that only 30 years' worth of extractable copper is left (Konishi et al 2014). Copper is the most abundant metal in the PCBs due to its use as the main electrical conductor which makes its recovery attractive.

There are various methods that can be used to extract copper from PCBs. The general steps taken in the copper recovery process from PCBs normally start with a pre-treatment method. The investigation of pre-treatment methods is very limited in literature as most studies focus on leaching the metal using finely ground PCBs. The pre-treatment methods are often not discussed in detail. However, the way a PCB is pre-treated has a huge effect on the recovery and therefore it is worth investigating the best method.

The pre-treatment method is then followed by either a pyrometallurgical or a hydrometallurgical process. Besides not being eco-friendly, most of these methods are energy intensive. Moreover, most of the current technologies are capital intensive due to the sophisticated infrastructure required. There is need to develop a process that is economically viable, that has less energy requirements and that is environmentally friendly.

Scope and Limitations of Study

The recycling of copper from PCBs is the hinge of this study. The investigation largely involves a comparison of eight pre-treatment methods. The comparison is based on recovery, environmental impact, safety, and practicality on a large scale. The only factor that is quantitatively studied is recovery. This will be done by exposing PCBs that are pre-treated differently to the same diagnostic leaching system to test the effectiveness of each pre-treatment method. All the other factors listed above are explored and evaluated qualitatively and semi-quantitively by using simple equations to score each method.

To avoid variability, the PCBs used in this study are a generic design supplied by a commercial manufacturer; Trax Interconnect (Pty) Ltd. The PCBs are 4 layered and are unpopulated i.e. they have no solders or any attached electronic components on them.

The recovery of metals from the leach solutions is not covered in the study but will only be discussed briefly.

Relation to Sustainability Development Goals

This research aims to fulfil some of the aspects of the sustainability developments goals (SDGs). The specific aspects that are met in this study are highlighted in italics (UN 2018)

1) Sustainability Development Goal 9: Industry, Innovation and Infrastructure:

- By 2030, upgrade infrastructure and retrofit industries to make them sustainable, with *increased resource-use efficiency* and greater *adoption of clean and environmentally sound technologies and industrial processes,* with all countries taking action in accordance with their respective capabilities

- *Enhance scientific research, upgrade the technological capabilities of industrial sectors* in all countries, in particular, developing countries, including, by 2030, encouraging innovation and substantially increasing the number of research and development workers per 1 million people and public and private research and development spending

2) Sustainability Development Goal 11: Sustainable Cities and Communities:

- By 2020, substantially increase the number of cities and human settlements adopting and implementing integrated policies and plans towards inclusion, *resource efficiency*,

mitigation and adaptation to climate change, resilience to disasters, and develop and implement, in line with the Sendai Framework for Disaster Risk Reduction 2015-2030, holistic disaster risk management at all levels.

3) Sustainability Development Goal 12: Responsible Consumption:

- *By 2030, ensure that all learners acquire the knowledge and skills needed to promote sustainable development, including, among others, through education for sustainable development and sustainable lifestyles,* human rights, gender equality, promotion of a culture of peace and non-violence, global citizenship and appreciation of cultural diversity and of culture's contribution to sustainable development.

Objectives

The objectives of this study are as follows:

1. Characterise the custom-made PCBs and measure the composition of the board.
2. Compare different pre-treatment methods and choose the most suitable.
3. Use the most suitable pre-treatment method to optimize the copper leaching process.

Key Questions

1. What is the composition of the PCBs?
2. What is the best way to pre-treat the PCBs?
3. What is the optimal process for leaching copper?

Research Approach

Literature will be explored for various methods of copper extraction from PCBs. This will give a guideline on the development of an optimal extraction process. The focus will be on how the PCBs are prepared for the leaching process which is normally referred to as pre-treatment. This pre-treatment stage is done to:

- Remove potentially toxic components
- Reduce size of PCBs to make the material more leachable
- Unlock the inner layers of the PCBs

Different pre-treatment methods will be compared against each other using a diagnostic leach test. The best pre-treatment method will then be used to optimise the leaching process.

Plan of Development

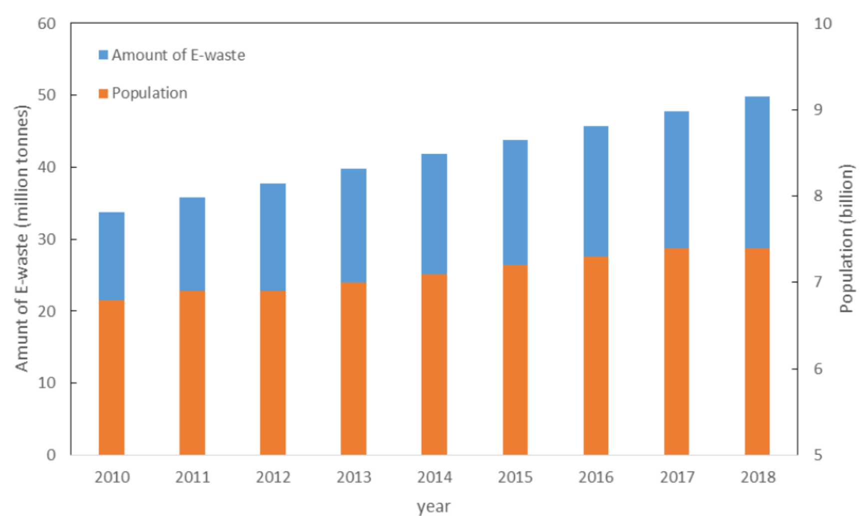
The background of the study has been spelled out and the main objectives have been highlighted. Following this is the literature review on copper recovery methods that have already been tested and these will be compared to each other. Thereafter, the methodology used to carry out the study will be explained. The methodology is written in three segments which correspond to each of the three objectives of the study. The procedure followed to meet the first objective is addressed first and then the second and third objectives follow respectively. The results will then be reported afterwards and then discussed. The report ends with the conclusions and recommendations from the investigation done.

2. LITERATURE REVIEW

Why Recycle Waste Printed Circuit Boards?

Technology has been advancing at a fast rate and this has led to shorter life spans for electric and electronic equipment (EEE) (Jadhav & Hocheng 2015; Cui & Anderson 2016). A good example is CPUs (central processing units) whose life-span decreased from 4 – 6 years to only 2 years from 1997 to 2005 (Deveci et al 2010). Some of the outdated EEE gets resold or refurbished but that is not the fate of the majority (Cui & Zhang, 2008). As aforementioned in the first chapter, there has been an increase of WEEE which ends up in landfills or is incinerated. Figure 2.1 is a graph that shows the amount of e-waste that is estimated to have been produced since 2010 and it has been projected up to the year 2018 (Cui & Anderson, 2016). The graph shows a steady increase in the amount of e-waste in a space of 9 years. As it appears in the graph, the growth in e-waste correlates with the population growth.

Figure 2.1 :E-waste Growth over the years (Cui & Anderson, 2016)



It is reported that in 2018, about 49.8 million tonnes of WEEE will be produced worldwide (Cui & Anderson, 2016). This is expected to increase by 3-5% per annum (Drechse, 2006) which could potentially result in detrimental effects on people's health and the environment. This is because most of the WEEE contains toxic substances such as flame retardants, plastic additives, heavy metals and chlorofluorocarbons (CFCs) (Cui & Anderson, 2016). It causes land pollution if WEEE is left to accumulate on landfills. Moreover, toxic substances may end up in water and air thereby causing water and air pollution. Recycling WEEE will result in the reduction of waste, thereby mitigating its problematic effects such as land, water and air pollution (Tuncuk et al, 2012). It should be noted that the reduction of pollution is heavily dependent on the technology used. Semi-formal recycling processes in most developing countries still have toxic waste streams. However, there are operations like Umicore in Belgium which still manage to recycle WEEE without polluting land, water or air.

Recycling WEEE provides a secondary source of metals which are estimated to be worth US$52 billion (Xu et al, 2016). Table 2.1 shows the various metals in e-waste and their corresponding London Metal Exchange (LME) price as of July 19th, 2010 (Deveci et al, 2010) and their more recent prices as of October 12th, 2018.

Table 2.1 : LME prices for July 19th, 2010 (Deveci et al, 2010) and October 12th, 2018(LME, 2018)

Metal	Fe	Cu	Al	Pb	Ni	Au	Ag	Pd
\$/ton[1] 2010	415	6,650	2,009	1,789	19,220	4.2 x 10^7	5.27 x 10^5	1.58 x 10^7
\$/ton[2] 2018	326	6,325	2,045	2,037	12,710	3.9 x 10^7	5 x 10^5	3.5 x 10^7
\$/ton[3] Diff	-89	-300	+36	+248	-6510	-0.3x 10^7	-1.27×10^5	+1.92 x 10^7

[1]Metal prices from London Metal Exchange Office (LME) official prices for cash seller and settlement (July 19th, 2010), (Deveci et al, 2010).

[2]Metal prices from London Metal Exchange Office (LME) official prices for cash seller and settlement (October 12th, 2018).

[3] Difference between the July 19th, 2010 prices and the October 12th, 2018 metal prices from London Metal Exchange Office (LME) official prices for cash seller and settlement.

The prices changed but the table shows just how much each metal in e-waste holds some value. The table above shows the price differences since 2010 with some metals having increased in value.

The focus of this study is on recycling PCBs which make up about 3 wt% of the WEEE (Robinson, 2009; Cui & Anderson, 2016). This is because they contain most of the desired base and precious metals (Cui & Anderson, 2016). There are various technologies that have been developed to recycle PCBs. The challenge is that there is a mix of various metals and non-metals in the PCBs and that the combination makes recycling very difficult (Tuncuk et al, 2012). There is need to understand the typical PCB composition and structure before delving into extraction methods.

Characterisation of the Printed Circuit Boards.

Structure of Printed circuit boards

There are three types of PCBs, single-sided, double-sided and multi-layered. They are made using both electric conductors and non-conductors. The conductive material is usually copper, and the non-conductive part is usually made of fibre-glass (dielectric). The single-sided boards only have one layer of conductive material and the rest is a non-conductive substrate. A double-sided PCB has two layers of conductive material usually on either side of the non-conductive layer. The multi-layered PCBs have alternating layers of conductive and non-conductive material. To connect the conductive layers, an electrical conductor such as copper is coated in the holes that are drilled through the layers of the PCBs. It is for this reason that most PCBs are highly rich in copper which averages 30 wt. % of the board (Bari et al, 2009; Cui & Anderson, 2016; Jadhav & Hocheng, 2015). To prevent the oxidation of the copper layers, a solder mask (epoxy) is applied to coat the exposed top and bottom layers (Jadhav & Hocheng, 2015). As technology is advancing, EEE is getting more complex and therefore the multi-layered PCBs are becoming more common.

Composition of Printed Circuit Boards

The composition of Printed Circuit Boards (PCBs) varies with the manufacturer, the type of board, the purpose of the board and the age of the PCB, (Tuncuk et al, 2012; Zhang et al, 2012).

Figure 2.2: Composition of various PCBs, Example1

Cu/%	23.73	23.47	20	20	26.8	10	15.6	22	17.85
Al/%	4.7	1.33	5	2	1.9	7	—	—	4.78
Pb/%	4.48	0.99	1.5	2	—	1.2	1.35	1.55	4.19
Zn/%	0.75	1.51	—	1	1.5	1.6	0.16	—	2.17
Ni/%	3.32	2.35	1	2	0.47	0.85	0.28	0.32	1.63
Fe/%	7.47	1.22	7	8	5.3	12	1.4	3.6	2.0
Sn/%	3.65	1.54	—	4	1.0	—	3.24	2.6	5.28
Sb/%	1.82	—	—	0.4	0.06	—	—	—	—
Au/ppm	800	570	250	1000	80	280	420	350	350
Pt/ppm	—	30	—	—	—	—	—	—	4.6
Ag/ppm	800	3301	1000	2000	3300	110	1240	—	1300
Pd/ppm	210	294	110	50	—	—	10	—	250
Total/%	~50	~33	~35	~40	~40	~21	~22	~30	~38

The Figure 2.2 above shows the composition of typical printed circuit boards. These board samples were taken from a blended sample of scrap PCBs. The samples are usually populated.

The tables was adapted from: (Hageluken, 2006; Hao et al, 2008; Iji & Yokoyama, 1997; Kim et al, 2004; Ogunniyi & Vermaak, 2007; Ogunniyi & Vermaak, 2009a; Ogunniyi & Vermaak, 2009b; Shuey et al, 2006; Sum, 1991; Yu et al, 2011; Zhang & Forssberg, 1997a; Zhang & Forssberg, 1997b; Zhang et al, 2012; Zhao et al, 2004)

The metals in total contribute to an average of about 34% of the full board. Of that, about 58% of the total metals is copper. Copper is the most abundant and it contributes an average of around 20% of the whole PCB.

Table 2.2 shows the weight percentage of different metals in various PCBs (Cui & Anderson 2016).

The PCBs were adapted from the following sources:

PCB1, (Birloaga et al, 2013), PCB 2, (Yang et al, 2009), PCB 3, (Oishi et al, 2007) and PCB 4, (Behnamfard et al, 2013).

Table 2.2: Composition of various PCBs, Example 2

Metal	**PCB 1**	**PCB 2**	**PCB 3**	**PCB 4**
Cu (wt %)	30.57	25.06	26	19.19
Al (wt %)	11.69	4.65	3.2	4.01
Fe (wt %)	15.21	0.66	3.4	1.13
Sn (wt %)	7.36	1.86	4.9	0.69
Ni (wt %)	1.58	0.0024	1.5	0.17
Zn (wt %)	1.86	0.04	2.6	0.84
Pb (wt %)	6.70	0.8	3.0	0.39
Mn (wt %)	-	-	0.11	0.04
Sb (wt %)	-	-	0.16	0.37
Au (ppm)	238	-	-	130
Ag (ppm)	688	-	-	704

The table displays that copper is always present and is the most abundant metal in PCBs. Although precious metals like gold and silver are of more value than copper, they are often absent in some boards and present only in very small amounts in others. Another example exhibiting the metal composition of a typical PCB is in table 2.3 (Jadhav & Hocheng, 2015).

Table 2.3: Composition of typical PCB, Example 3

Metal	Metal content (mg/g)	Corresponding % out of total metal in PCB
Cu	117 (±0.28)	65.31 (±0.16)
Zn	28.97 (±0.81)	16.13 (±0.45)
Sn	12.62 (±0.27)	7.02 (±0.15)
Ni	10.41 (±0.45)	5.79 (±0.25)
Pb	9.34 (±0.49)	5.19 (±0.27)
Fe	0.62 (±0.006)	0.34(±0.003)
Al	0.325 (±0.004)	0.18 (±0.002)
Ag	0.02 (±0.002)	0.01(±0.001)
Pd	0.012 (±0.0008)	0.006 (±0.004)
Au	0.0075 (±0.0004)	0.004 (±0.002)

As shown in the table above, copper contributes to more than 65% of the metals in the PCB. This shows that copper makes the bulk of the metallic part of the board. Another example of a PCB that is rich in copper is reported by Bari et al. (2009) and that is shown in table 2.4.

Table 2.4: Composition of a typical PCB, Example 4 (Bari et al, 2009)

Metal	Mg/mg	Corresponding %
Cu	227.4	85.39
Ni	4.1	1.54
Zn	20.3	7.62
Fe	11.2	4.21
Pb	1.8	0.68
Al	0.6	0.23
Sn	<0.1	<0.04
Mg	<0.1	<0.04
Mn	0.2	0.07
Ag	<0.1	<0.04
Co	<0.1	<0.04
Cd	<0.1	<0.04
As	<0.1	<0.04
Sb	<0.1	<0.04

The table above shows that more than 85% of the metals in the particular PCBs is copper. The fact that most of the metallic components of the PCB are made of copper makes its recovery very attractive. It is to be noted that average copper ore grade for China is 0.8% wt. % (Xu et al, 2016). This means that most PCBs are more than 25 times richer in copper than the traditional mineral ores. If copper can be recycled with less or no emissions it will diminish the carbon footprint of copper which is around 4 kg of CO_2 per kilogram of copper (Hayes, 1993). Furthermore, there is only 30 years' worth of mineable copper and it would be beneficial to recycle the copper that is disposed as waste (Konishi et al, 2014).

Options for Recovery Steps

Various methods and technologies have been applied for the recovery of metals from WEEE. These include physical methods, pyrometallurgy, hydrometallurgy, bio-technology, microwave treatment and supercritical fluid technology to mention a few (Zhang et al, 2012). The figure below illustrates that there are different stages and options available for the metal recovery process from PCBs (Cui & Anderson, 2016).

Figure 2.3: Flow Diagram for Metal Recovery from PCBs (Cui & Anderson, 2016)

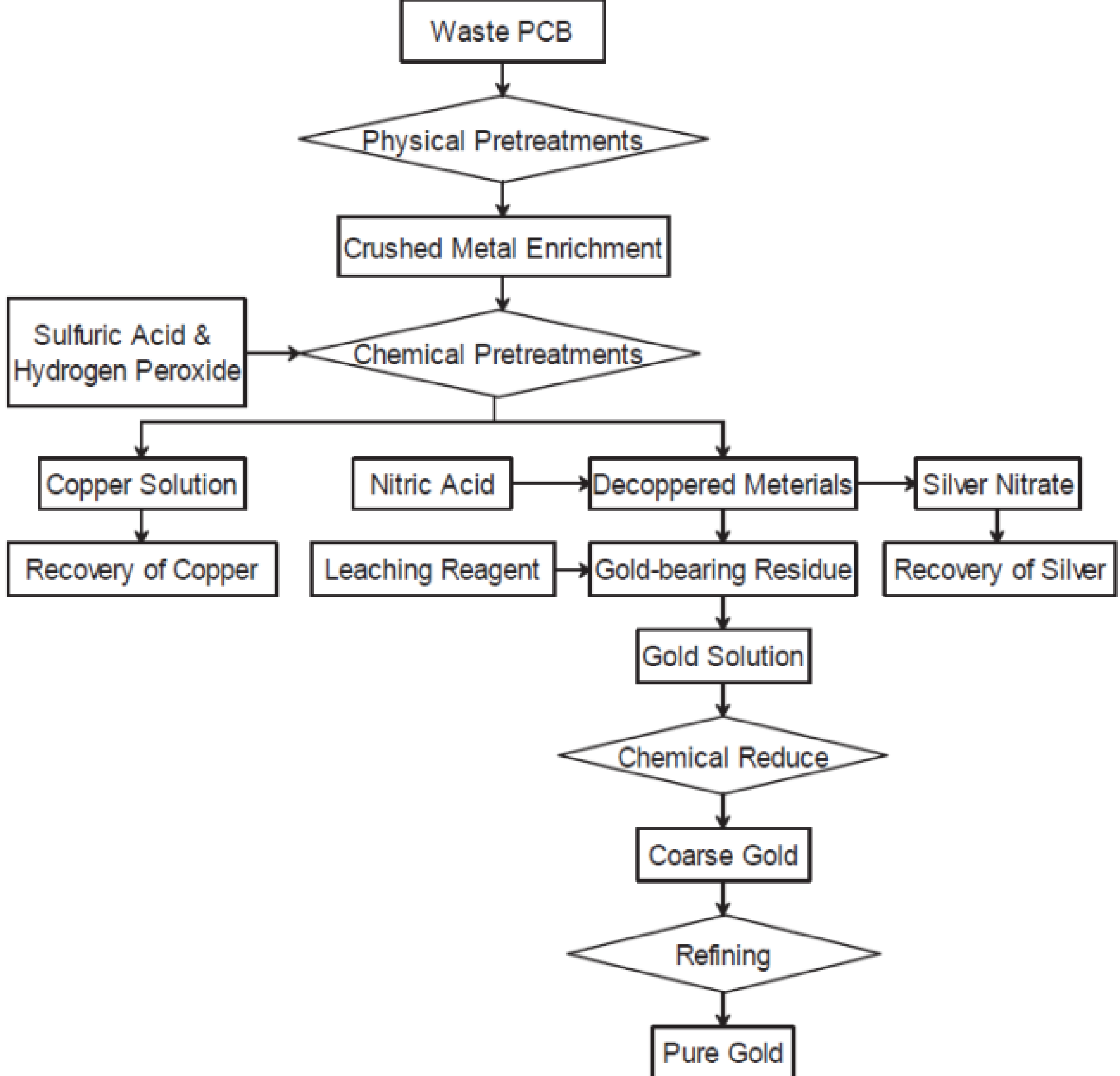
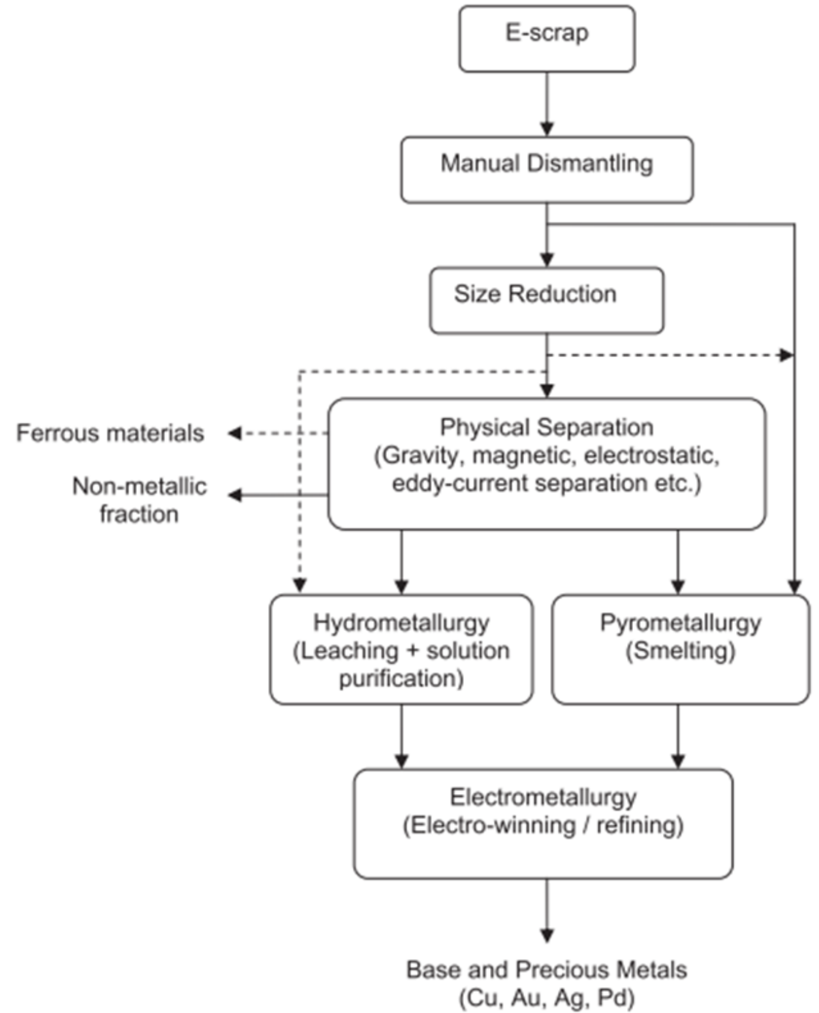


Figure 2.3 demonstrates that there is always a physical pre-treatment stage prior to metal recovery. This is followed by metal enrichment then chemical pre-treatment. A more generic process for recovering metals from e-waste is illustrated in the following figure, (Tuncuk et al, 2012).

Figure 2.4: Process for Metal Recovery from e-waste (Tuncuk et al, 2012)



In the diagram in Figure 2.4 , the pre-treatment stage includes manual dismantling, size reduction and physical separations. Pre-treatment is intended to be the stage where there is a concentration of the desired metal by either separating metals from non-metals or magnetic material from non-magnetic material. Moreover, hazardous components can also be removed at the dismantling stage (Tuncuk et al, 2012). Pre-treatment is then followed by either pyrometallurgy or hydrometallurgy and ends with a refining stage which is usually done by electro-winning. There is need to compare the different available methods at each stage to come up with the best method.

The Pre-treatment Stage

The necessity of a pre-treatment method.

Printed circuit boards have a myriad of materials in them and this poses a challenge when it comes to recycling. The metal fractions of the PCBs are very diverse and are often embedded in the non-metal fractions which include plastics, glass fibre, or ceramics (Cui & Anderson, 2016). Pre-treatment is hence a requisite stage as it liberates the desired metals from other parts of the board. Due to pre-treatment, the subsequent recovery processes become more efficient.

The pre-treatment of WEEE or PCBs is not only limited to physical processes but can be any method that results in the accessibility of the desired metal. This aids the lixiviants to better reach the metal of interest. There are various ways that PCBs can be pre-treated prior to metal recovery.

Different types of Pre-treatments available

Most of the research done is not explicit about the pre-treatment stage and instead focuses more on the subsequent stages of leaching and metal recovery. Some of the methods mentioned in literature have not yet been tested in much depth.

Literature mainly discusses two types of pre-treatment methods which are physical and chemical (Zhang et al, 2012). Physical methods involve breaking or crushing PCBs whereas chemical methods make use of chemicals to dissolve some parts of the PCBs and leave the rest of the board intact.

Physical methods are separation methods that exploit the different physical properties of the components of the PCBs such as specific gravity separation, eddy current separation, magnetic separation and electrostatic separation. When particles of the PCBs are too fine, gravity separation, magnetic separation and electrostatic separation are not as effective because the physical qualities of the particles become too similar. Flotation has been tried on fine particles and it resulted in concentrated metals. The problem with flotation was that a lot of Cu, Ni, Pb and Sb were found in the froth, which contributed to severe consequences of disposal and loss of metals (Cui & Anderson, 2016; Mäkinen et al, 2015).

There are reports on using supercritical water but however this requires extreme operating conditions like 374 °C and 218 atm and costly equipment to operate at these conditions (Cui & Anderson, 2016). Lee et al. (2010) researched using pre-treatment methods such as roasting and managed to get complete recovery of the desired metal. Another type of pre-treatment method studied is the pyrolysis of PCBs which increased metal dissolution (Madenoglu, 2005; Sheng & Etsell, 2007). Roasting and pyrolysis can be energy intensive due to the need for high temperature which can be up to 850 °C for roasting (Lee et al, 2010) and up to 900 °C for pyrolysis (Havlik et al, 2010). Although with roasting the PCBs can act as the fuel unlike in pyrolysis, both methods may also require sophisticated machinery which will incur high capital and operational costs. In addition, there are weight losses between 5 – 35% after the use of thermal pre-treatment methods such as pyrolysis (Havlik et al, 2010).

One pre-treatment method that is often done involves the size reduction/crushing of PCBs into powder (pulverisation) (Castro & Martins, 2009; Jadhav & Hocheng, 2015; Lee et al, 2010; Oh et al, 2003; Tuncuk et al, 2012; Yoo et al, 2009; Zhang et al, 2012). Fine particles are, however, not suitable for some recovery technologies such as bioleaching. If PCB powder is used, there is a risk of passivation, which inherently inhibits the microorganisms (Adhapure et al, 2014; Jadhav & Hocheng, 2015).

It is suggested that pulverising PCBs is ideal for hydrometallurgical metal recovery (Tuncuk et al, 2012). It is reported that the combination of mechanical crushing and hydrometallurgy is the most competitive technology for recycling waste PCBs (Zhang et al, 2012). However, Tuncuk et al (2012) also highlights the high metal losses associated with such aggressive physical methods.

The losses are said to be caused by the production of fines which get lost as airborne dust. Furthermore, due to the intimate association of metals with non-metals it can result in the insufficient liberation of metals. The material losses can be up to 35 wt% (Deveci et al, 2010; Tuncuk et al, 2012). This could translate to losing almost 35% of the value that the PCBs hold. Losing such a large amount of material before a recovery step is not economically sound. The production of dust also poses health hazards to the workers. In industry there would be a need to install infrastructure that collects the dust such as extractors with dust cyclones to reduce the loss of material. However, these will add to the capital and operational costs of the process. Moreover, crushing the PCBs into powder entails the use of a lot of energy. This may require heavy machinery and hence high capital and operational costs (Cui & Anderson, 2016; Cui & Zhang, 2008).

There is no mention of any losses due to size reduction in some literature. In the study done by Castro & Martins (2009), PCBs were crushed using a ball mill for 8 minutes until 90% of the particles were finer than 0.208mm particle size. However, no losses were reported. This may be because it is a closed laboratory mill. Similarly, Deveci et al (2010) also reduced the PCB until the d80 was 100 µm using a tema mill but did not mention any losses. Oh et al. (2003) also did no report on any losses due to crushing PCBs to pieces smaller than 1mm.

Adhapure et al. (2014) and Jadhav & Hocheng (2015) brought forward the idea of leaching composite boards without pulverising them. Using large pieces of PCBs has not been explored much thus there is very little known, but it potentially has several advantages. Firstly, it has low energy requirements since there is no crushing required. It also makes it easier to recycle the non-metal part as it will still be intact and can be used as building material (Cui & Anderson, 2016). The chances of contamination when recovering metals from leach liquors also reduces (Jadhav & Hocheng, 2015).

The challenge with using whole large pieces in the recovery process is that the boards have a protective coat made of epoxy. This layer contains the bromine base flame retardants. Its key purpose is to protect the metals on the board and hinder any substances from reaching them. It is for that reason that Jadhav & Hocheng (2015) applied the same technology as Adhapure et al. (2014) which is the use of sodium hydroxide to remove the chemical coating (epoxy) on printed circuit boards. In Jadhav & Hocheng's (2015) study10M NaOH was used for 24hrs under static conditions and room temperature and the epoxy got completely removed exposing the metal that was underneath it. It also resulted in the significant dissolution of Aluminium, (911 (±0.85) µg/g). However, very minute amounts of other metals were dissolved. Table 2.5 details the extent of dissolution for most of the metals that were on the PCBs.

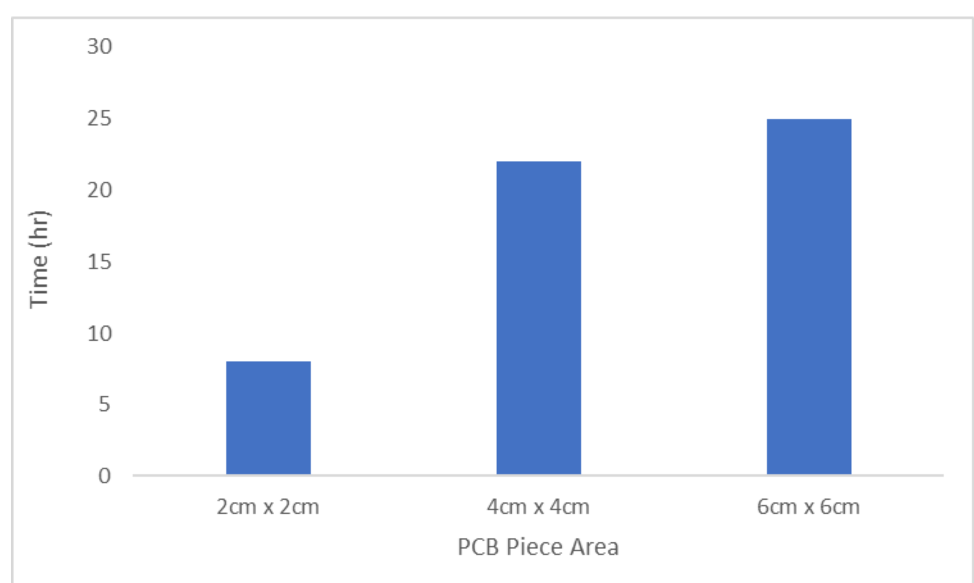
Table 2.5: Extend of dissolution for metals in NaOH (Jadhav & Hocheng, 2015)

Metal	**Initial (mg/g)**	**Dissolved (µg/g)**	**% Dissolved**
Zn	28.97 (±0.81)	27 (±0.10)	0.093
Sn	12.62 (±0.27)	21 (±0.04)	0.166
Fe	0.62 (±0.006)	10 (±0.370)	1.612
Pb	9.34 (±0.49)	4 (±0.02)	0.043
Cu	117 (±0.28)	0.43 (±0.001)	0.0004
Ni	10.41 (±0.45)	0.11 (±0.003)	0.001

Except for iron which had 1.6% dissolution, all the metals had a dissolution of less than 1%. It was also reported that Ag, Pd and Au did not dissolve at all. That is beneficial because the NaOH is very selective to aluminium and epoxy and leaves the rest of the board intact making it easier to recycle the non-metal parts after leaching.

When it comes to leaching large PCBs, the question rises on just how large the pieces should be. Jadhav & Hocheng (2015) studied the effect of PCB size and this was done based on the time it will take different board sizes to reach complete recovery when subjected to similar conditions. Figure 2.5 is the graph that unveils their findings.

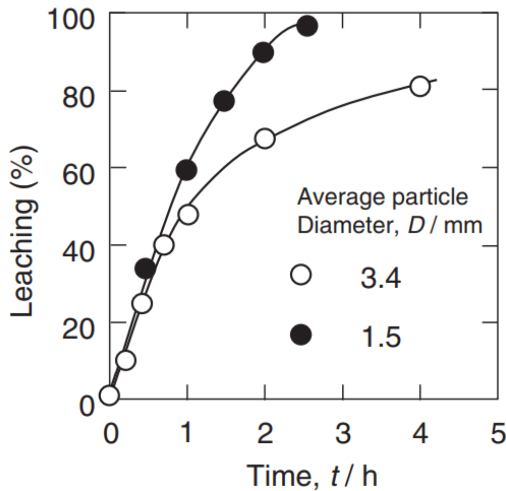
Figure 2.5: Effect of PCB size on Leaching, Example 1 (Jadhav & Hocheng, 2015)



It is clear that the rate of recovery increases with decreasing board size; thus, it takes less time to reach complete recovery with smaller board pieces. There is not much difference between the 4 cm x 4 cm pieces (requires 22 hrs) and the 6 cm x 6 cm pieces (requires 25 hrs); the difference is only 3 hours. There is a significant difference, however, when the size is reduced to 2 cm x 2 cm pieces which took only 8 hours. This trend suggests that the smaller the PCB pieces, the faster the recovery process. This might be as a result of the exposure of a larger surface area when PCBs are reduced in size which ultimately makes metals more accessible. It may be the reason why most researchers prefer using pulverised PCBs despite their associated drawbacks.

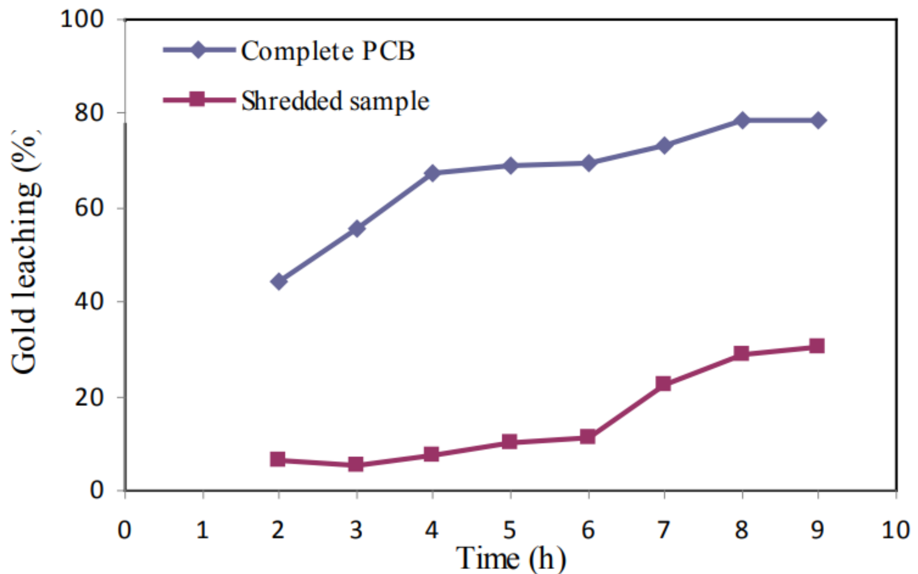
Figure 2.6 shows the comparison of different particle sizes that were leached in the same conditions (Koyama et al, 2006).

Figure 2.6: Effect of PCB size on Leaching, Example 2 (Koyama et al, 2006)



In the graph in Figure 2.6 , the smaller particles (1.5 mm) leached faster than the larger particles (3.4 mm). This supports the conclusion reached by Jadhav & Hocheng (2015). However, a comparison between pulverised and whole PCBs was done by Tripathi et al. (2012). Figure 2.7 is the graph that shows the comparison.

Figure 2.7: Gold Leaching; Shredded vs Complete PCB (Tripathi et al, 2012)



The recovery of gold from the complete PCB is significantly higher than that of the shredded sample. The size of the complete boards was not specified but they were taken as they were from mobile phones. Only 56.7% gold recovery was achieved with fine particles whereas 78.8% gold recovery was achieved with composite boards. The low recovery for fine PCB particles may have been due to material loss during size reduction. This seems to counter what Jadhav & Hocheng (2015) and Koyama et al. (2006) found concerning the relationship between the size of the board and leaching rate and recovery.

Jadhav & Hocheng's (2015) study mostly applies to single or double-sided boards where the only barrier to the copper layers is epoxy. There is a challenge when it comes to multi-layered boards since the copper in the inner layers remains inaccessible even after removing the surface

coating. It is not only covered with the coating (epoxy) but also covered by the non-metal substrate. The NaOH does not seem to affect the substrate and it is therefore unlikely that the copper between two substrate layers will be exposed.

There is need to develop a sustainable pre-treatment method that is applicable to many types of PCBs. Besides metal leaching, there are other factors that need to be taken into account when choosing the most suitable pre-treatment method. The ideal PCB pre-treatment method will be one that is quick, liberates all the metals, leaves the non-metallic parts intact, not energy intensive, has no loss of material, economically viable, practical and environmentally friendly. The optimal pre-treatment method is one that has the best trade-off and compromise between these aspects.

Metal Recovery Methods

Pre-treatment methods such as physical separation do not sufficiently liberate metals and therefore there is need for pyrometallurgical or hydrometallurgical processes to further recover metals (Tuncuk et al, 2012). Cui & Anderson (2016) mention that pre-treatment and pyrometallurgy are the main technologies applied industrially so there is need for comparison, including other possible methods. Table 2.6 summarises the advantages and disadvantages of different processes from various Literature (Cui & Anderson, 2016; Cui & Zhang, 2008; Jadhav & Hocheng, 2015; Tuncuk et al, 2012; Zhang et al, 2012)

Table 2.6: Comparison of different metal recovery technologies

Methods	Advantages	Disadvantages
• Hydrometallurgy & Bioleaching	• Methods are available to clean the effluent streams • High selectivity possible (Cui & Anderson, 2016) • Relatively low capital cost (Jadhav & Hocheng, 2015; Tuncuk et al, 2012) • Reduced environmental impact on land (by reducing WEEE on landfills) (Tuncuk et al, 2012) • High metal recoveries (Jadhav & Hocheng, 2015; Tuncuk et al, 2012) • Suitable for small scale applications (Jadhav & Hocheng, 2015; Tuncuk et al, 2012) • Suitable for low grade feed (Jadhav & Hocheng, 2015; Tuncuk et al, 2012) • Flexible for upscaling (Jadhav &	**Hydrometallurgy:** • large amounts of toxic, highly acidic or alkaline or flammable reagents with the generation of voluminous solid wastes and effluents **Bioleaching:** • hard to cultivate • Long leaching cycles limiting large-scale application (Adhapure et al, 2014; Tuncuk et al, 2012) • Low Pulp density of less than 20% (Jadhav & Hocheng, 2015; Tuncuk et al, 2012) • Metal Toxicity can inhibit microorganisms (Jadhav &

	Hocheng, 2015) • Easily controllable (Jadhav & Hocheng, 2015)	Hocheng, 2015; Tuncuk et al, 2012) • Leaching agent consumption (Jadhav & Hocheng, 2015)
Pyrometallurgy	• High Purity Product • High reaction rate (Konishi et al, 2014)	• Energy intensive due to high temperatures (Jadhav & Hocheng, 2015) • High capital and operating cost (Jadhav & Hocheng, 2015) • Require high grade feed (Jadhav & Hocheng, 2015) • Halogenated flame retardants used in PCBs lead to the formation of dioxins and furans, volatile metals and dust (Jadhav & Hocheng, 2015)
Physical Methods	• Some have low capital and operating costs (Tuncuk et al, 2012)	• 10-35% valuable metal loses (Tuncuk et al, 2012) • Pollution due to dust (Tuncuk et al, 2012) • Insufficiently liberate metals, (Tuncuk et al, 2012)
Other • supercritical fluid • microwave • pyrolysis • plasma melting		• Not much literature on it • Little metal recovery

After delving into the comparison of different types of metal recovery processes, hydrometallurgy seems to have advantages that outweigh its disadvantages. Although the extraction of copper using hydrometallurgy is well established for the copper ore, there is no

industrial flowsheet applicable for its recovery from PCB's (Cui & Anderson 2016). There are various hydrometallurgical processes that make use of different chemicals as lixiviants for copper recovery.

The ideal leaching agent is one that is:

1) Capable of achieving high recovery in a short time
2) Selective
3) Cheap
4) Not hazardous to human health and the environment

There are two main types of lixiviants that are worth looking into i.e. alkaline and acid leaching (Jadhav & Hocheng, 2015).

Acid Lixiviants

There are a number of acids that have been used to study metal recovery from PCBs. Acid leaching with an oxidant is commonly used to recover base metals. Habbache et al. (2009) mentions that chloride, nitrate and sulfate ions are common elements for metal removal. Copper leaching has been done using acids with some of these ions such as sulphuric acid (H_2SO_4), nitric acid (HNO_3), hypochlorous acid (HClO) and aqua regia with oxidants such as hydrogen peroxide (H_2O_2), oxygen (O_2), iron (III) (Fe^{3+}) and chlorine (Cl_2) (Cui & Anderson, 2016). Sulfuric and hydrochloric acid solutions are the common leaching agents, but they have low selectivity which in turn makes separation processes after leaching more complicated (Koyama et al, 2006). Typically, sulphuric acid (H_2SO_4) and hydrogen peroxide (H_2O_2) are used and a copper rich solution is made. The reaction that occurs is as below:

$$Cu^0 + H_2O_2 + H_2SO_4 \rightarrow Cu^{2+} + SO4^{2-} + 2H_2O$$

The pregnant solution is later sent for solvent extraction and the final stage is the electro-winning of copper (Cui & Anderson, 2016). There are several studies on the use of sulphuric acid as a lixiviant.

Table 2.7 shows one example where sulphuric acid was used as a lixiviant for copper recovery.

Table 2.7: Sulphuric Acid as a lixiviant, Example 1 (Castro & Martins, 2009)

Parameter	Amount
H_2SO_4 Concentration	2.18 N = 1.09 M
Cu Recovery	>0.01%
Sn Recovery	2.7 ± 0.04%
Time	120 minutes (2 hours)
Temperature	60±2 ºC
Solid: Liquid ratio	1 g/10 ml
Agitation	Very High (not specified)

The study by Castro & Martins (2009) only focused on tin and copper and therefore the leach solutions were not analysed for other metals. The recovery is very low for both copper and tin and this may be due to the short leach time i.e. 2 hrs. This may also be due to the absence of an oxidant such as hydrogen peroxide. A similar study was done by Jadhav & Hocheng (2015) using 1M H_2SO_4 for a longer period without an oxidant as shown in Table 2.8. Although they

managed to recover more copper with a longer leaching time, the recovery was still very low due to the inadequacy of the oxidising agent. The results are as follows:

Table 2.8: Sulphuric Acid as a Lixiviant, Example 2 (Jadhav & Hocheng, 2015)

Parameter	**Amount**
H_2SO_4 Concentration	1 M
Cu Recovery	8.8%
Time	96 hours
Temperature	Room temperature
Solid: Liquid ratio	unknown mass 4 cm x 4 cm PCB: 100 ml
Agitation	150 rpm

A study in which an oxidising agent (H_2O_2) was used is the one done by Deveci et al. (2010). The conditions and results are as follows:

Table 2.9 : Sulphuric Acid as a Lixiviant, Example 3 (Deveci et al, 2010)

Parameter	**Amount**
H_2SO_4 Concentration	0.45 M - 1.6 M
H_2O_2 Concentration	0.2 - 0.8 M
Cu Recovery	15.5 – 98.2%
Time	4 Hours
Temperature	32 - 68°C
Solid: Liquid ratio	1g/75 ml
Agitation	140 rpm

High copper extraction of 98.2% was reached at the highest concentrations and temperature. Deveci et al. (2010) concluded that the concentration of H_2SO_4 had insignificant effect on the copper recovery. The high recovery is therefore due to the presence of hydrogen peroxide and perhaps also the high temperature, solid: liquid ratio and agitation. There were other metals that were in the PCBs, but the extent of their dissolution was not disclosed. The 15.5% recovery was at the lowest temperature tested. High temperatures are therefore necessary for effective leaching even in the presence of an oxidant as this affects the breakdown of hydrogen peroxide and hence the quantities needed to maintain an effective concentration.

Sulphuric acid in the presence of an oxidant is effective for copper recovery, but it is also effective for the recovery of other metals as seen in the study by Oh et al. (2003). Table 2.10 summarises their findings.

Table 2.10: Sulphuric Acid as a Lixiviant with H_2O_2 oxidant (Oh et al, 2003)

Parameter	Amount
H_2SO_4 Concentration	2 M
H_2O_2 Concentration	0.2 M
Cu Recovery	95%
Time	48 hours
Temperature	85 °C
Solid: Liquid ratio	1g/100 ml
Agitation	150 rpm

A 95% recovery of copper was also accompanied by a 95% recovery of Fe, Zn, Ni and Al. This shows that the sulphuric acid is not selective to copper but dissolves other base metals. According to Lee et al. (2010), sulphuric acid is also capable of completely dissolving some precious metals in the presence of thiourea and ferric sulphate.

Comparably, HCl can recover 98% copper (Havlik et al, 2010).

Table 2.11: HCl as a Lixiviant, Example 1 (Havlik et al, 2010)

Parameter	Amount
HCl Concentration	1 M
Cu Recovery	98%
Time	180 minutes (3 hours)
Temperature	80 ºC
Solid: Liquid ratio	1 g/133.33 ml
Agitation	Constant but not mentioned

In the study done by Castro & Martins (2009) only 20% of copper was recovered using three times the concentration i.e. 3M HCl. This may be due to factors summarised in the table below such as a low solid: liquid ratio or shorter leaching time.

Table 2.12: HCl as a lixiviant, Example 2

Parameter	Amount
HCl Concentration	3 N = 3 M
Cu Recovery	33.2 ±1.1%
Sn Recovery	89.1 ± 3.5%
Time	120 minutes (2 hours)
Temperature	60±2 ºC
Solid: Liquid ratio	1 g/10 ml
Agitation	Not specified

Jadhav & Hocheng (2015) reported 100% copper recovery using 1 M HCl in just 22 hours at room temperature and 150 rpm. However, the HCl was not selective because it also dissolved 100% of all the other metals on the PCBs namely, Zn, Sn, Ni, Pb, Fe, Al, Ag, Pd and Au.

Another acid which is commonly studied is nitric acid (HNO_3). Its selectivity is also as poor as HCl. 100% recovery of Cu, Zn, Sn, Ni, Pb, Fe, Al, Ag, Pd and Au was achieved with 1M HNO_3 at room temperature after 96 hours (Jadhav & Hocheng, 2015). Nitric acid has been said to be capable of recoveries over 90% for copper and other metals such as lead and nickel (Kinoshita et al, 2003; Mecucci & Scott, 2002).

Aqua regia is another acid that is commonly used in the recovery process and recoveries are normally high (Madenoglu, 2005; Quinet et al, 2005; Sheng & Etsell, 2007). Castro & Martins (2009) reported recoveries as high as 90% for copper in aqua regia systems as shown in Table 2.13.

Table 2.13: Aqua Regia Leach (Castro & Martins, 2009)

Parameter	**Amount**
HCl + HNO_3 (aqua regia) Concentration	3 N = 3 M HCl + 1 N = 1 M HNO_3
Cu Recovery	93.2 ± 2.4%
Sn Recovery	98.1 ± 3.3%
Time	120 minutes (2 hours)
Temperature	60±2 ℃
Solid: Liquid ratio	1g/10 ml
Agitation	Not Specified

The recovery achieved by aqua regia is also high for metals that are difficult to dissolve such as gold. This results in aqua regia not being selective as it is strong enough to dissolve almost every metal. Table 2.14 shows that aqua regia has high recoveries for copper and precious metals.

Table 2.14: Aqua regia Recoveries for different metals

Copper	**Palladium**	**Gold**	**Silver**	**Reference**
100%	Not reported	100%	88.51%	(Lee et al, 2010)
Not reported	93%	97%	98%	(Park & Fray, 2009a)

The use of HCl + H_2SO_4 as a lixiviant was also done by Castro & Martins (2009) where there was a primary and a secondary leach. The difference between the two is that the secondary leach was done with PCBs that had been leached before. The first round of leaching; which is the primary leaching, did not dissolve much copper or tin. The assumption was that the initial composition of the PCBs did not change after the first leaching round. The results of the primary leach are as follows in Table 2.15:

Table 2.15: Sulphuric acid + HCl as lixiviant, Example 1

Parameter	**Amount**
H_2SO_4 + HCl Concentration	2.18 N = 1.09 M H_2SO_4 + 3 N = 3 M HCl
Cu Recovery	8.9 ± 0.4%
Sn Recovery	59.3 ± 2.3%
Time	120 minutes (2 hours)
Temperature	60±2 ºC
Solid: Liquid ratio	1g/10 ml

The secondary leaching had better results as seen in Table 2.16:

Table 2.16: Sulphuric acid + HCl as lixiviant, Example 2

Parameter	**Amount**
H_2SO_4 + HCl Concentration	2.18 N = 1.09 M H_2SO_4 + 3 N = 3 M HCl
Cu Recovery	12.3 ± 0.4%
Sn Recovery	90.5 ± 3.0%
Time	120 minutes (2 hours)
Temperature	60±2ºC
Solid: Liquid ratio	1g/10 ml

The secondary leach was done on the PCBs that were treated using the primary leach stage thereby lengthening their time in the lixiviant. The higher recovery for the secondary leach could be due to longer exposure of the PCBs to the lixiviant. It could also be the fact that the primary leaching acted as a pre-treatment method by exposing more of the desired copper and tin.

Jadhav & Hocheng (2015) made use of biodegradable acids such as acetic acid ($C_2H_4O_2$) and citric acid ($C_6H_8O_7$). They had poor copper recoveries of 9.89% and 19.57% respectively. They also have low boiling points and decompose at low temperatures which is a disadvantage as it shrinks the range of temperatures that copper leaching can be done. Jadhav & Hocheng (2015) also relate the low copper dissolution to the lack of anions from the organic acids.

Most acids, however, achieve very high, and sometimes complete, recovery of metals but they have very low copper selectivity. Having a mix of metals in the leach solution complicates downstream processes such as electro-winning (Koyama et al, 2006). In addition, some acids like HNO_3 have toxic emissions such as nitric oxides. Moreover, complete removal of some acids such as HNO_3 from the solution prior to metal separation is required. This further complicates the process and incurs huge operating costs (Jadhav & Hocheng, 2015).

Acids are generally corrosive and if they are to be used industrially for the recovery of copper, there is need to use corrosion-resistant materials like stainless steel for the equipment, thereby prompting higher capital costs.

As previously discussed, the most dominant drawback for acids, however, is their low selectivity. There is need to use a lixiviant that can allow sequential leaching of metals which

later simplifies the downstream processes such as electro-winning. Another crucial downside is that they are highly corrosive. To avoid high capital costs, non-corrosive lixiviants are preferred as these can be industrially used in equipment made of cheaper materials.

Alkali Systems

Using alkaline systems for copper recovery is the alternative to acids. Alkaline systems are less commonly used than the acids and therefore there is limited literature on them. Ammoniacal systems are the most employed alkaline lixiviants. They comprise of an ammonia-ammonium salt buffer system. The ammonium salts that are used are either ammonium chloride, ammonium sulphate or ammonium carbonate. Ammoniacal systems are often oxidative with oxidants such as oxygen or Cu(II) ions (Tuncuk et al, 2012). For the stability of Cu(I) and Cu(II) in neutral or alkaline solutions, complexing agents such as NH_3 or CN^- are needed (Koyama et al, 2006). The ammoniacal systems are relatively more selective than acids for instance, iron and aluminium are not dissolved in ammonia solution (Konishi et al, 2014). However, some metals such as nickel and zinc may also be dissolved and form ammine complexes.

There are advantages of using the ammoniacal system that were noted (Koyama et al, 2006).

- High copper selectivity since metals such as iron and aluminium are not dissolved.
- No supplementary oxidants are required due to the Cu(II) produced at the anode. The Cu(II) acts as the oxidant.

A study focusing on the dissolution of metallic copper (Cu^0) was experimented in two different ammoniacal system and were compared by Konishi et al (2014). The experiments were done at temperatures between 25 ℃ and 80 ℃. It was found that the concentration of the ammonia had substantial effects on the copper dissolution compared to the concentration of other reagents (Konishi et al, 2014). The rate of leaching was higher in a leaching system with ammonium chloride than one with ammonium sulphate (Konishi et al, 2014).

Aqueous $CuSO_4$ – (NH_3) – $(NH_4)_2SO_4$ and the $CuCl_2$ – (NH_3) – NH_4Cl solution were used in Konishi's study (2014). The Cu(II) ion is stable in these solutions and the reaction that normally takes place in the pH range of 8 – 10 is

$$Cu + Cu(NH_3)_4^{2+} \rightarrow 2Cu(NH_3)_2^{2+}$$

$Cu(NH_3)_4^{2+}$is capable of oxidising metallic copper in an ammoniacal alkaline solution. This is because the oxidation-reduction potential of $Cu(NH_3)_4^{2+}$/ $Cu(NH_3)_2^{2+}$ is greater than that of $Cu(NH_3)_2^{2+}$/Cu. The Cu(II)-ammine complex $Cu(NH_3)_4^{2+}$ significantly enhances the leaching rate whereas the Cu(I)-ammine complex $Cu(NH_3)_2^{2+}$ slightly depresses it (Koyama et al, 2006).

The ammonia – ammonium sulphate conditions are presented in Table 2.17.

Table 2.17: Ammonia-Ammonium Sulphate System (Konishi et al 2014)

Parameter	Amount
NH_3 Concentration	7 $kmolm^{-3}$ = 7 M
$(NH_4)_2SO_4$ Concentration	1 $kmolm^{-3}$ = 1 M
$CuSO_4$ Concentration	0.5 $kmolm^{-3}$ = 0.5 M
Cu Recovery	100%
Solid: Liquid ratio	Not specified

The temperature and agitation were varied, and it showed that the copper leaching rate increased with increasing agitation and temperature. The rate tripled when the stirring rate was increased from 0 to 600 rpm. Increasing the temperature from 313 K (40 ℃) to 353 K (80 ℃) also more than doubled the rate of leaching from 0.8 $kgm^{-2}h^{-1}$ to 1.65 $kgm^{-2}h^{-1}$ at a stirring speed of 600 rpm. Konishi et al. (2014) postulated the equation:

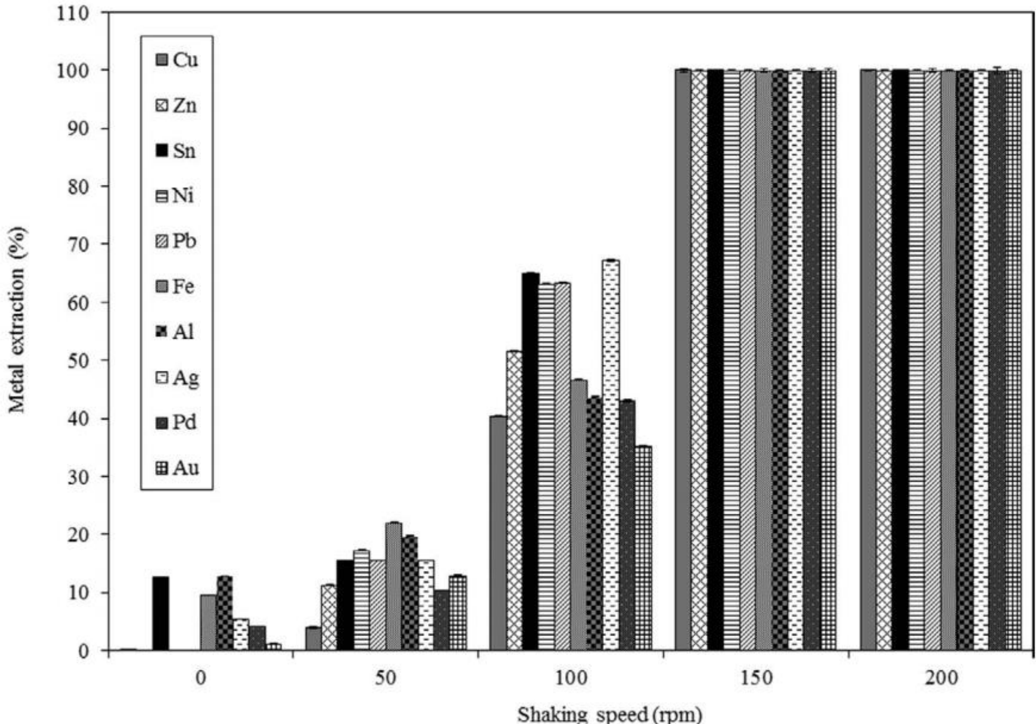
$$\text{Leaching Rate} = k\,[Cu(NH_3)_4^{2+}]^{0.5}\,V^{\frac{2}{3}}$$

Where V is the stirring speed and k is the rate constant.

This suggests that at constant temperature, the only factors that contribute to the leaching rate is concentration of the $Cu(NH_3)_4^{2+}$ ligand and the stirring speed. From the equation, the stirring has a greater effect on the leaching rate than the copper-ammine complex concentration. However, in other studies which use different systems, the leaching rate is not significantly influenced by agitation. This may be because the ammonia reacts faster or due to other factors which are not explicitly discussed such as the difference in configuration of the vessel and impeller.

Figure 2.8 which shows the effect of agitation/shaking speed on the recovery of various metals (Jadhav & Hocheng, 2015).

Figure 2.8: Effect of Agitation/Shaking on Metal Recovery (Jadhav & Hocheng, 2015)



The experiments were all done within 22 hrs at similar conditions except for the agitation. It is clear from the figure above that an increase in agitation increases the rate at which copper is recovered. However, speeds beyond 150 rpm do not seem to have an additional effect. This suggests that within the 22 hrs that the experiment was run, the agitation at 150 rpm was no longer a limiting factor.

Below are diagrams showing the effect of agitation (0 – 600 rpm) & temperature 313 K (40 ºC) & 353 K (80 ºC) respectively

Figure 2.9: Temperature at 313K (40ºC)

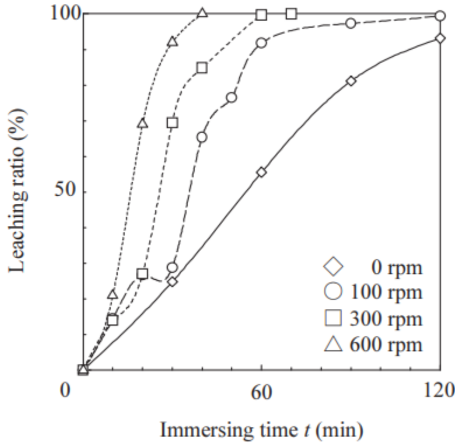
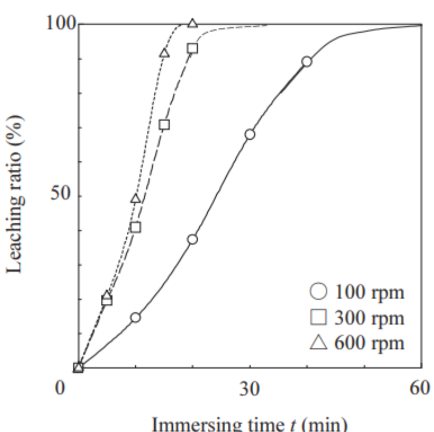


Figure 2.9: Temperature at 353K (80 ºC)

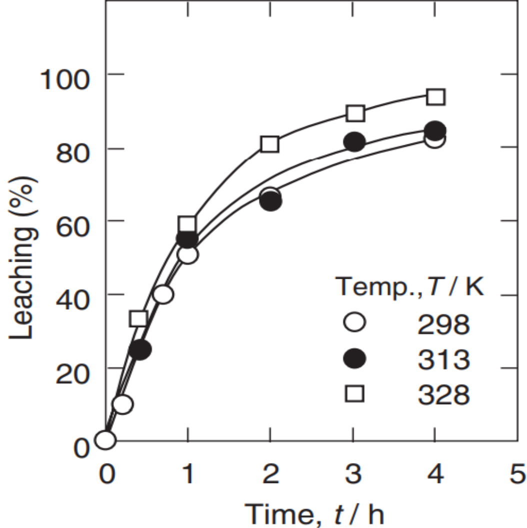


The graphs show that increasing agitation increases the leaching rate. Collating the two, it shows that the runs done at a higher temperature (80 ºC) have a faster leaching rate than those done at a lower temperature (40 ºC). Temperature is said to be one of the most influential factors affecting metal extraction from e-waste (Tuncuk et al, 2012).

The equation postulated by Konishi et al. (2014) indicates that temperature does not have appreciable influence on the rate of leaching. However, their study proposes that increasing temperature increases the rate of ion diffusion and decreases the viscosity of the solution making the diffusion quicker. Furthermore, the experimental findings demonstrate that increasing temperature does modestly increase the leaching rate and extent of the reaction.

The graph in Figure 2.10 also shows the correlation between temperature and the leaching rate from a different study (Koyama et al, 2006).

Figure 2.10: Effect of Temperature on Leaching Rate (Koyama et al, 2006):



Although higher temperatures result in the increase of both recovery and leaching rate as shown in the graph, the difference is not too pronounced. The rate and degree of leaching was higher for the run at 328 K (55 ℃) and lower at 298 K (25 ℃).

In the Chloride System shown below, the following conditions were used.

Table 2.18: Ammonia- Ammonium Chloride system (Konishi et al 2014)

Parameter	Amount
NH_3 Concentration	2 kmolm^{-3} = 2 M
NH_4Cl Concentration	1 kmolm^{-3} = 1 M
$CuSO_4$ Concentration	0.5 kmolm^{-3} = 0.5 M
Temperature	313 K = 40 ℃
Cu Recovery	100%
Solid: Liquid ratio	Not specified

The leaching rate increased with an increase of NH_3 from 1 M to 2 M. Thereafter, there was no significant effect of changing the NH_3 concentration as shown in the figure. On top of that, increasing the NH_4Cl concentration resulted in an increased leaching rate but it had no significant effect beyond 0.5M as shown in Figure 2.11 (Konishi et al, 2014).

Figure 2.11: Effect of NH3 Concentration

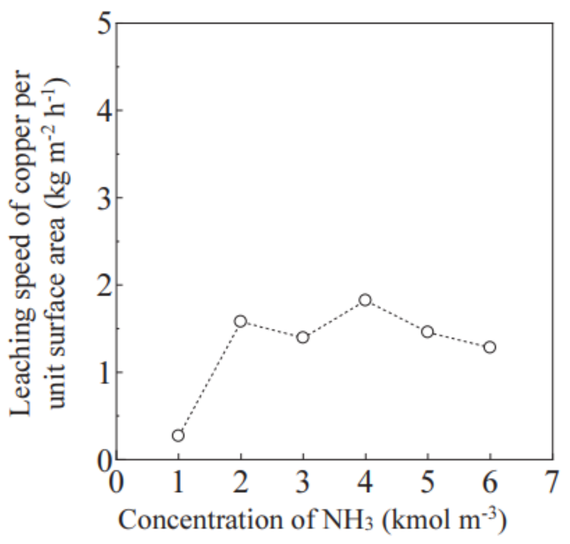
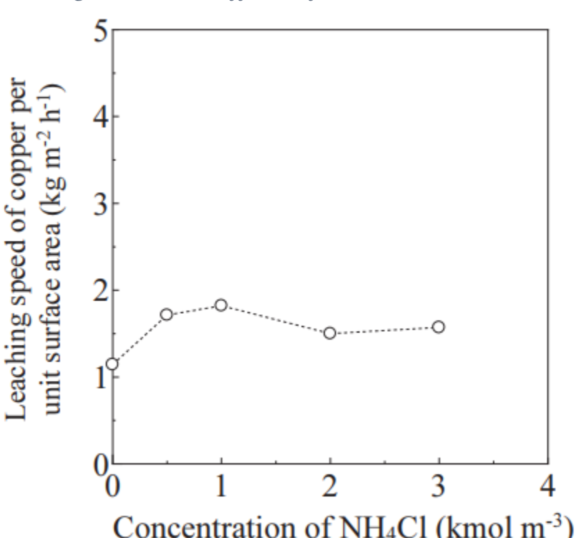


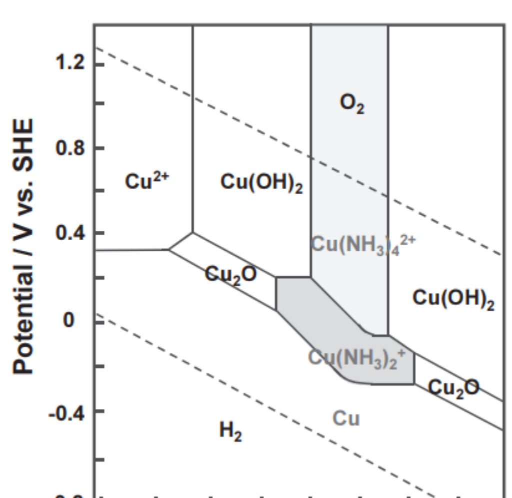
Figure 2.11: Effect of NH4Cl Concentration



Interestingly, increasing either the NH_3 or the NH_4Cl sometimes decreases the leaching rate as the two graphs unveil. At 4 M NH_3, 1 M NH_4Cl, 0.5 M $CuSO_4$ 353 K (80 ℃) and 600 rpm the copper leaching rate that resulted was 3.98 kgm^{-2}h^{-1} which exceeded that obtained with higher NH_3 concentration with the sulphate salt by a factor of more than 2.4 (Konishi et al 2014). This may be because the kinematic viscosity of the chloride system is 70% of that of the sulphate system, which makes ion diffusion much easier in the chloride system (Konishi et al 2014). It is suggested that the higher diffusivity was due to the presence of Cu(I)/ NH_3/Cl complexes.

The potential-pH diagram below is for the Cu – NH_3 – H_2O system obtained for copper activity of 0.5 and a total NH_3 and NH_4^+ of 7 M.

Figure 2.12: Eh- pH Diagram of the Ammoniacal System (Konishi et al, 2014):



The reaction happens within the dotted lines and for this study the pH was kept in the bounds of 8 and 11 which is the region shaded in grey. There is a possibility of copper precipitating to form $Cu(OH)_2$ if the pH drops below 8 or above 11.

The extracted copper may precipitate out of solution to form as per the equation below.

$$CuSO_4 + 2NH_4OH \rightarrow (NH_4)_2SO_4 + Cu(OH)_2$$

The ammonia concentration directly affects the pH of the system and thus should be monitored to keep it in the required range. To minimise the precipitation of copper the pH is to be kept between 8 and 11 by adding ammonia since any pH outside that range is favourable for the reaction.

The following equation occurs to form the copper (II) tetraamine complex when there is enough free ammonia.

$$Cu(OH)_2 + (NH_4)_2SO_4 + 2NH_4OH \rightarrow [Cu(NH_3)_4] + 4H_2O$$

The above equations show that adding ammonia into the solution results in less precipitation of copper.

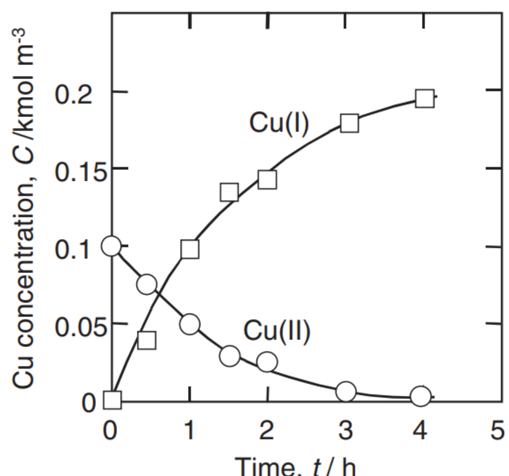
Koyama et al. (2006) did a study using the ammonia – ammonium sulphate system using Cu(II) as an oxidant. The following table shows the conditions that were used:

Table 2.19 Ammonia – Ammonium sulphate system with Cu(II) oxidant

Parameter	**Amount**
NH_3 Concentration	5 M
$(NH_4)_2SO_4$ Concentration	1 M
$CuSO_4$ Concentration	0.1 M
Agitation/Stirring Speed	200 rpm
Temperature	298 K (25 ℃)
Solid: liquid Ratio	1g/20 ml
Time	4 hours

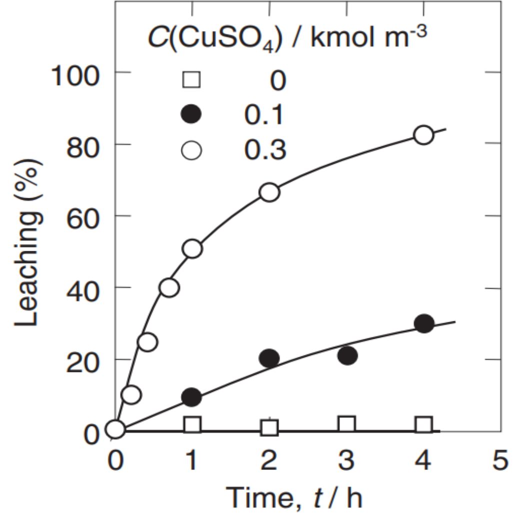
They found that the colour of the solution changed from navy blue to pale blue. This is because the navy-blue Cu(II)-ammine complex concentration decreased as the colourless Cu(I)-ammine complex increased (Koyama et al, 2006):

Figure 2.13: Concentration Profile of Cu(I) & Cu(II) (Koyama et al, 2006):



The effect of CuSO4 concentration was experimented and the graph in Figure 2.14 shows the results that were obtained (Koyama et al, 2006).

Figure 2.14: Effect of CuSO4 Concentration (Koyama et al, 2006):



On the graph, three different concentrations of $CuSO_4$ were tried; 0 M, 0.1 M and 0.3 M. The solution with 0 M $CuSO_4$ did not leach out anything. There was an improvement with the solution with 1 M $CuSO_4$ as this leached out some copper. The best leaching result is from the highest concentration of $CuSO_4$ which is 0.3 M which improved both the leached copper amount and the leaching rate.

Bari et al. (2009) tested a range of lixiviants for the selective leaching of copper and Table 2.20 shows the results.

Table 2.20: Recoveries of Different Reagents (Bari et al, 2009):

Leaching agent, 1M	**NH3, M**	**Cu, mg/g**	**Ni, mg/g**	**Zn, mg/g**	**Fe, mg/g**
Aqua regia	0	277.40	4.13	20.36	11.25
Leaching agent, 1M	NH3, M	Cu, %	Ni, %	Zn, %	Fe, %
Sulfuric acid	0	29.74	26.15	42.93	24.26
Nitric acid	0	83.87	66.34	71.56	67.82
Hydrochloric acid	0	37.29	16.70	28.14	9.60
DL tartaric acid	5	0.28	0	1.72	4.62
	0	3.18	8.72	3.44	75.46
Oxalic acid	5	65.32	6.78	40.91	0
	0	2.47	14.28	3.43	65.77
Acetic acid	5	65.46	7.99	39.44	0
	0	0.04	0	0.73	27.11
Sodium chloride	5	69.74	19.85	58.98	0
	0	0	0	3.59	1.42
Sodium sulfate	5	75.41	12.35	49.36	0
	0	0.07	0	1.49	0.17
Sodium nitrate	5	80.45	17.43	72.34	0.44
	0	0.06	0	4.62	1.51
Ammonium thiocyanate	5	58.37	60.29	58.49	0
	0	2.44	5.32	1.27	0
Ammonium carbonate	5	92.62	18.64	67.70	0
	0	25.08	0	3.38	0.62
Ammonium nitrate	5	76.40	7.99	57.76	0
	0	28.64	4.60	4.12	0.53
Ammonium chloride	5	72.89	11.38	53.33	0
	0	23.58	4.60	5.89	0.53
Ammonium sulfate	5	64.31	2.20	48.14	0
	0	15.99	0	3.24	0
Ammonium persulfate (0.5M)	5	98.93	9.68	60.70	0
	0	27.14	54.70	10.90	65.60

The table shows that acids are capable of high recoveries but they are not as selective as the alkali. The lixivinat that had the best recovery (98.93%) and selectivity of copper was found to be the solution with 5M ammonium – 1M ammonium thiosulphate solution. However, the PCBs used by Bari et al. (2009) did not contain much gold and thus not much was leached. However, in Tripathi's study, gold was leached with a recovery of upto 78.8% using the same lixiviant, ammonia – ammonium thiosulfate (Tripathi et al, 2012). This suggests that the ammonia – ammonium persulphate might not be as selective when there is significant precious metals in the PCB.

Rating from Bari's study, the other lixiviant that has high copper selectivity is the 5M with ammonium carbonate which recovered 92.62% and therefore this system is worth exploring. The most explored ammoniacal system in literature is the ammonia – ammonium sulphate solution with $CuSO_4$ as the oxidant. Bari et al. (2009) reported a copper recovery of only 64.31% which is relativey lower than what is reported in literature.

There are several parameters that were experimented on, and they affect copper recovery. These include,

- Concentration of reagents such as ammonia
- Agitation; shaking or stirring speed
- Temperature
- Solid: Liquid Ratio
- pH
- Type of ammonium salt

After leaching, the lixiviant is loaded with the ions of the desired metals and the recovery of the metals from the pregnant solution is usually done by solvent extraction, adsorption on activated carbon, and electrowinning (Tuncuk et al, 2012).

Since the most common alkaline lixiviant is the ammonia – ammonium sulphate with $CuSO_4$ as the oxidant is the most common lixiviant for the selective leaching of copper, it will be used for the comparison of different pre-treatment methods. Once the best method is determined, the leaching conditions can be optimised by changing some of the parameters.

Research Outlook based on Literature

Composition of the PCBs

Literature showed that there are many types of PCBs that widely vary in composition. In order to compare the pre-treatment methods and leaching parameters, a particular custom-made PCB is going to be used in the research to avoid variability. The PCB is going to be characterised to fulfil the first objective.

Pre-treatment Stage

There are quite a number of pre-treatment methods that are used in literature and they all have different attributes. The intended end result is the accessibility of metals on the PCBs. A comparison of all these methods under the same conditions is necessary. The pre-treatment methods can be grouped in two groups.

1. PCBs pre-treated with size reduction

This has been done by milling, shredding or cutting the boards into small pieces.

2. PCBs pre-treated as whole boards

Whole boards are cut into large pieces, roasted or treated with NaOH to remove the epoxy which contains CFCs.

A comparison of the combination of some the above-mentioned methods and other new ways that could potentially expose the copper on the PCBs is going to be done. These methods are to be employed on similar custom-made PCBs of known structure and composition. This will in turn fulfil the second objective.

Leaching Optimisation

To improve the diagnostic leach, a different salt is going to be explored and 2 factors are going to be varied thus; ammonia concentration and the liquid to solid ratio. The optimal conditions are going to be chosen to fulfil the third objective.

Hypothesis

- Copper recovery from printed circuit boards (PCBs) varies depending on the pre-treatment method used. The optimal pre-treatment method is one that reduces the size of the PCB which exposes more metal to the lixiviant.
- The choice of salt, liquid: solid ratio and ammonia concentration affects the rate of copper recovery. The type of salt affects the amount of copper that is dissolved because different salts have different buffering effects to the ammoniacal system. Ammonium carbonate is expected to improve the copper recovery as it is a better buffer. Decreasing the liquid: solid ratio decreases rate of recovery due to the reduction in the lixiviant molecules available for reaction. Increasing the ammonia concentration improves the recovery as that increases the free ammonia molecules available to make complexes with the copper on the PCBs.

3. METHODOLOGY

Overview of Methodology

In this study there are 3 objectives that will be fulfilled. The layout of the methodology chapter corresponds with the main objectives. The steps done to meet the objectives are summarised below.

1. *Characterise the Printed Circuit Boards and measure the composition of the board.*

Steps taken:

- Understanding the manufacturing process
- Using QEMSCAN to observe the surface
- Using 3D X-ray CT Scan to study the metallic part
- Using Aqua Regia Leach for head grade

2. *Compare different pre-treatment methods and choose the most suitable.*

Steps taken:

- Describing the 8 different pre-treatment methods explored
- Describing the Diagnostic Leach test used to compare them

3. *Use the best pre-treatment method to optimize the copper leaching process.*

Steps taken:

- Detailing on the parameters changed

Objective 1: Printed Circuit Board Characterisation

The key aim is to understand the structure and composition of the printed circuit boards that are used in the study.

Manufacturing Process of the Printed Circuit Boards

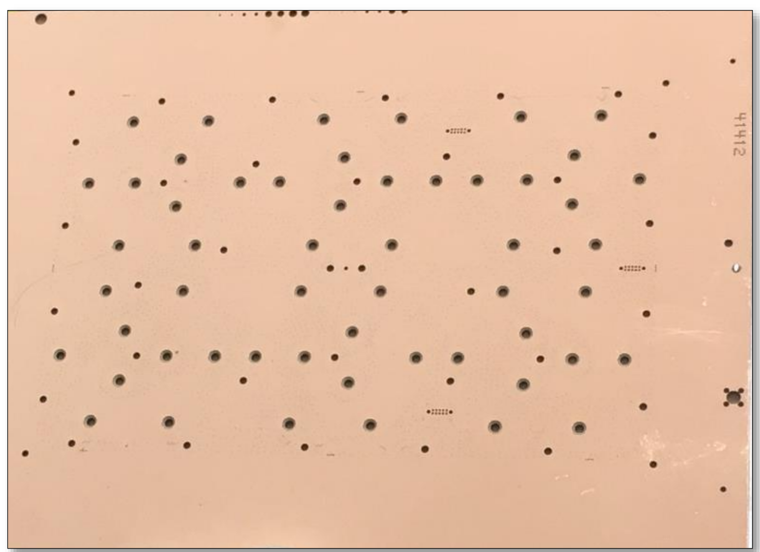
A key problem with PCBs is their extreme inhomogeneity as the literature review indicates that PCBs widely vary in composition. Although a degree of homogenisation can be achieved with milling a sample to fine powder, other methods of pre-treatment ought to be explored without milling. In this initial study identical custom-made PCBs are used instead of waste PCBs that may have different composition. These are unpopulated as populating them will complicate the recovery process. A study on copper extraction on populated PCBs is planned for the next stage into developing the process.

TraX Interconnect (pty) Ltd manufactured PCBs with a design analogous to that of a generic board commonly used in many high-end control devices. The PCBs are 4 layered comprising of a laminate of FR4 (Fibreglass with epoxy resin) inner core sandwiched by two copper foils 17µm in thickness. The copper layers on either side are then followed by a layer of laminate and an additional layer of copper sheet for each side. The outer two layers are made of copper foil that is added on either side of the laminate at a later stage in the manufacturing process.

Designing and Drilling Holes on the Board

The first step is to design the PCBs using commercially available software and this involves the outlining of tracks, holes, materials to be used and the general detail of the PCBs. Subsequent to this, holes are drilled on the copper foil which is held in place by mounting aluminium foil over it and fixing the two together using masking tape. The purpose of the aluminium foil is to lubricate the tungsten drill bits and to protect the copper foil from heat damages when drilling holes. The aluminium is then removed, and any aluminium usually reported in leaching is in-fact residual aluminium from the copper-aluminium foil contact. The smallest drilled holes are 0.2mm in diameter and drilling takes place purely on an X and Y coordinate with one side of the board drilled at a time. Figure 3.1 is an image of a drilled FR4 laminate.

Figure 3.1: Drilled FR4 Laminate



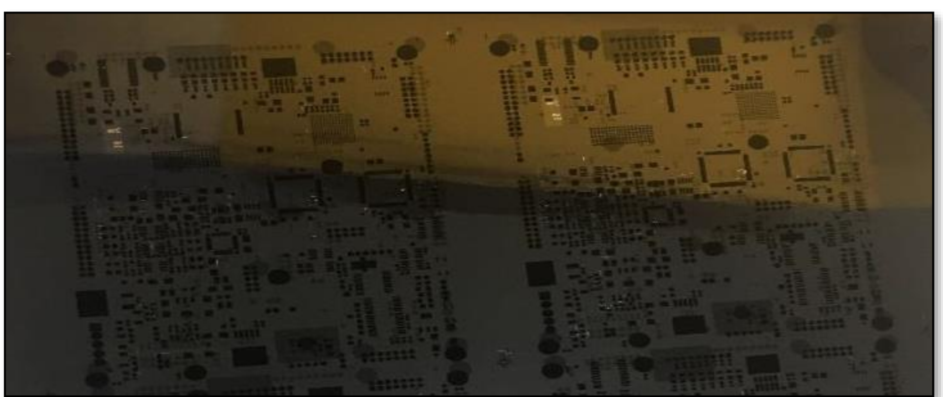
Fibreglass is non-conductive so after drilling, the holes must be lined with copper for conductivity. This permits the current to flow between the top and bottom copper layers. Graphite paste is put on the fibreglass to enable the attachment of copper. After this, the sheets are put in the electro-plating line and copper sulphate solution is used to electroplate the walls of the holes.

Putting Tracks on the board

After the holes are drilled, tracks must be put on the copper layers. This is done by printing the design of the tracks on photoresist material made of silver halide to create negatives.

Figure 3.2 is an image of the photoresist material with track designs printed on it

Figure 3.2: Photoresist with track Designs



The material is laid on each of the copper foils and then they are exposed to Ultra-Violet light creating the image on them. There are dust collectors to reduce amount of dust entrapped within the sheets. The conditions must be vacuum-like and such that no light can penetrate. The Ultra-

Violet light will then shine and expose the image on the photoresist material. Every exposed area goes dark and hardens (cures) otherwise it stays clear.

The photoresist material is easily removed in all the areas that are uncured (have not hardened) to show the copper. Extra copper is electroplated onto the exposed copper to form the tracks. The sheet originally has 17 µm of copper and a further 17 µm is electroplated on the uncured parts of the copper making them 34 µm thick. This method is used for the inner layers of the board.

Figure 3.3 PCB with Printed Photoresist

Figure 3.3 shows a board with track designs printed on it using photoresist material. The alternative method that is used for the outer layers is to take a 34µm thick copper foil and print the reverse design (of the first method) using photoresist material. The areas left uncured are where a thickness of 17 µm of copper is etched off until the board has 17 µm of copper left where the tracks should be. This method is not used much as it would be a waste of copper seeing that it might not be fully recovered.

During etching, the boards should be covered in tin on the parts that are not to be etched to protect the copper that is to be left there. The tin is electroplated onto the copper. During etching, the boards do not get soaked for long in the ammonia but instead pass through a conveyer belt. The speed of the conveyer belt is determined by the thickness of the copper.

Figure 3.4 shows a board covered with tin where the copper should not be plated.

Figure 3.4: PCB covered with Tin during Copper Etching

After drilling holes and putting tracks on the board, the first thing to be removed is the cured photoresist laminar using caustic soda (NaOH). Subsequently, ammonia is used to remove any excess copper. The last thing to be removed is the tin using nitric acid. The boards are rinsed after each stage.

Combining Inner Layers and Outer Layers

A Vacuum Transfer Press is used to attach the two outer copper foil layers to the inner layer (FR4 core laminate). Uncured FR4 normally called pre-preg is put between the FR4 core and the outer copper foils. This is then put on a steel plate. The stack is pressed hard in a vacuum at controlled temperatures as high as 300 °C so that the pre-preg melts and creates a strong physical bond. The pre-preg hardens as it becomes cured and thus becomes similar to the FR4 in the core. The bond between the cured FR4 and the copper foils make the PCBs become multi-layered boards.

Quality Control

Before adding ink or more value to the boards, they are checked for voids and short circuits by optical inspection. This is because sometimes the etching does not take all the copper away or takes away some that should remain. For boards with thin tracks, specialised machinery is used to analyse the boards. The machines can check up to 15 μm comparing the output with the original designs. It will then remove the copper that did not etch away. However, if there is copper to be added e.g. voids, the boards are scrapped as rejects.

Masking the Boards

The ink mask is sprayed on the boards while covering the whole board. They come in different colours but the green one was used for the PCBs in this study. The ink is a photo-imageable ink and is put through photo imaging so that only the parts that are to be covered are cured.

The rest is washed off using 5% potassium carbonate to dissolve the ink and it takes around 3 days to remove it. The temperature should be between 32 °C – 35 °C.

Nickel and Gold plating

The last stage is to electroplate all the exposed copper with nickel and then electroplate the nickel with gold. The gold is there to protect copper from oxidising. There are also silver-gold finishes, but this does not work on FR boards.

The final product

Figure 3.5 is the front and Figure 3.6 is the back of the final PCB manufactured for this study. The PCBs are 10cm x 15cm in size.

Figure 3.5: Front of the Final PCB

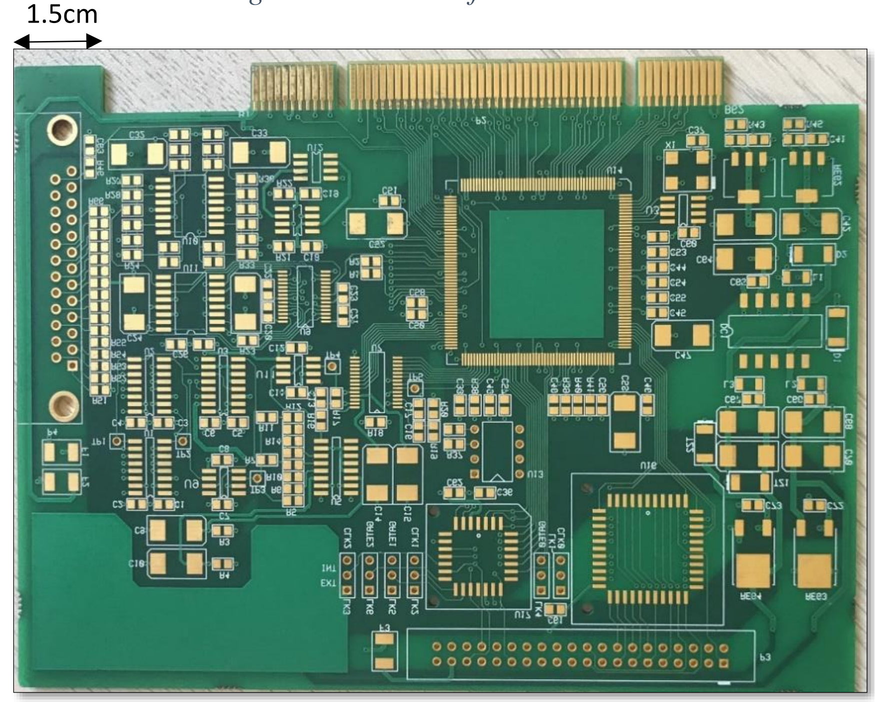
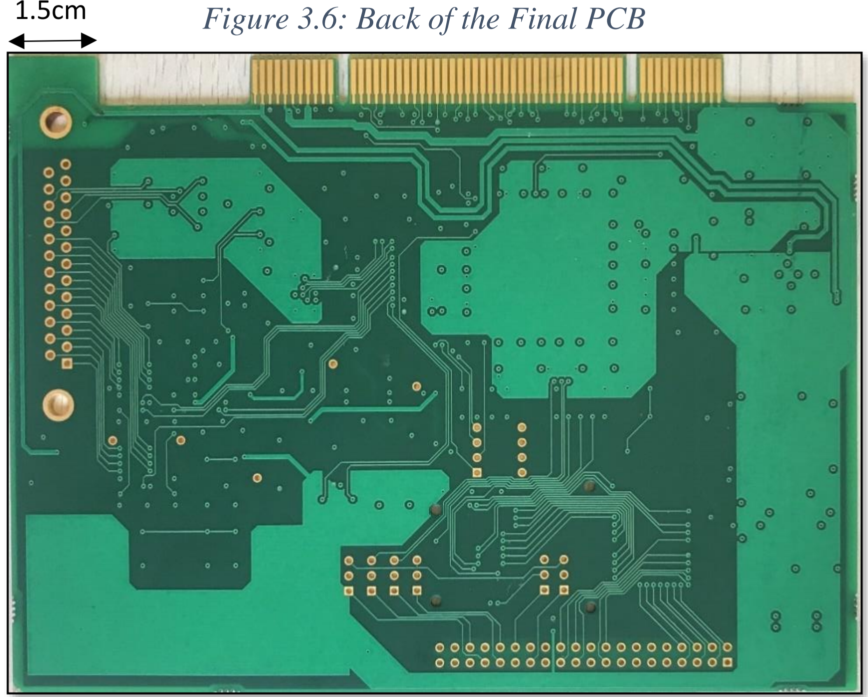


Figure 3.6: Back of the Final PCB



The boards are mostly covered by the top mask and have the nickel/gold plating on the surface and no copper is exposed.

Blueprint of the printed circuit boards

From the manufacturing process, a blueprint of the PCBs was also produced. Analysing the blueprint helps in understanding the structure of the PCBs.

The Board Layers

As aforementioned, the PCBs have 4 copper layers. The top and bottom are covered with a mask. The inner layers are connected to the outer layers by the pre-preg (uncured FR4 resin) which cures when the layers are combined.

Figure 3.7 is a cross-sectional schematic diagram of the PCBs

Figure 3.7: Cross-Sectional Schematic Diagram of the PCB

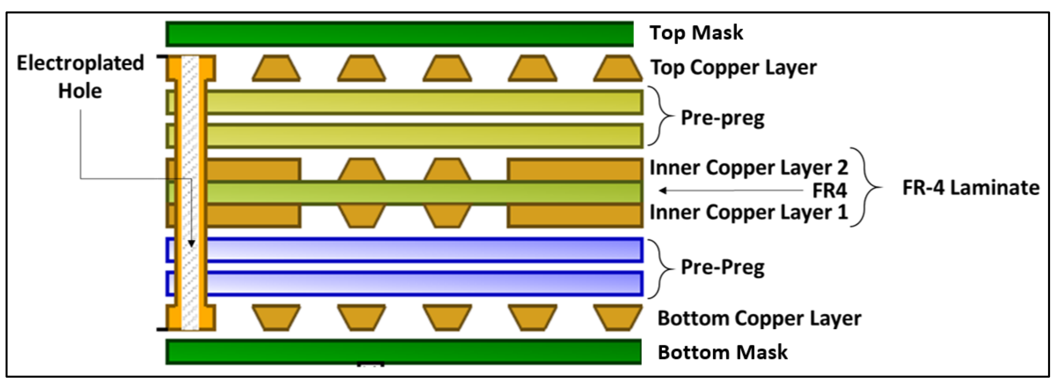


Figure 3.11 is the blueprint of the Top Outer (left) and Top Inner (right) Copper Layers

Figure 3.8: Top Copper Layers

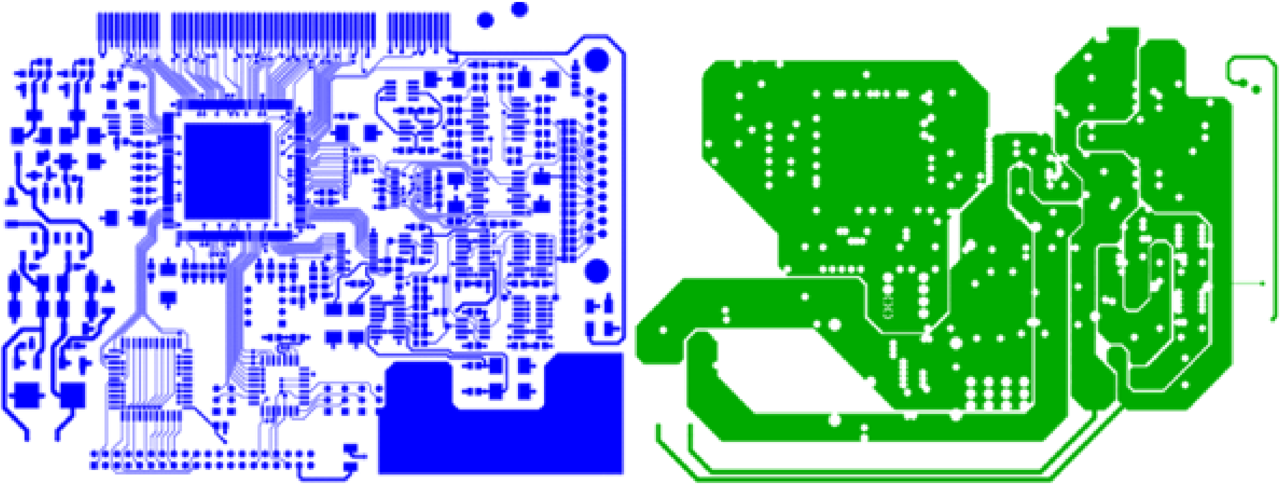


Figure 3.12 is the blueprint of the Bottom Outer (left) and Bottom Inner (right) Copper Layers

Figure 3.9: Bottom Copper Layers

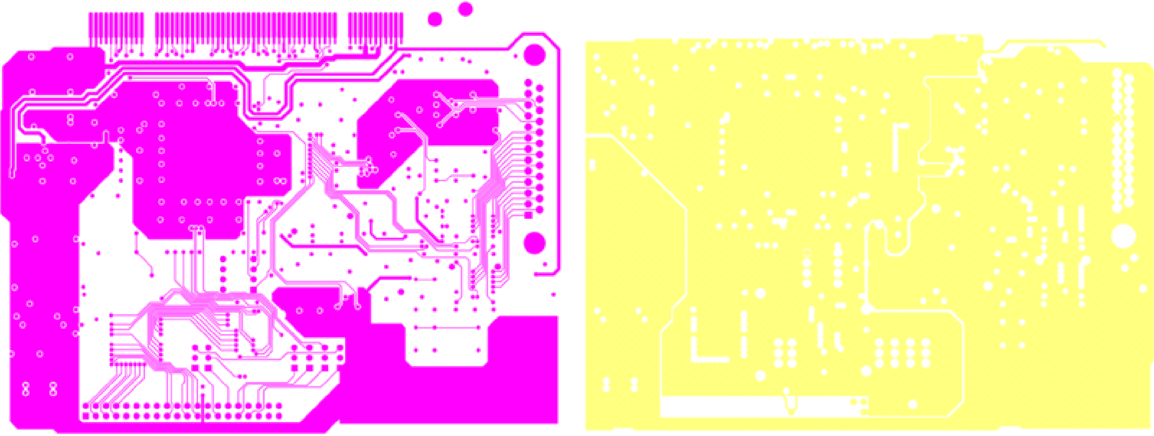
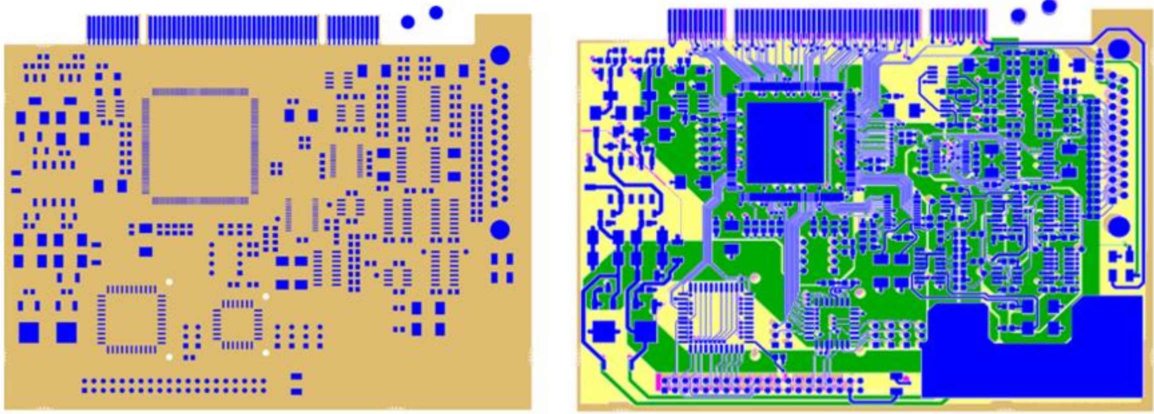


Figure 3.13 is the blueprint of the Mask (left) and all the board layers combined (right)

Figure 3.10: Mask of PCB (left) and Combined Layers of the PCB (right)



The blueprint of the printed circuit boards

The blueprint of the printed circuit boards (PCBs) only give information on the general distribution of the materials on the PCBs. It does not give any quantitative information and therefore there is need for further analysis.

The shape and distribution of the copper layers is shown accurately and in detail. Visual analysis of the blueprint can give a guideline as to how much each layer has.

QEMSCAN

There are numerous techniques that are routinely used for the characterisation of traditional mineral ores that can similarly be applied to the PCBs. Some of these techniques include Quantitative Evaluation of Minerals by Scanning Electron Microscopy (QEMSCAN) and X-Ray Computated Tomography Scans (X-Ray CT Scan). In this study, QEMSCAN was used to characterise printed circuit boards to determine the amount and distribution of material on the board.

QEMSCAN Model and Settings

The QEMSCAN used for this study is the FEG (field emission gun) QEMSCAN 650 F, with high resolution BSE (Back scattered electron), Bruker Energy Dispersive Spectrometers (EDS) and a Spectral Analysis Engine (SAE) usually used to analyse rocks and other samples (Centre for Minerals Research, University of Cape Town).

The QEMSCAN has two Bruker XFlash 6130 detectors that run on the applied potential of 25kV. The carbon coater is a Quorum coater that disperses the electron charge to prevent the build-up of charge during the SEM (Scanning Electron Microscope) measurement.

The beam current in the QEMSCAN is optimised at 10 nA on the Faraday Cup. A Faraday cup is a metal (conductive) cup designed to measure the actual beam current. The chamber vacuum is to remove particulates and gases and must be at $<1x10^{-4}$ Pa to perform any measurements on the samples. Back scattered electrons are produced by the interaction between the electron beam and the sample in the QEMSCAN. The BSE values vary between 0 and 255, measured on grey scale. The BSE values give information about their densities as this is based on the relative brightness. Heavy elements will appear as a bright white colour and light elements appear black. A backscatter electron detector (BSD) detects scattered electrons. These electrons are higher in energy from atoms below the sample surface. Using a BSD allows for lower vacuum levels, reducing sample preparation requirements and minimizing beam damage. BSE is calibrated with the Gold standard at 232, the Quartz standard at 42 and the Copper standard at 130.

QEMSCAN uses a mineral library system, called SIP (Species Identification protocol) which is basically a library of specified materials. The SIP determines how the elemental information measured by the SEM (Scanning Electron Microscope) scanning a sample, is classified into a mineralogical composition or species. The SIP consists of a list of entries (SIP definitions), each with a set of user-specified criteria to match the X-ray spectra and BSE (Back Scatter Electron) data from a measurement point to a mineral species. As each point on a sample is scanned, its spectrum is converted to element information which is compared to the entries in the SIP list until one is found with parameters matching the scanned material. If the elemental information does not match any of the SIP definitions, the pixels is grouped into the "unclassified" SIP definition at the bottom of the list. It was necessary to make a new mineral list that shows what components are on the PCBs some of which include pure nickel.

Some measurements that the QEMSCAN performed in this study are:

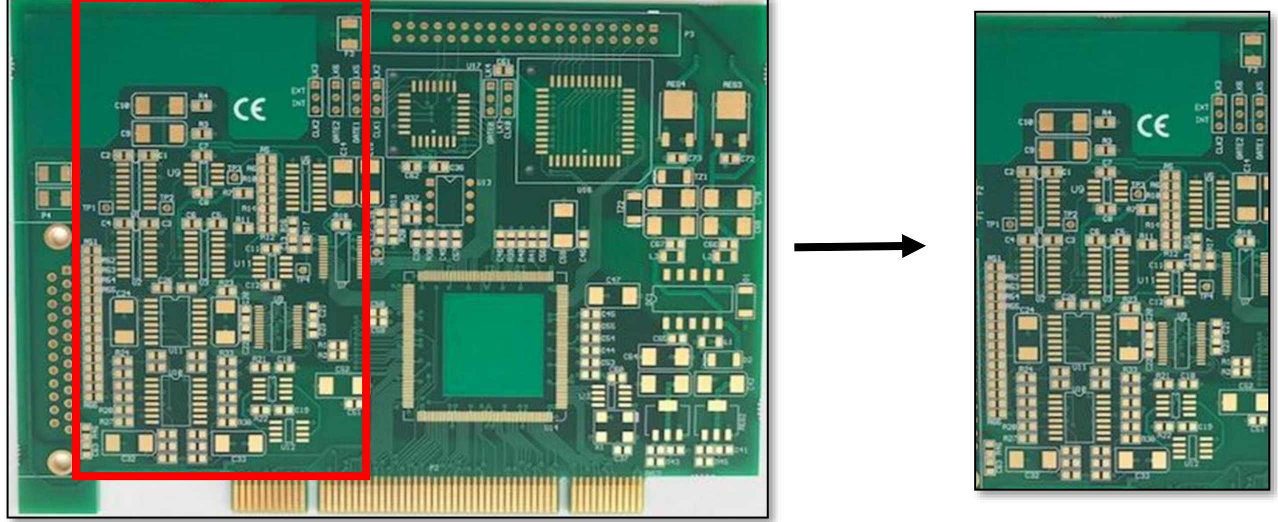
- Particle Mineralogical Analysis (PMA) – detailed particle information, important analysis for PCBs to identify any pure gold or a nickel-gold alloy.

- Trace Mineral Search (TMS) – detailed particle information on traced spots (e.g. Au, Ni) Field scan – detailed mapping of larger samples to see which elements were on a specific spot.

In this study, field images of 4000, 2500, 2000 and 1500 µm were made with FEG Steps of 25 microns. The field size determines the magnification that is used. The step size is essentially the pixel sizes being used in creating the new mineral map. A false colour map is created for each particle; each colour represents a mineral or chemical grouping.

Sample Preparation
The part of the circuit board that was scanned is shown in Figure 3.11:

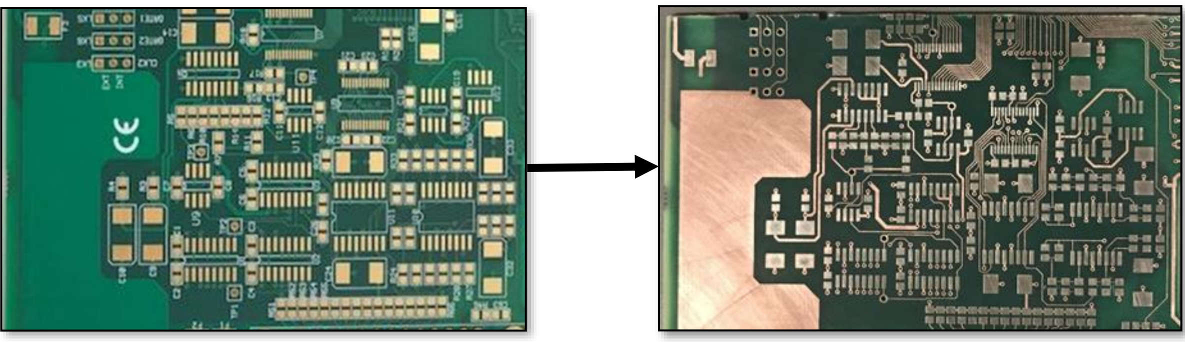
Figure 3.11: Section of the PCB used for QEMSCAN



QEMSCAN only scanned the surface and therefore to get more information about the inner layers of the board, the board was polished using sandpaper to expose the copper layer below the mask. The ink mask stayed intact where there was no copper underneath but all the mask that covered the copper got removed.

Figure 3.12is an image of the piece of PCB that was polished to expose the some of the top copper layer.

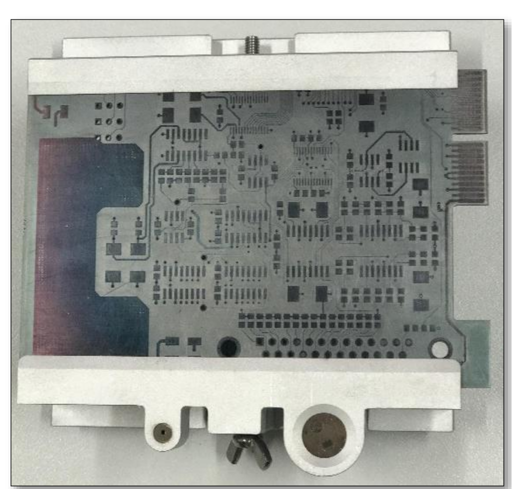
Figure 3.12: Unpolished to Polished



Before the QEMSCAN can be used to analyse the board, the PCB needs to be carbon coated. Coating of samples is required to enable or improve the imaging of samples. Firstly, ethanol is used to clean any dirt and dust on the PCB. The PCB sample is then put in a Quorum carbon coater and is coated in a thin coating of carbon. The carbon coating is important as it disperses the electron charge building up from the electron beam. The PCB pieces are then put in the rough rock holder (RRH) and that is then put into the vacuum chamber of the QEMSCAN.

Figure 3.13 shows the polished PCB piece that is covered in graphite and put in a rough rock holder (RRH).

Figure 3.13: PCB Coated in Graphite



The downside of QEMSCAN is that only a small piece of the board could be scanned at a time due to the size of the rough rock holder. Additionally, QEMSCAN only has surface detection therefore any materials below the surface cannot be detected. That poses a limitation to how much information can be obtained.

3D X-Ray Computed Tomography Scan

X-ray computed tomography can be defined as a non-destructive technique for visualizing interior features within solid objects, and for obtaining digital information on their 3D geometries and properties (DTIC, 2014). The digital x-ray scanner is mounted and rotates producing 2D panoramic views of the object being scanned. These 2D images are stacked together as slices in the x, y and z axes forming the 3D image of the object. The resolution is dependent on how far the image is from the x-ray source and how big the object is. The smaller the object and the shorter the distance to the source is, the higher the resolution and vice versa. In this study, 3D x-ray CT scan is used to determine the distribution of metals on the PCB.

The PCB was cut into 5cm x 5cm pieces in a bid get a higher resolution. Two of the pieces were also scanned after leaching to compare with the images before Leaching. Each PCB piece was scanned using the settings in Appendix A. The results where filtered to only show the threshold corresponding mostly to copper (155 to 255). This therefore means that most of the metallic parts shown in the 3D images is copper. The voxels that represent copper were then taken note of for each layer.

The model and settings

The XT Software, SuitBuild XT 3.1.9 (Copyright © 2004-2013 Nikon Metrology NV), Version=V3.1.5071.19115 was used. The settings used to scan the PCBs are in Appendix A.

Aqua Regia Leach

The previous methods discussed showed the qualitative composition of the printed circuit boards (PCBs) and detailed on the distribution of the materials on the PCBs. However, they did not give an accurate quantitative analysis of the PCBs since the imaging cannot differentiate the materials accurately for instance, the 3D x-ray cannot distinguish between the non-metals and air due to their low density. To get the accurate composition of the board, aqua regia leaching was used. The composition determined by this method will be used as the head grade of the PCBs.

The Experimental Setup

The experiments were set up in a fume hood. The leaching was done in conical flasks and each conical flask sat on a hot plate that also works as a magnetic stirrer. In each flask there is a thermometer to measure the temperature.

The Leaching Process

The experiment was carried out as follows:

Preparation of the PCB samples:

1) 1 PCB (15cm x 10cm) was cut into 2 cm x 1.5 cm pieces using a band saw
2) The PCB pieces were put in a ring mill to be pulverised
3) The pulverised samples were split into 4 using a splitter (each of the 4 samples were leached separately and all the powder was recovered)

Preparation of the Aqua Regia Solution (done in a fume hood):

4) 10 M HCl (Merk) and 11 M HNO_3 (Merk) were mixed in the ratio of 4:1 (HCl to HNO_3)
5) The mixture was mixed with a stirrer until it was pale green (the pale green solution is the aqua regia).

Running the experiment (done in a fume hood):

6) 55 ml of the aqua regia was used for every 1g of printed circuit board (solid liquid ratio of 1g per 55 ml)
7) The mixture of the PCB powder and aqua regia was mildly stirred to ensure the lixiviant reaches all the solids.
8) The temperature was monitored not to exceed 60 °C by adjusting the hotplate
9) The experiment was stopped 15 minutes after the green/yellow fumes stopped forming which indicated that the reaction was done.
10) The residue was filtered out. And left to air dry
11) The dried residue was analysed using X-ray Fluorescence (XRF).
12) Samples of the clear green solution were taken for analysis using Atomic absorption spectroscopy (AAS).

Summary of the AAS analysis in the lab

The samples were filtered using 0.2 μm filters and diluted to a suitable concentration and subsequently analysed using AAS. AAS uses the absorption of optical radiation (light) by free atoms in the gaseous state to quantitatively determine chemical species. To prepare the ten times dilution, 2 wt% nitric acid (HNO3) is employed to dilute a one ml of sample to ten ml. For the 100 ml dilution, series dilutions are prepared from the previous dilution. For copper analysis, element standards of 0.2, 0.5, 1, 2, 5 and 10 ppm copper are used for calibration. The

samples containing 1 and 5 ppm, are used to confirm that the calibration is acceptable. The emission line is chosen for each element based on a high intensity signal.

Objective 2: Pre-treatment Methods

In this study, eight different pre-treatment methods were compared. Most of these methods are from literature and some were developed as a way to liberate copper on PCBs using somewhat primitive methods and consuming relatively less energy. This chapter summarises the individual pre-treatment methods and the diagnostic leach conditions that were used for the comparison.

Pre-treatment Reagents Preparation

The only chemical used for some of the pre-treatment methods of the printed circuit boards (PCBs) is NaOH. It was prepared as follows:

1) 80 g of NaOH (Merk) pellets was measured (to make ~2 M NaOH)
2) The 80 g of NaOH pellets were transferred to a 1000 ml (1 L) Volumetric Flask
3) Deionised water was added to the volumetric flask until it reached the 1000 ml mark.
4) Adding water was done while mixing the solution with a magnetic stirrer.
5) The solution was mixed until it was clear and until the temperature was at room temperature.

Method 1

The first method (Method 1) was done by taking the custom-made PCB and cutting it into 5cm x 5cm pieces using a band saw. There was no significant material loss.

Figure 3.16 shows PCB pre-treated by method 1

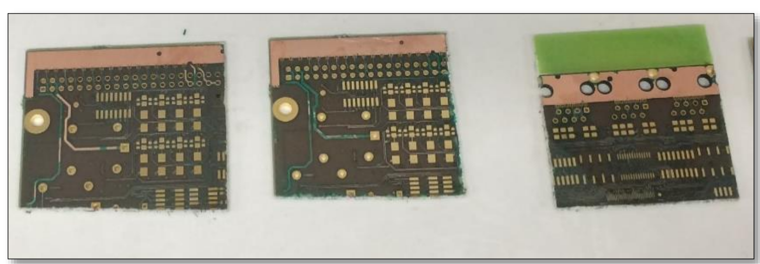
Figure 3.14: PCB Pre-treated by Method 1

Method 2

1) A band saw was used to cut the board into six equal pieces which are 5cm x 5cm.
2) The 5cm x 5cm board pieces were soaked in 200 ml of 2 M NaOH for 24 hours at 40 °C. This method is similar to the one used by Jadhav and Hocheng (2015).
3) After soaking the board pieces in NaOH, they were washed with water until all the top coating made of green epoxy washed off.
4) The PCB pieces were then left to air dry

All six pieces that make up one whole PCB were treated using method 2 and Figure 3.15 is an image of some of the pieces after the pre-treatment.

Figure 3.15: PCB Pieces Pre- treated by Method 2

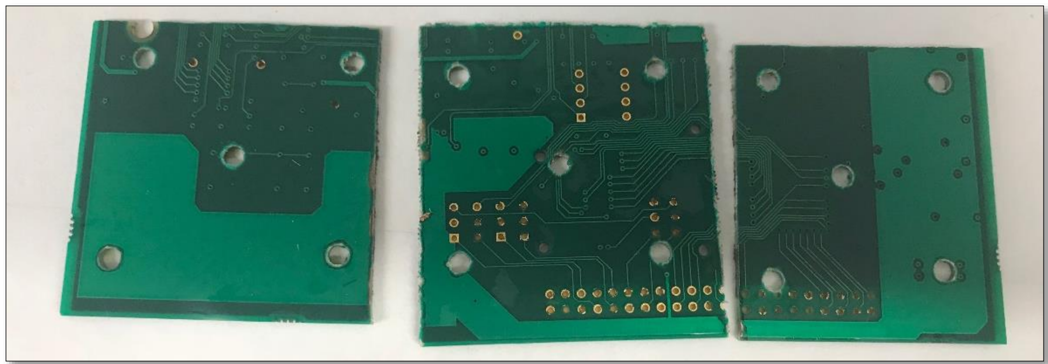


Method 3

1) A band saw was used to cut the PCB into six equal pieces which are 5 cm x 5 cm.
2) Each 5 cm x 5 cm Board piece was drilled 5 times with a 3.5 mm drill bit. One hole at each of the four corners and one at the centre.

The whole PCB was cut and drilled. Figure 3.18 shows some of the PCB pieces that were cut and drilled.

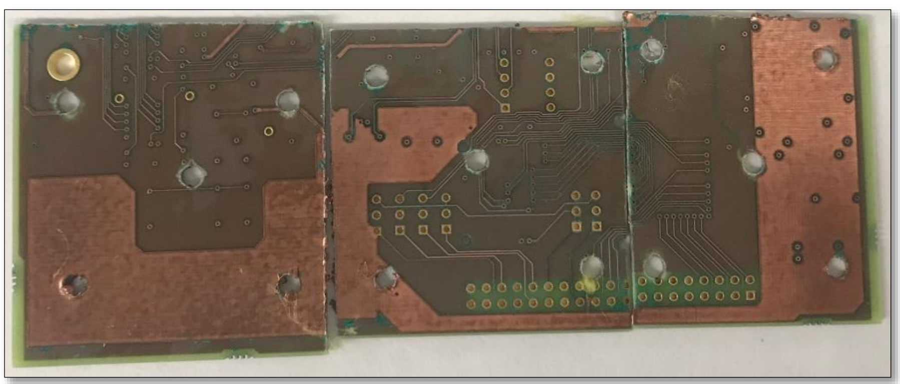
Figure 3.16: PCB Pieces that are cut & Drilled



3) The 5 cm x 5 cm board pieces were soaked in 200 ml of 2 M NaOH for 24 hours at 40 °C.
4) After soaking the PCB pieces, they were washed with water removing the top coating made of green epoxy.
5) The PCB pieces were then left to air dry.

Figure 3.19 shows some of the board pieces that were pre-treated using Method 3

Figure 3.17: PCB Pieces Pre- treated by Method 3



Method 4

1) A band saw was used to cut the custom-made PCB into 50 pieces which are 2 cm x 1.5 cm each.

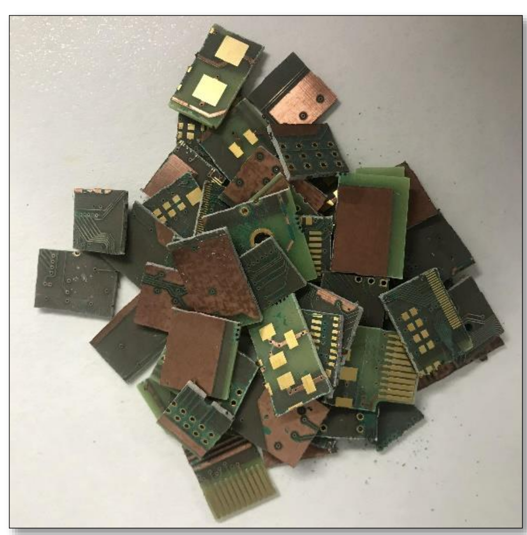
Figure 3.18 is an image of some pieces of a PCB cut into 2 cm x 1.5 cm pieces

Figure 3.18: PCB cut into 2cm x 1.5cm pieces

2) The 2cm x 1.5cm board pieces were soaked in 200 ml of 2 M NaOH for 24 hours at 40 °C
3) After soaking the PCB pieces, they were washed with water until all the top coating made of green epoxy washed off.
4) The board pieces were then left to air dry

Figure 3.19 is an image showing PCB pieces after pre-treated with Method 4

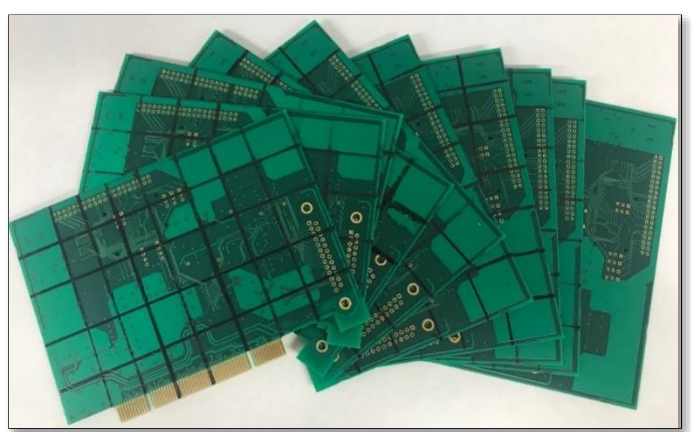
Figure 3.19: PCB after Pre-treatment with Method 4



Method 5

1) A saw was used to cut 10 boards into equal pieces which are 2 cm x 1.5 cm. Each Board had 50 each.

Figure 3.20: 10 PCBs cut into 2cm x 1.5cm Pieces



2) The 500 pieces which are 2 cm x 1.5 cm were then put into a hammer mill to further reduce the size.

Figure 3.21 is an image of the PCBs after size reduction in the hammer mill

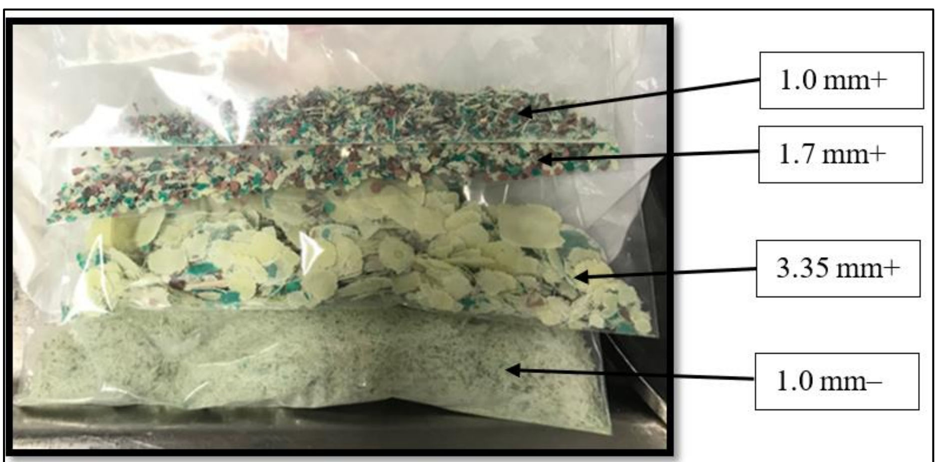
Figure 3.21: PCBs after Size Reduction in a Hammer Mill

3) The shredded sample had different size particles and was put in a sieve to separate the different size particles.
   The following sieve sizes were used:
   - 3.35 mm
   - 1.7 mm
   - 1.0 mm

   There were 4 different samples with the following size distribution:
   - 3.35 mm+
   - 1.7 mm+
   - 1.0 mm+
   - 1.0 mm–

Figure 3.22 is an image of the 4 different size samples

Figure 3.22: PCBs Shredded to 4 different size



4) Each of the 4 shredded samples of different particle sizes was put into a splitter and split into 10 equal samples. This resulted in each size distribution having 10 equal samples each.

5) A sample from each size distribution was mixed with a sample from the other size distributions to make 10 mixed samples with all size particles.
6) Each of the 10 mixed samples represented one full shredded board.

Method 6

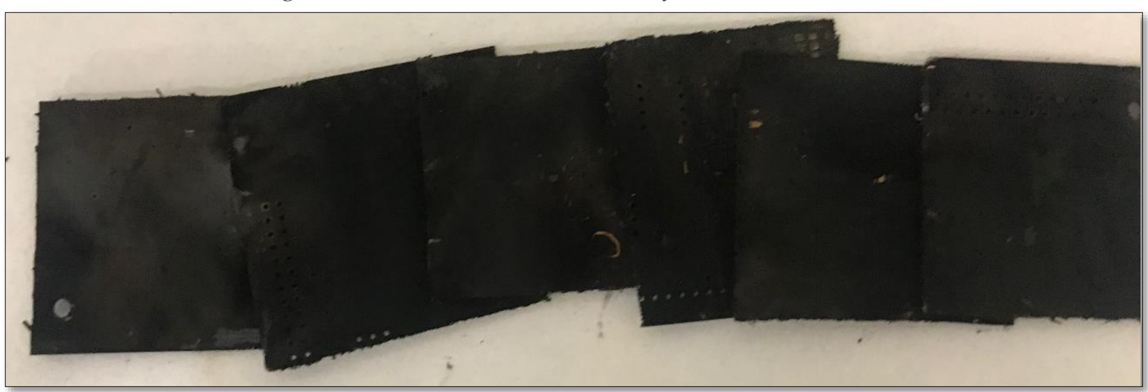
1) From Method 5, three mixed samples which represented 3 full shredded boards were taken.
2) Each shredded board sample was put in a ring mill for pulverisation.

Method 7

1) A saw was used to cut the board into six equal pieces which are 5 cm x 5 cm.
2) The PCBs were heated using a Bunsen Burner in a fume hood. Each piece was put in an open flame for 5 minutes each and they were held using tongs.

Figure 3.23 is an image of one board that was burnt in an open flame.

Figure 3.23: PCB Pre-treated by Method 7



Method 8

1) A band saw was used to cut the board into six equal pieces which are 5 cm x 5 cm.
2) The board pieces were put in a crucible and heated using a Bunsen Burner in a fume hood. This was to ensure that all the smoke that can be produced from heating the board is released.

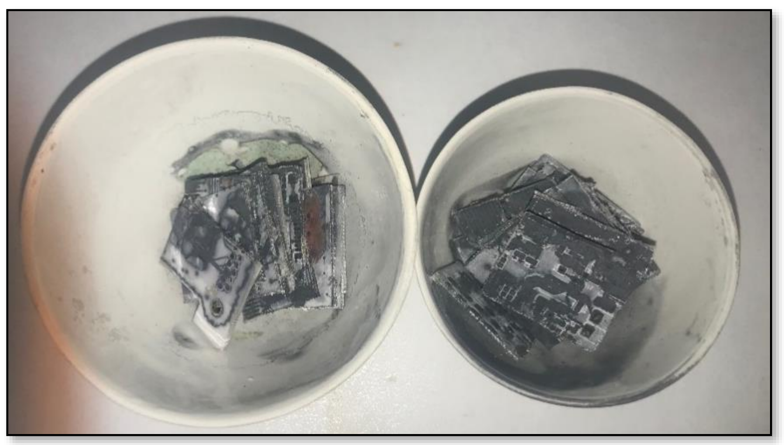
Figure 3.24 is an image of the PCB pieces being burnt in a crucible

Figure 3.24: PCB being Burnt in Crucible

3) The board pieces were then placed in a Labofurn furnace for further heating at 200 °C for an hour.

Figure 3.25 is an image of 2 PCBs after being pre-treated with Method 8.

Figure 3.25: 2 PCBs Pre-treated with Method 8



Diagnostic Leach test

To compare the effectiveness of each pre-treatment method, a diagnostic copper leach was done on the PCBs.

Making the Lixiviant

1) 264.28 g of Ammonium Sulphate was measured and put in a 1000 ml volumetric flask.
2) 0.392 g of Copper Sulphate Pentahydrate were measured and added to the 1000 ml volumetric flask containing the ammonium sulphate from step 1.
3) Using a measuring cylinder 298.4 ml of 25% Ammonia Solution (Merk) was measured and put in the 1000 ml (1 L) Volumetric Flask containing ammonium sulphate and copper sulphate from step 2.
4) Deionised water was added to the mixture in the 1000 ml volumetric flask from step 3. The mixture was mixed with a magnetic stirrer until the solids dissolved and the solution was clear and blue.

Table 3.1 summarises the diagnostic conditions:

Table 3.1: Diagnostic Leach Conditions

Parameter	Condition
25% Ammonia Solution (Merk) Concentration	4 M
Ammonium Sulphate (Merk) Concentration	2 M
Copper Sulphate (Merk) Concentration	~100 ppm
Temperature	25 °C
pH	8 - 11
Agitation	500 rpm
Volume	1000 ml
Liquid: Solid Ratio	1000 ml per PCB (~50 g), 20:1
Time	120 hrs+

The Copper Leaching

1) 1L of the lixiviant was transferred to a jacketed glass reactor.
2) The jacketed reactor was connected to a water bath and the temperature of the circulating water was set at 25 °C.
3) An overhead stirrer was put in the reactor to mix up the reactor contents. It was set at 1 which is equivalent to 500 ppm.
4) Some air was bubbled in the reactor using a small rubber pipe at a flowrate more than 5ml/min.
5) The set-up was left that way until the lixiviant in the reactor reached 25 °C.
6) A sample of the lixiviant was taken so that the Cu content and pH could be measured to know the starting point (blank solution).
7) When the lixiviant in the jacketed glass reactor reached 25 °C, the pre-treated boards were added to the reactor.
8) Samples of the lixiviant (~10 ml) were taken after short time intervals (between 5minutes to 1 hour) which got progressively longer in the first 3 hours.
9) Thereafter, samples were taken after progressively longer time intervals (between 2 and 24 hours) until it went down to once per day.

10) The copper content of the samples was analysed using AAS or ICP-OES depending on the expected concentration range of the sample.
11) The pH was measured and kept between 8 and 11 by adding about 150 ml ± 50 ml of 25% ammonia solution (Merk) to the reactor.
12) The volume of the reactor contents was also kept at 1000 ± 10 ml.
13) The Leaching Process ended after at least 120 hrs.
14) The PCB was then removed from the lixiviant and washed with deionised water.
15) The leach residue was then left to dry.

Experimental Setup

Below is figure 3.26 showing the schematic diagram of the experimental set-up

Figure 3.26: Schematic Diagram of Experimental Set-up

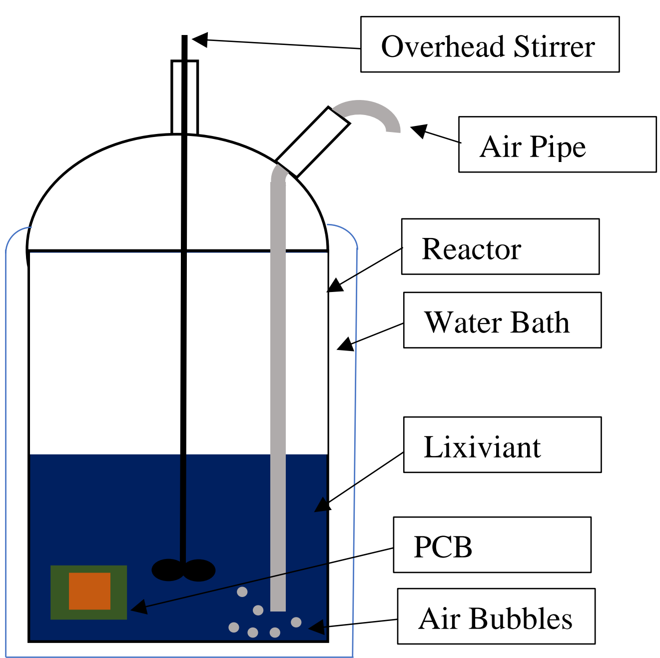
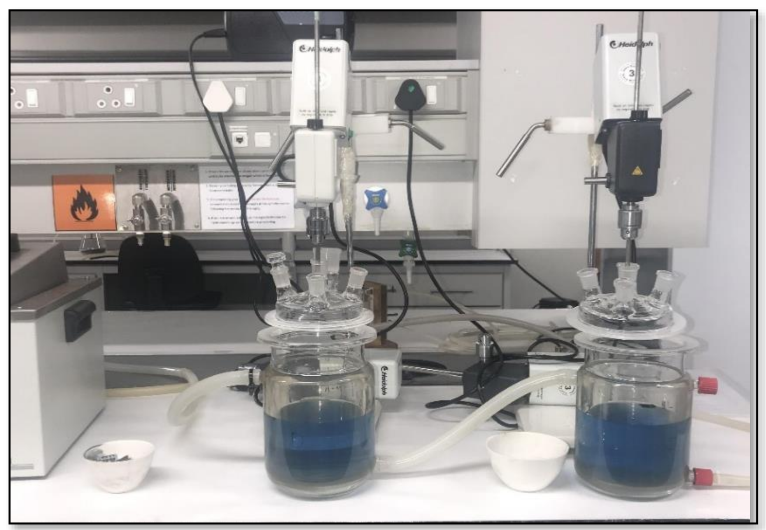


Figure 3.27: Experimental Setup for Diagnostic Leach shows the experimental set-up before leaching (left) and after leaching (right):

Figure 3.27: Experimental Setup for Diagnostic



Objective 3: Optimisation of the Leaching Parameters

Parameter 1: Type of Salt

The first parameter to be changed was the type of ammonium salt. Ammonium carbonate was to be used since it has high recoveries in literature. The leaching conditions stayed the same except for the salt. Samples were taken for analysis by AAS throughout the experiments.

Making the Lixiviant

1) 192.12g of Ammonium Carbonate was measured and put in a 1000ml volumetric flask.
2) 0.392g of Copper Sulphate Pentahydrate were measured and added to the 1000ml volumetric flask containing the ammonium sulphate from step 1.
3) Using a measuring cylinder 298.4 ml of 25% Ammonia Solution (Merk) was measured and put in the 1000 ml (1 L) Volumetric Flask containing ammonium sulphate and copper sulphate from step 2.
4) Deionised water was added to the mixture in the 1000 ml volumetric flask from step 3. The contents of the volumetric flask were then mixed with a magnetic stirrer until the solids dissolved and the solution was clear and blue.

Leaching Conditions

Table 3.2: Leach Conditions; Changing the salt

Parameter	Condition
25% Ammonia Solution (Merk) Concentration	4 M
Ammonium Carbonate (Merk) Concentration	2 M
Copper Sulphate (Merk) Concentration	~100 ppm
Temperature	25 °C
pH	8 - 11
Agitation	500 rpm
Volume	1000 ml
Liquid: Solid Ratio	1000 ml per PCB (~50g) = 20:1

Parameter 2: Ammonia Concentration

Making the Lixiviant

1) 192.12g of Ammonium Carbonate was measured and put in a 1000 ml volumetric flask.
2) 0.392g of Copper Sulphate Pentahydrate were measured and added to the 1000 ml volumetric flask containing the ammonium sulphate from step 1.
3) Using a measuring cylinder, 410.3 ml of 25% Ammonia Solution (Merk) was measured and put in the 1000 ml (1L) Volumetric Flask containing ammonium sulphate and copper sulphate from step 2 to make 5.5 M solution. For the 7 M solution, 522.2 ml of 25% Ammonia Solution (Merk) was used instead.
4) Deionised water was added to the mixture in the 1000ml volumetric flask from step 3. The mixture was mixed with a magnetic stirrer until the solids dissolved and the solution was clear and blue.

Leaching Conditions

Every other parameter was kept the same except for the ammonia concentration and the conditions were as follows.

Table 3.3: Leach Conditions; Changing NH3 Concentration

Parameter	Condition
25% Ammonia Solution (Merk) Concentration	Varied (5.5 M and 7 M)
Ammonium Carbonate (Merk) Concentration	2 M
Copper Sulphate (Merk) Concentration	~100 ppm
Temperature	25 °C
pH	8 - 11
Agitation	500 rpm
Volume	1000 ml
Liquid: Solid Ratio	1000 ml per PCB (~50 g) = 20:1

The following ammonia concentrations were compared:

1) 4 M
2) 5.5 M
3) 7 M

Samples were taken for analysis by AAS throughout the experiments.

Parameter 3: Liquid: Solid Ratio

Making the Lixiviant

1) 192.12 g of Ammonium Carbonate was measured and put in a 750 ml volumetric flask. A 500 ml volumetric flask was used for the 500 ml to 50 g liquid to solid ratio (LTSR).
2) 0.392 g of Copper Sulphate Pentahydrate were measured and added to the 750 ml volumetric flask containing the ammonium sulphate from step 1. A 500 ml volumetric flask was used for the 500 ml to 50 g LTSR.
3) Using a measuring cylinder 298.4 ml of 25% Ammonia Solution (Merk) was measured and put in the 700 ml Volumetric Flask containing ammonium sulphate and copper sulphate from step 2. A 500 ml volumetric flask was used for the 500 ml to 50 g LTSR.

4) Deionised water was added to the mixture in the 750 ml volumetric flask from step 3. The mixture was mixed with a magnetic stirrer until the solids dissolved and the solution was clear and blue. A 500 ml volumetric flask was used for the 500 ml to 50 g LTSR.

Leaching Conditions

All the other parameters were kept constant except liquid solid ratio. The Conditions were as follows:

Table 3.4: Leach Conditions; Changing Liquid to Solid Ratio

Parameter	**Condition**
25% Ammonia Solution (Merk) Concentration	4M
Ammonium Carbonate (Merk) Concentration	2 M
Copper Sulphate (Merk) Concentration	~100 ppm
Temperature	25 °C
pH	8 - 11
Agitation	500 rpm
Volume	Varied (750 ml and 500 ml)
Liquid: Solid Ratio	Varied (15:1 and 10:1)

The volume of liquid per PCB was

1) 1000ml
2) 750ml
3) 500ml

Samples were taken for analysis by AAS throughout the experiments.

4. RESULTS AND DISCUSSION

Overview of Results

The findings are laid out such that they align with the main three objectives and the approached laid out in the methodology chapter.

2. *Characterise the Printed Circuit Boards and measure the composition of the board.*

Results Shown and Discussed:

- The blueprint from the manufacturing process
- The QEMSCAN images of the printed circuit board
- The 3D X-ray CT Scan Images of the Boards
- The head grade of the Printed circuit boards after leaching with aqua regia

4. *Compare different pre-treatment methods and choose the most suitable.*

Results Shown and Discussed:

- The leaching curves of the 8 different pre-treatment methods explored
- Comparison of other factors to choose the optimal pre-treatment method

5. *Use the best pre-treatment method to optimize the copper leaching process.*

Results Shown and Discussed:

- The leaching curves for the different parameters used

Objective 1: Characterising the Printed Circuit Boards

QEMSCAN

Before classifying the pixels and making a new mineral list, the field image looked like a chaos of coloured pixels. After carefully classifying the pixels, the field images looked like the blue print of the PCB (Figure 3.10).

Unpolished PCB piece

The first PCB to be scanned was the board that was not polished, and it therefore only showed the surface. The surface of the PCB consists of only the mask.

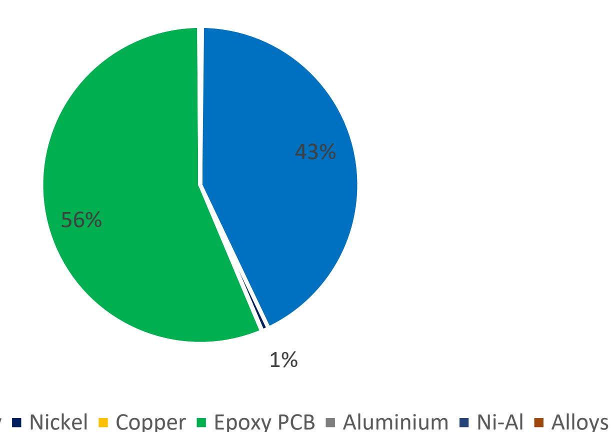
The unpolished PCB piece looked like the image in Figure 4.1

(25micron spacing, 70 x 60 field image)

Figure 4.1: QEMSCAN Image of Unpolished PCB Piece

The unpolished PCB piece has the distribution shown in figure 4.2

Figure 4.2: Material Distribution on an Unpolished PCB Piece



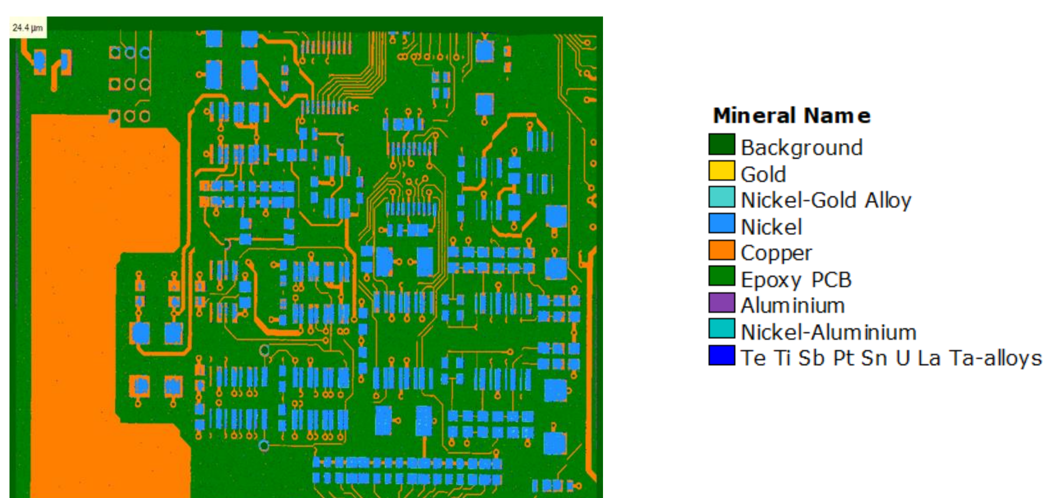
The QEMSCAN image in figure 4.1 shows that the surface mostly contains epoxy (green) and the Nickel- Gold Alloy (Blue). The presence of the Nickel Gold alloy is as expected and agrees with how the PCB was made thus electroplated with nickel and then with gold for the protection of copper. It shows that the epoxy covers 56% of the surface while the alloy covers 43%. The rest of the surfaces are traces of Nickel (1%) and other alloys of various metals.

The unpolished PCB is comparable to the blueprint of the PCB. QEMSCAN is not as accurate and it misses some details, but it shows the general distribution of the materials on the surface of the PCB.

Polished PCB Piece

After polishing the PCB piece, the top copper layer was exposed as shown in figure 4.3

Figure 4.3: QEMSCAN Image of the Polished PCB Piece



The distribution of the polished PCB piece is shown in figure 4.4

Figure 4.4: Material Distribution on the Polished PCB Piece

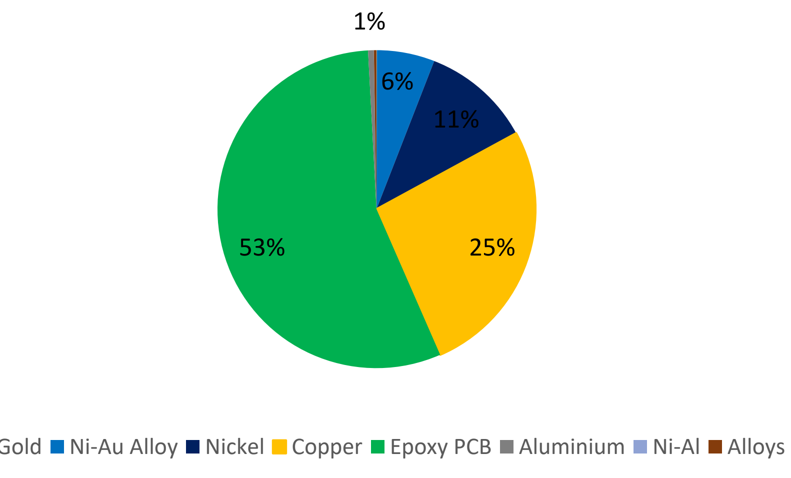
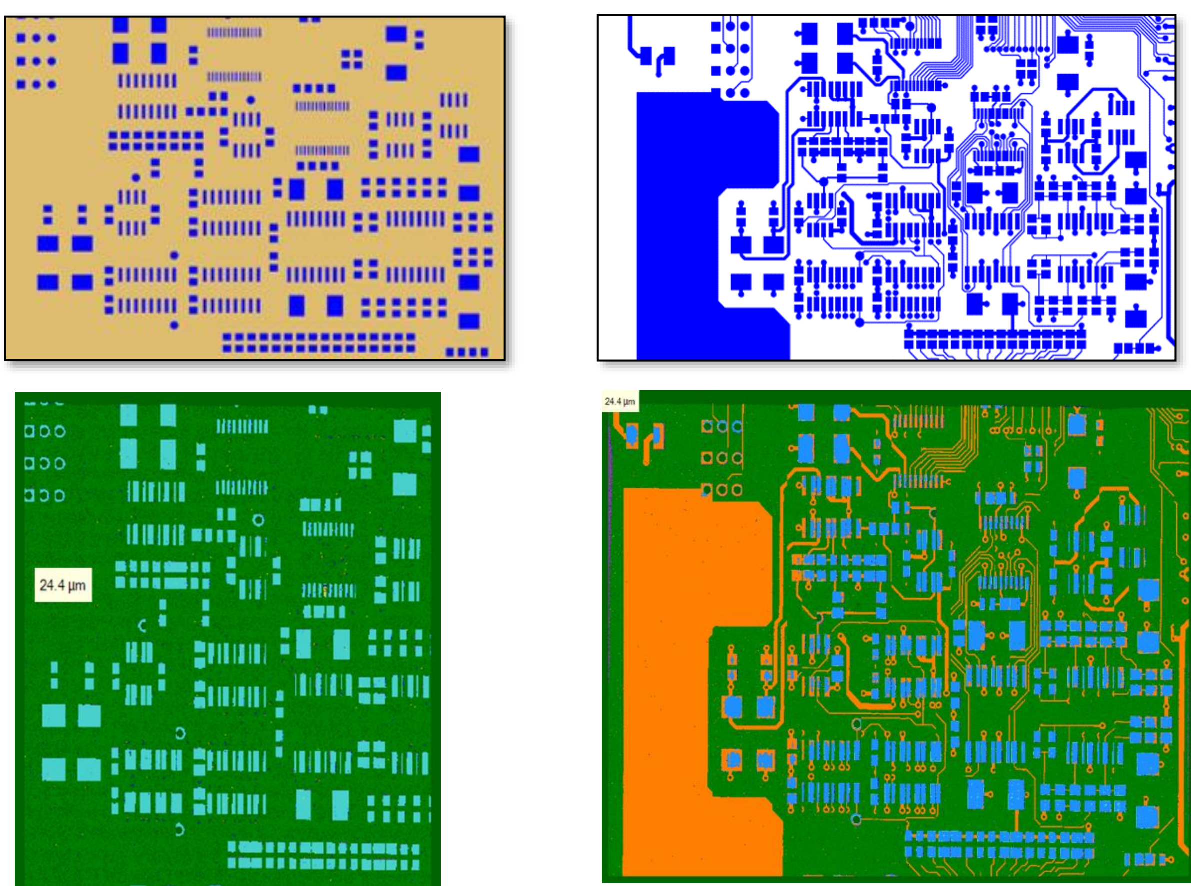


Figure 4.5 is the blueprint of part of the board that was scanned unpolished (right) and polished (left)

Figure 4.5: Comparison between the blueprint (top) and QEMSCAN image (bottom) for 2 sections of the PCB



The QEMSCAN images have a different aspect ratio when compared to the blueprint but they look very similar in the details shown.

The polished PCB revealed more about the layer below the mask. It exposes part of the top copper layer. The distribution of the materials shows that there is 53% epoxy, 25% copper, 11% nickel, 6% nickel- gold alloy. The rest are traces of aluminium (1%), gold and other alloys.

The epoxy went down from 56% to 53% because some of it was removed in the polishing process. There are also inaccuracies that may have resulted in less epoxy being detected by the QEMSCAN for instance it possible that the QEMSCAN also detected some FR4 as epoxy. Additionally, more copper is visible and contributes to 25% of the surface.

In the unpolished PCB, the nickel-gold alloy had been covering the copper to protect it from oxidation. The percentage of the Ni- Au alloy went from 43% on the unpolished PCB to 6% on the polished PCB. After the PCB was polished, the sandpaper removed most of the Ni- Au alloy to expose the copper.

During the manufacturing process, the nickel and the gold are electroplated separately and not as an alloy. The nickel is put first then the gold is electroplated onto the nickel. When the PCB

got polished, more nickel got exposed. Although the aim was to remove it all and expose the copper, some of it remained visible because the sand paper did not remove it all. This explains why there is only 1% nickel that is visible on the unpolished PCB and there is 6% nickel on the polished PCB.

Other materials on the PCB

Other materials on this custom-made PCB are residues such as aluminium. The traces may be due to the fact that the PCBs are aligned with an aluminium frame when they are being drilled in the manufacturing process. Additionally, there are traces of metals like tin which is used to protect the desired copper during etching. Other traces of impurities can be traced back to upstream processes of the manufacturing process of the board that are beyond the scope of this study.

Limitations of the Results

QEMSCAN gives insufficient information and cannot adequately characterise the PCBs. One of the limitations is the size of the PCB that can be scanned at a time. Since the material distribution of the PCB is not uniform across the PCB, a small potion if the board is not representative of the full board.

Another drawback is the fact that QEMSCAN only analyses the surface of the PCB and does not penetrate to the inner layers in the case of multi-layered PCBs. The PCBs in the study has 4 copper layers but with some board polishing, only 1 layer could be partially analysed with QEMSCAN.

3D X-ray CT Scan

Since the PCBs were scanned in 5cm x 5cm pieces, this meant that there are 6 pieces see Appendix B. All of them were scanned to get a collective semi-qualitative and semi-quantitative result about the copper distribution. Only one piece of the PCB (piece 5) was pre-treated and studied further after leaching. A similar PCB piece (piece 5) was also pre-treated with a different pre-treatment method and studied afterwards with 3D XCT Scan to determine where the copper is leached. For this reason, although there are 6 pieces, the image of piece 5 is shown last for easier comparison with the leached pieces from a similar Boards which are also piece number 5.

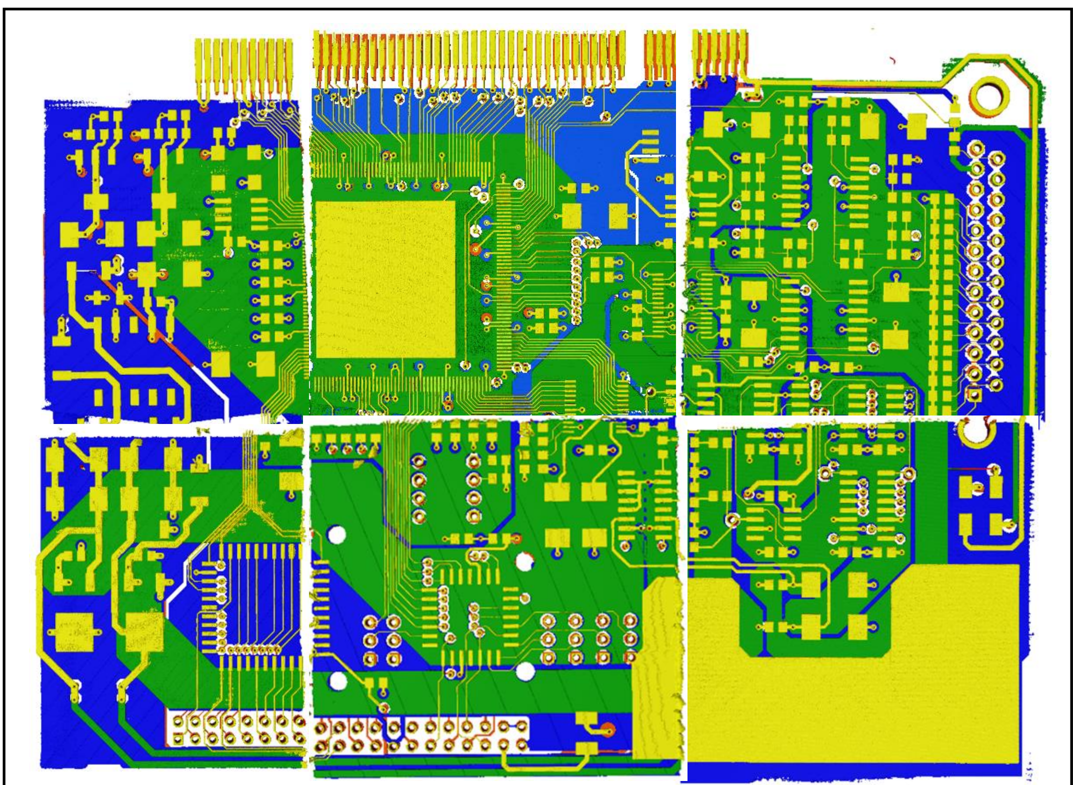
3D X-ray CT Scan results are shown below.

Key

The full PCB

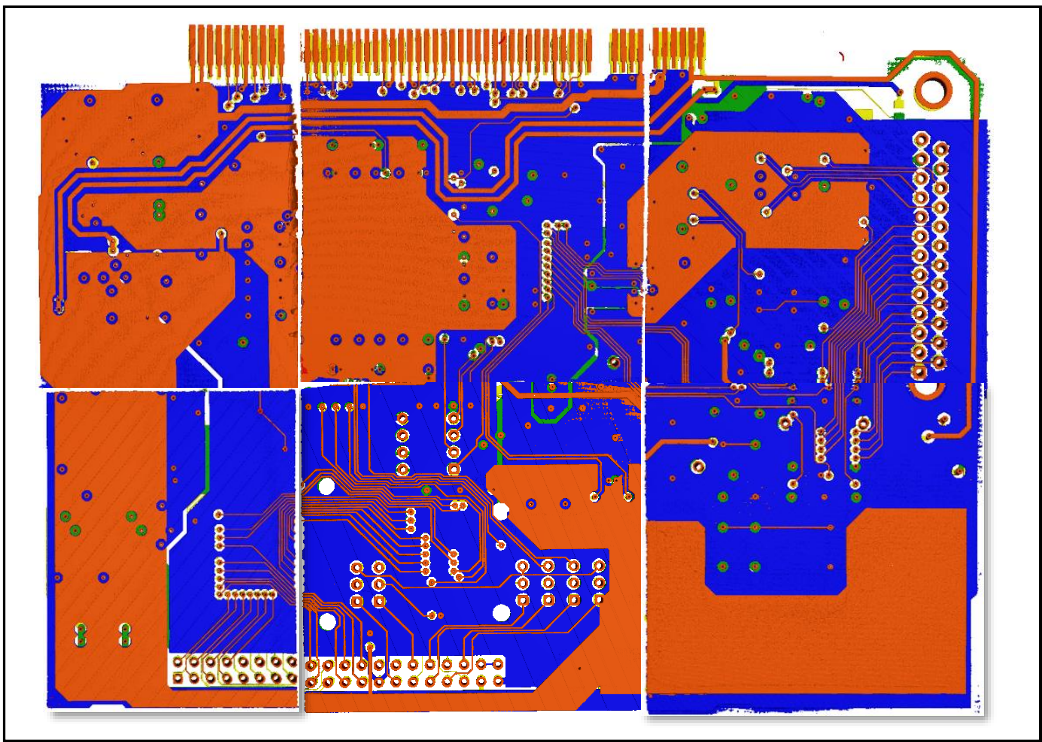
The full board made up of the individual pieces joined at front in figure 4.6 (piece 5 – top middle)

Figure 4.6: 3D CT Scan of Front of PCB



The full board made up of the individual pieces joined at the back in figure 4.7 (piece 5 – top middle)

Figure 4.7: 3D CT Scan of Back of PCB

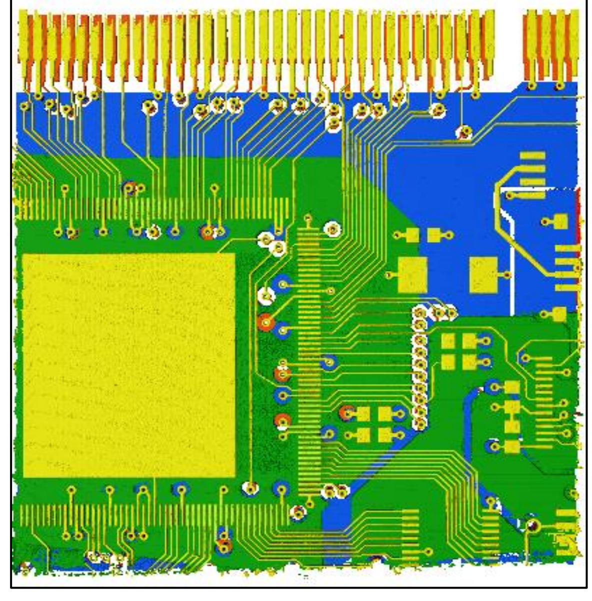


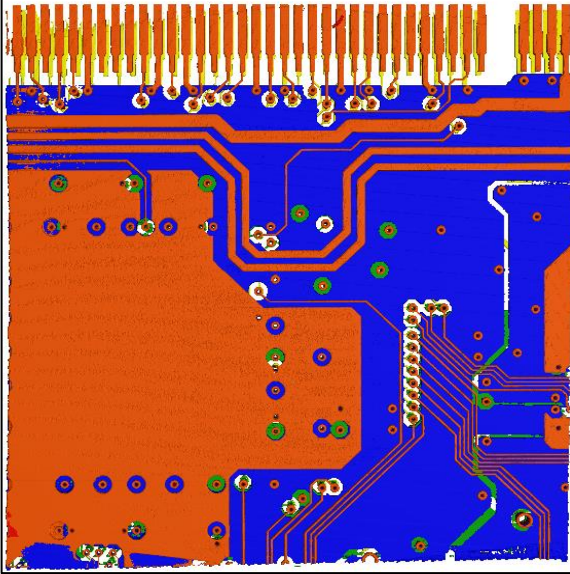
Although the 6 images of the PCB pieces do not perfectly stitch together, the combined image looks similar to the blueprint (figure 3.10) and the actual PCB (figure 3.5 and figure 3.6). Metals, particularly copper, form the bulk of the PCB as the general shape of the PCB image is not too compromised without the non-metallic parts showing.

All the coloured parts of the 3D XCT scan images are copper because the artificial colours were only applied to a threshold that corresponds to copper. From the images, the 4 layers of copper are clearly visible on all the pieces. These copper layers are held together by fibreglass which is not visible. Non-metals are invisible on the images because their x-ray density is negligible compared to that of metals and hence they are not detected by the equipment. The images only give the general idea of the copper distribution across the layers. The detail and resolution are such that on some pieces, rough edges can be seen due to the cutting that was done to the PCB with a bandsaw. The resolution allows some of the internal structures to be detectable, for instance, the copper that was plated in the walls of holes through the PCB (connectors). In figure 4.9 it is clear that the cylindrical shape of the copper in the connectors can be observed. Moreover, the layers are distinguishable even though they are mostly 17µm thin and practically bonded tightly together.

Pre-treated PCB Piece 5
Image of untreated PCB Piece 5 Front (left) and Back (right) in figure 4.8 below

Figure 4.8: PCB Piece 5

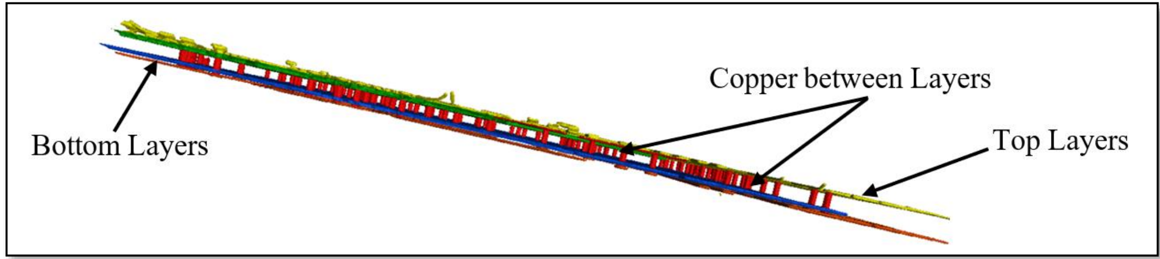




All the PCB pieces have copper between the top and bottom layers. The image below shows the copper in between the top and bottom layers of the PCB piece.

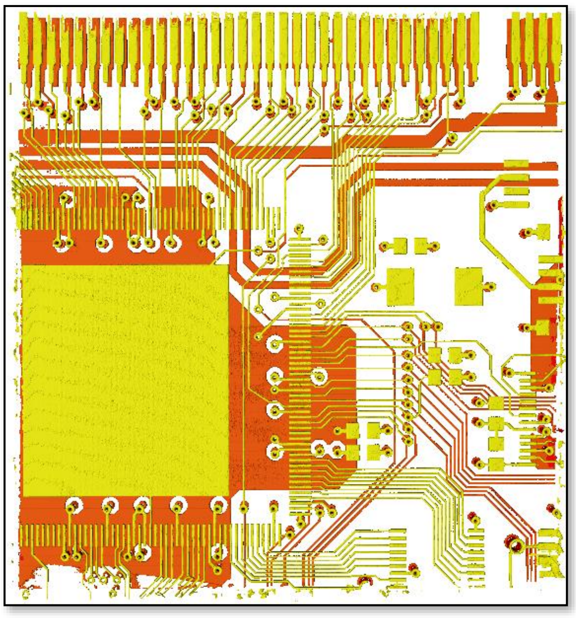
Image of the untreated PCB piece 5 (at an angle) showing the copper between the top and bottom layers in figure 4.9.

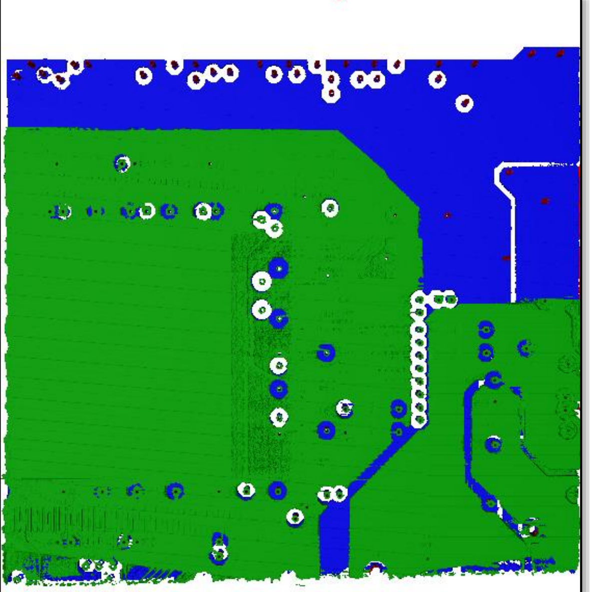
Figure 4.9: PCB Tilted to Show Copper Between Layers



The Outer Layers (Left) and Inner Layers (right) of untreated PCB piece 5 in figure 4.10

Figure 4.10: PCB Outer Layers (left) and Inner Layers (right)

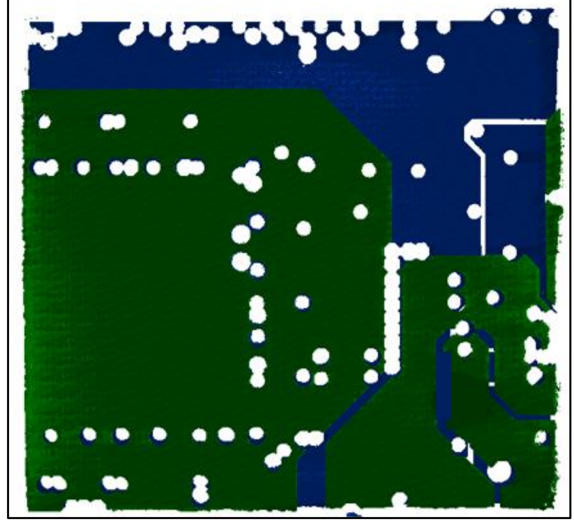




After the PCB shown above was pre-treated with Method 2 (Cut 5cm x 5cm, NaOH treatment) it was leached using the diagnostic leach, the X-ray CT Scan showed the following images (figure 4.11, figure 4.12, figure 4.13 and figure 4.14).

PCB piece 5 pre-treated with Method 2 and leached; Top (left) & Bottom (right) in Figure 4.11

Figure 4.11: PCB Piece 5 Pre-treated with method 2 and Leached



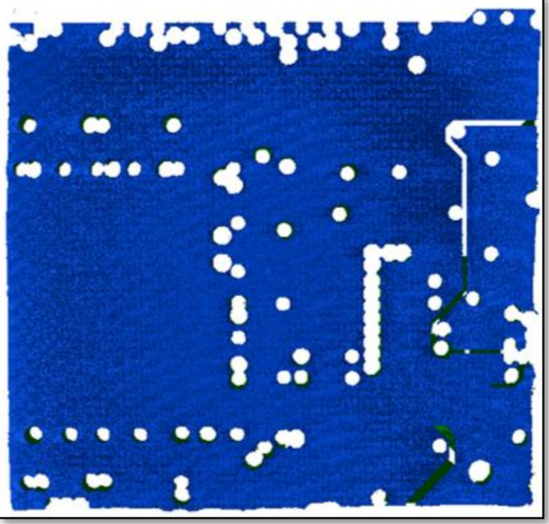


Image of the PCB piece 5 after pre-treatment method 2 and diagnostic leaching showing the no copper between the top inner and bottom inner layer in figure 4.12

Figure 4.12: PCB Piece 5 Pre-treated with Method 2 with no copper between layers

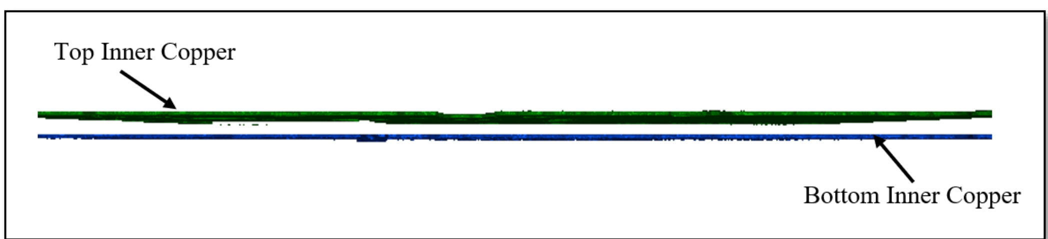
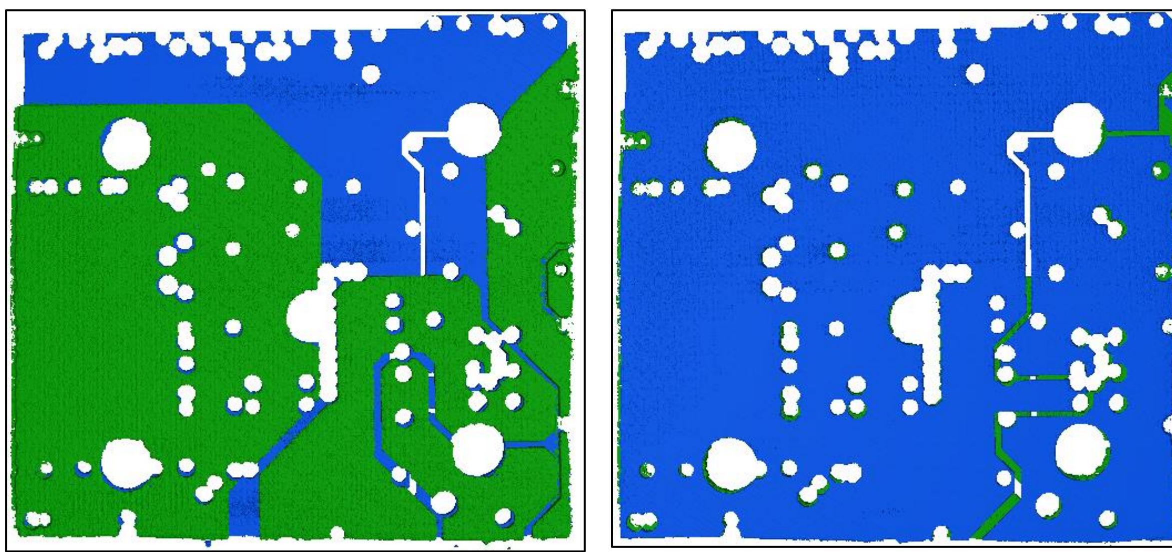


Figure 4.11and 4.12 show that the PCB piece only has 2 layers of copper left after leaching. The top and bottom layers got dissolved in the lixiviant, leaving only the inner layers. The inner layers remained intact since they are covered by the fibreglass. The outer top and bottom layers became exposed when NaOH was used to dissolve the top mask. On figure 4.12, the copper channels between the layers are not visible, meaning that they have been leached.

After a similar PCB piece 5 was pre-treated with Method 3 (Cut 5cm x 5cm, NaOH treatment and drilled) it was leached using the diagnostic leach. The X-ray CT Scan showed the following image.

PCB piece 5 pre-treated with pre-treatment Method 3 and leached Top (Left) & Bottom (right) in figure 4.13.

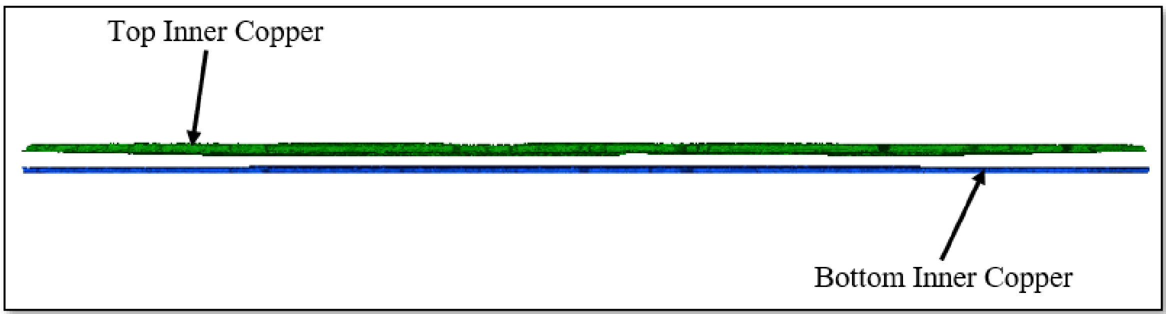
Figure 4.13: PCB Piece 5 Pre-treated with Method 3 and Leached



The 5 holes that were drilled for pre-treatment were measured using a physical vernier calliper as well as using one in the 3D XCT Scan software and both still measure 3.5mm diameter for each hole. It seems there has been virtually no penetration from the holes laterally into the inner layers

Below in 4.14is an image of the PCB piece 5 after pre-treatment method 3 and leaching showing no copper between the top and bottom layer.

Figure 4.14: PCB Piece 5 Pre-treated with Method 3 with no copper between layers



Similar to the PCB pre-treated with method 2, only the inner top and bottom layers are left on the PCB piece. The outer top and bottom copper layers were leached from the PCB piece. The small cylindrical copper structures between the copper layers are also not on the PCB piece as in Figure 4.14. This also means they were dissolved along with the outer copper layers.

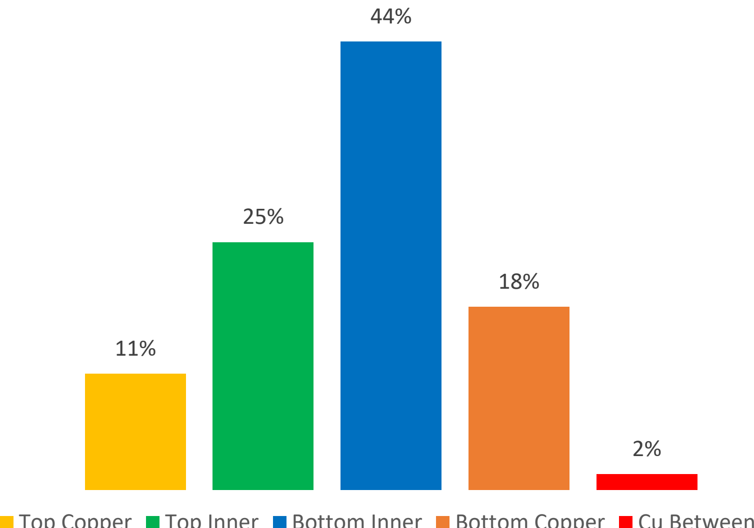
After the PCB piece was leached, the holes were measured again with a physical vernier callipers and the vernier callipers in the 3D XCT scan software. The holes still measure 3.5mm in diameter. This goes to show that the holes had no effect on the leaching of the PCB pieces.

The copper distribution on the PCB

As aforementioned in the methodology chapter, the threshold of the Images was limited to that corresponding to copper. This therefore means that most of the metallic parts shown in the 3D images are copper.

The graph below in figure 4.15 summarises how much copper is on each layer for the whole board.

Figure 4.15: Copper Distribution on the PCB Layers



The voxels that formed each copper layer show how most copper is in the inner layers.

The graph in Figure 4.15 reports that 44% of the copper is on the bottom inner layer. This is then followed by the top inner layer which has a quarter (25%) of the copper. This essentially means that a lot of the copper is on the inner layers of the PCB. Combined, the top and bottom inner layers hold 69% of the copper on the PCB. The outer layers only contain a total of 29% of the copper with 11% on the top and 18% at the bottom. The internal copper between the copper layers is only 2%. About 69% of the copper is covered with RF4 and the rest is only covered by the mask.

The various pre-treatments methods that were tested aim to make all the copper layers accessible. Pre-treatment methods 2 and 3 done on PCB piece 5 do not seem promising because they only exposed the outer layers of copper as well as that in the drill holes. this means that the leached copper is around 32%, i.e. the internal copper (2%), the top (11%) and bottom (18%) copper layers.

3D X-ray CT Scan vs QEMSCAN

Although they both show limited information about the PCB, the 3D XCT scan gives more information than the QEMSCAN. Unlike the QEMSCAN, 3D XCT Scan analyses more than the surface of the board. Combined, they show a much clearer picture of the PCB. The metallic parts are shown in detail from the 3D XCT scan while the top mask is also shown in detail by

the QEMSCAN. Most of the PCB is shown except for the fibreglass which is not shown by either method.

The advantage of the X-ray CT scan is that the sample preparation is simple and there is nothing added or removed from the PCB. For the QEMSCAN, the PCB had to be cleaned with alcohol and coated with graphite. Additionally, the board had to be polished with sandpaper to reveal the top copper layer whereas with 3D XCT Scan, all the layers are visible without any polishing.

The contrast of the 3D XCT images is better compared to that of QEMSCAN. There is more detail that the 3D XCT scan shows that is not shown on the QEMSCAN.

Limitations of the 3D CT Scan

Metals have higher density than the non-metals which essentially makes the non-metals indistinguishable from the background or air around the PCB due to their relatively low density. Consequently, the 3D CT Scan only shows the metallic parts of the board. The metals are also indistinguishable from each other.

Furthermore, with CT Scans, the higher the resolution, the smaller the field view. There is a need to trade off the two. Similar to QEMSCAN, only a small piece of the PCB can be scanned at a time in order to get good resolution.

Aqua Regia Test

The custom-made PCB was dissolved in aqua regia to get quantitative information about the elemental distribution on the board. This was for four different samples and the average was taken, See Appendix C.

Elemental Composition of the PCBs

The following table shows the elemental compositions of the PCB

Table 4.1: Elemental Composition of the PCBs

	Al	Au	B	Ba	Ca	Co	Cu	Fe	K	Mg	Mo	Na	Ni	Pb	Si	Sr	Zn
%	7.37	0.11	1.19	0.31	27.11	1.44	55.45	3.37	0.24	0.36	0.01	0.23	1.57	0.39	0.21	0.10	0.52

Each PCB weighs an average of 50 g and has 55.45% mass of copper. This means that there is 27.725 $\pm$ 2 g of copper on every board. The second most abundant element on the board is calcium which is 27.11% of the mass of the PCB due to the FR4 and the ink mask used to make the PCB. The chemical composition of the FR4 and top mask has most of the elements that are in table thus all the non-metals and metals such as aluminium, zinc, magnesium, potassium, lead, iron and sodium.

The copper on the board is protected by a layer of nickel and the nickel is 1.57% mass of the PCB. For every PCB of 50 g, there is about 0.785 g of nickel which means the nickel layer is very thin.

Gold makes up only 0.11% mass of the PCB which is 0.055g of gold per PCB of 50 g. This translates to about 1.1kg of gold per ton of PCBs which is relatively rich.

Scan Results vs Aqua Regia Results

It is clear that unlike the QEMSCAN or the 3D X-ray CT Scan, aqua regia analysis gives more quantitative results. Moreover, the is more qualitative information about what is on the board. Although the scans are not as accurate when distinguishing between elements, they help to see how the non-metals and metals are distributed on the board. They map out the structure of the board.

Summary of Results for Objective 1

The objective was to characterise the board and to determine the composition and structure of the PCB.

The objective was fulfilled, and the summary of the results is as follows:

1) There are 4 copper layers on the PCB
2) About 69% of the copper lies on the inner layers, 29% on the outer layers and 2% internally
3) 55.45% mass of the PCB is copper thus 27.725 g per PCB of 50 g

Objective 2: Comparing pre-treatment Methods

In the following section; are graphs showing the results of the diagnostic leach tests on PCBs that were pre-treated eight different ways. Also shown are the corresponding pH profiles. Each leach test was done in duplicate (See Appendix D).

Each experiment was run at least twice. Firstly, the data sets for each method are checked statistically using the coefficient of variance. It reflects how the data points are dispersed from the mean. The coefficient of variance was calculated for each data set. Any data set which had an average coefficient of variance of more than 20% was not used.

Table 4.2 summarises the pre-treatment methods.

Table 4.2: Summary of the Pre-treatment Methods

Number	Method
1	Cut into 5 cm x 5 cm
2	Cut into 5 cm x 5 cm + NaOH treatment
3	NaOH Treatment & Drilled
4	Cut into 2 cm x 1.5 cm + NaOH treatment
5	Shredded
6	Shredded then Pulverised
7	Burnt in an Open Flame
8	Burnt in a Furnace

The diagnostic leach conditions are also summarised in table 4.3 below.

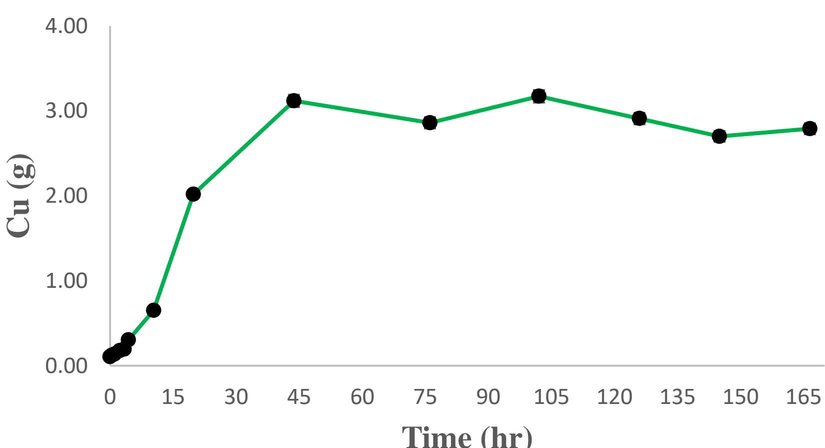
Table 4.3: Summary of Diagnostic Leach

Parameter	Condition
25% Ammonia Solution (Merk) Concentration	4 M
Ammonium Sulphate (Merk) Concentration	2 M
Copper Sulphate (Merk) Concentration	~100 ppm
Temperature	25 °C
pH	8 - 11
Agitation	500 rpm
Volume	1000 ml
Liquid: Solid Ratio	1000 ml per PCB (~50g), 20:1
Time	120 hrs+

The highest copper recovered on the leaching curve for each method is reported as the copper recovery. In some instances, the copper in solution decreases due to the pH changes and minor precipitation. This will be disregarded since the copper would have dissolved off the PCB. As seen in the Eh-pH diagram, some of the extracted copper may precipitate out of solution to form $Cu(OH)_2$. To minimise the precipitation of copper the pH was kept between 8 and 11 by adding ammonia to reduce precipitation. The addition of ammonia results in pH fluctuations throughout the experiments. When the ammonia is added there is a sudden increase in pH.

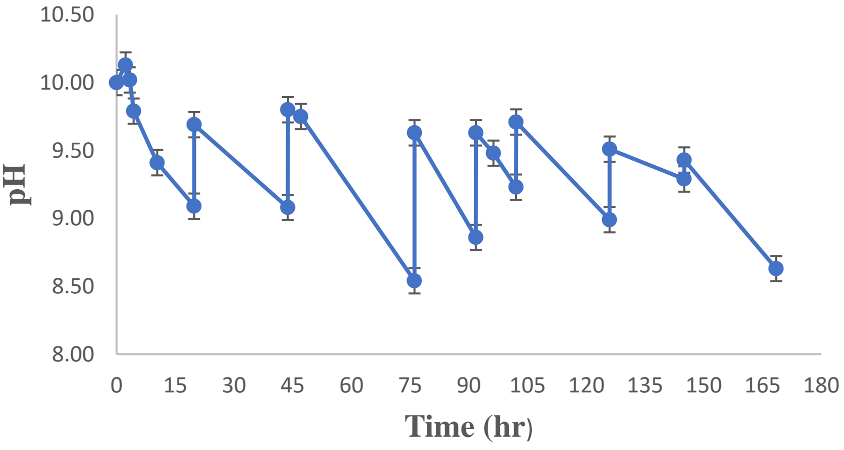
Pre-treatment Method 1

Figure 4.16: Leach Curve for Method 1



The pH Profile is as below

Figure 4.17: pH Profile for Method 1



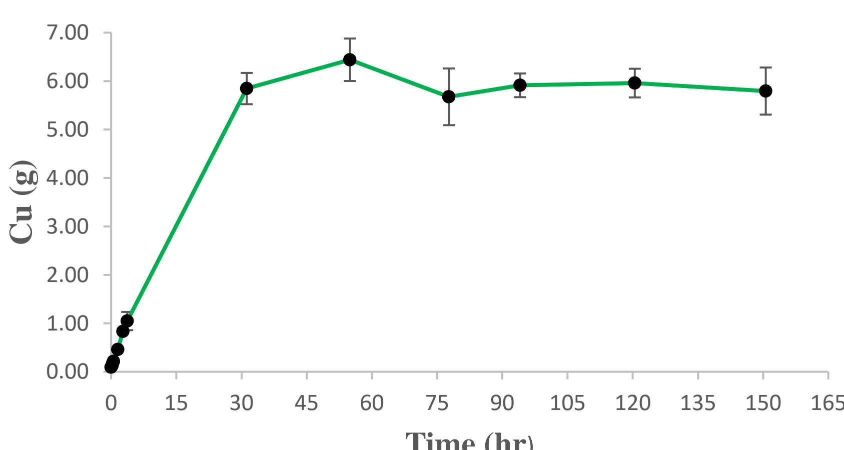
It can be seen from Figure 4.16 that the bulk of the extraction happens in the first 45 hours.. Thereafter, there seems to be no significant copper extraction. The small error bars indicate that the results are repeatable. For these PCBs, the recovery of copper only got as high as 3.17 g of copper after 43.75 hours which equated to 11.43% recovery. This is very low, and it may be due to the fact that the top and bottom mask still covered the copper and acted as a protective layer against the lixiviant, barring it from reaching any copper underneath it. There is a need to remove the top and bottom mask to allow the lixiviant to reach the copper on the PCBs which is what was done in method 2.

In Figure 4.17, the pH was kept in the bounds of 8 and 11 as recommended in literature. The fluctuations are due to the addition of ammonia throughout the experiments. In instances like

at 75 hours where the pH went very low, the pH drop may have triggered precipitation which would explain the Cu decline on the extraction curve.

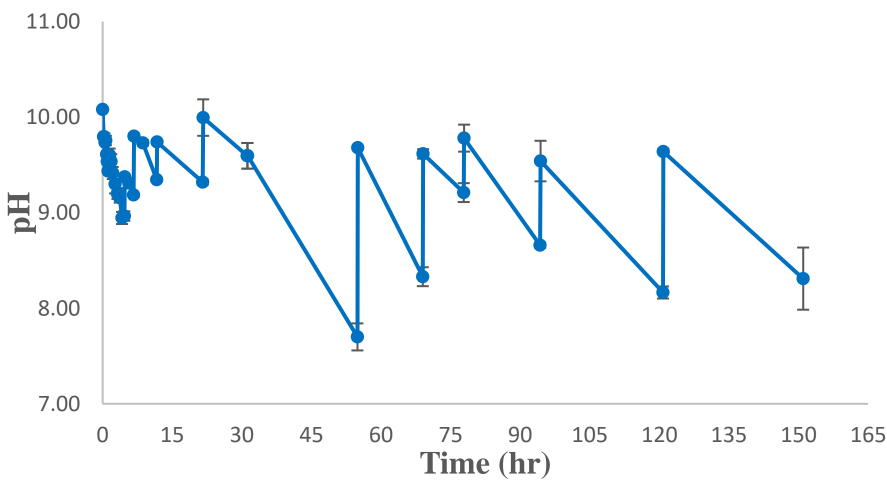
Pre-treatment Method 2

Figure 4.18: Leach Curve for Method 2



The corresponding pH profile is as follows.

Figure 4.19: pH Profile for Method 2



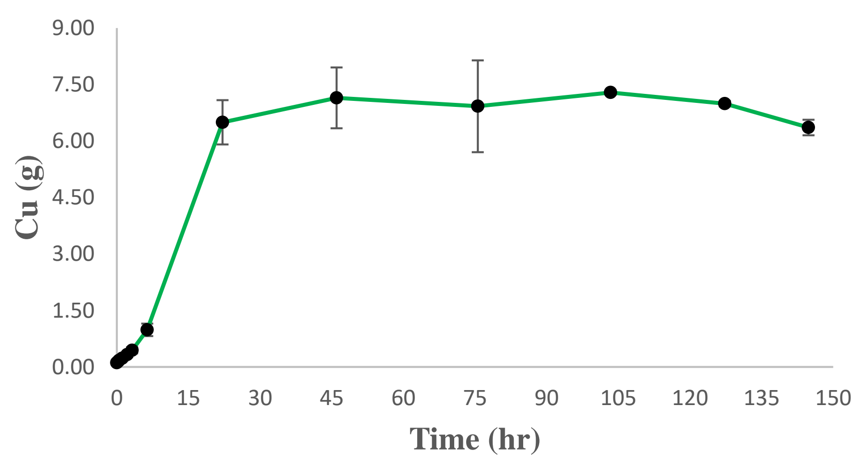
Removing the top and bottom masks allowed the copper to be more accessible. This is shown by the higher recovery that resulted which is 6.44 g of copper after about 55 hours. Most of the extraction happens in the first 30 hrs of the experiment. The copper recovery is about 23% which is more than double that of the PCBs pre-treated with method 1. However, the recovery is still relatively low compared to the recoveries reported in literature, for instance Jadhav et al

(2015) used method 2 and achieved 100% recovery. However, it is important to note that the PCBs they used are single sided but the PCB in this study is multi-layered

As seen through the 3D analysis of the PCBs, about 69% of the copper lies on the inner layers. This means that the exposed copper layers are therefore only about 31%. The rest of the copper is still underneath the FR4 and inaccessible to the lixiviant. The 3D image of the PCB piece that was treated with method 2 showed that only the top and bottom outer layers were leached. The copper that was electroplated in the walls of the holes also got leached as it is not covered by any mask or FR4. If only the accessible layers are considered, the 6.44 g leached would be about 74.93% of the accessible copper. This is still a relatively low recovery of the exposed copper. There is a need to expose the copper that lies in the inner layers to improve recovery.

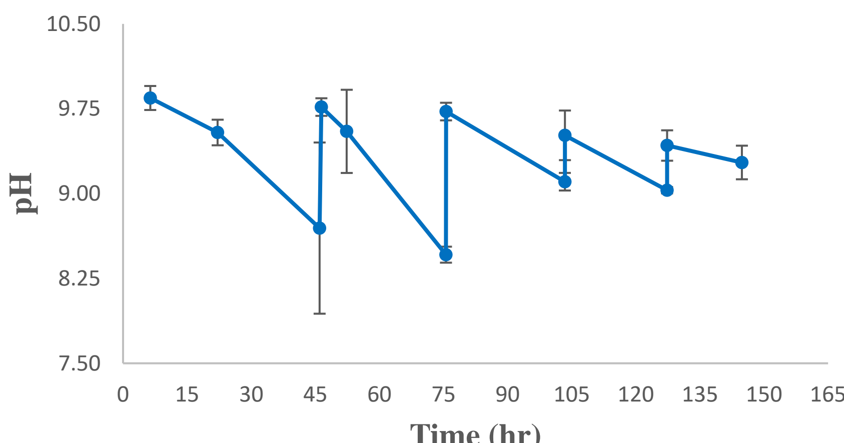
Pre-treatment Method 3

Figure 4.20: Leach Curve for Method 3



The pH profile is as below.

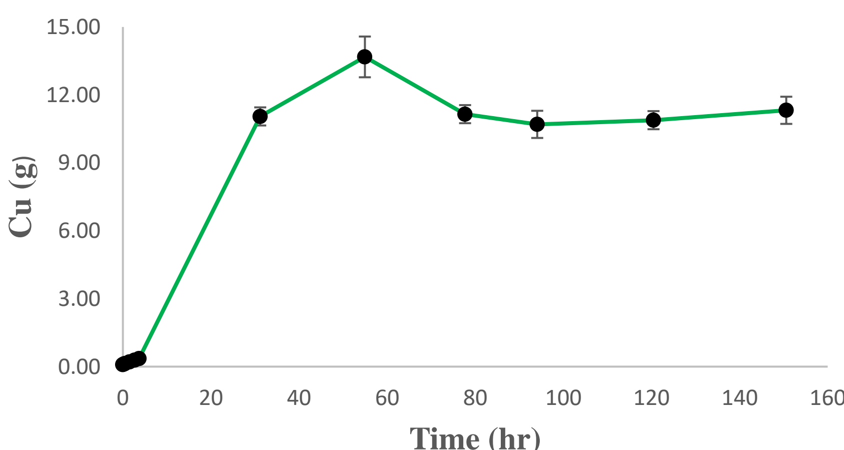
Figure 4.21: pH Profile for Method 3



For this method, 3.5 mm holes were drilled in order to expose the inner layers by creating an entry point for the lixiviant. 7.29 g of copper was leached after 103.4 hours. Although it took longer, the was a slight increase in the amount of copper as this is 26.29% recovery. From the 3D analysis of one of the PCB pieces treated with this method and leached, it showed in figure 4.14 that only the outer layers and the copper plated in holes got leached. Considering only 31% of the copper was accessible, 84.82% of the exposed copper got leached. Drilling holes resulted in a 10% increase in recovery. For industrial application, drilling holes not only increases the energy, machinery and labour, it also results in the loss of valuable material. The PCBs were weighed after drilling and they had lost about 2.7 g which translates to 5.4% mass loss.

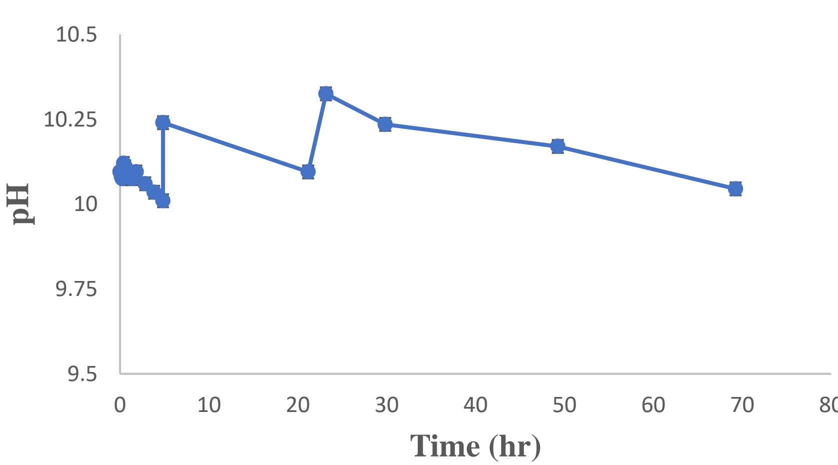
Pre-treatment Method 4

Figure 4.22: Leach Curve for Method 4



The pH profile is shown below

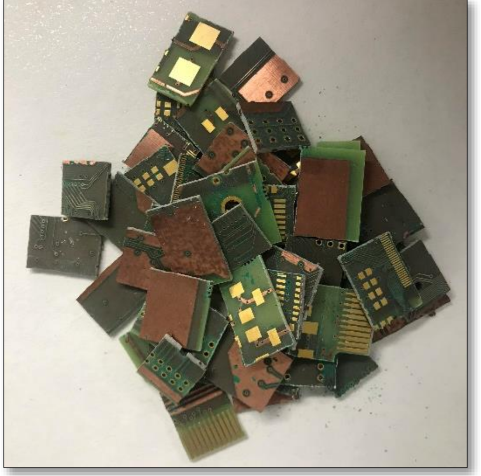
Figure 4.23: pH Profile for Method 4



Jadhav et al (2015) found that by reducing the size of the PCB pieces, the recovery and leaching rate improved. This is the aim for method 4, the PCBs were cut into 2 cm x 1.5 cm pieces. The top and bottom mask was removed by NaOH and then the PCBs were leached. After 54.53 hours, 13.68 g of copper was leached. This is a significant improvement from method 1, 2 and 3. Cutting the pieces into 2 cm x 1.5 cm resulted in a 49.34% recovery. Since the outer copper layers and the copper electroplated in connectors both contribute about 31%, that means that some of the inner copper layers were leached.

Figure 4.24 is an image of the PCBs before leaching (left) and after leaching (right)

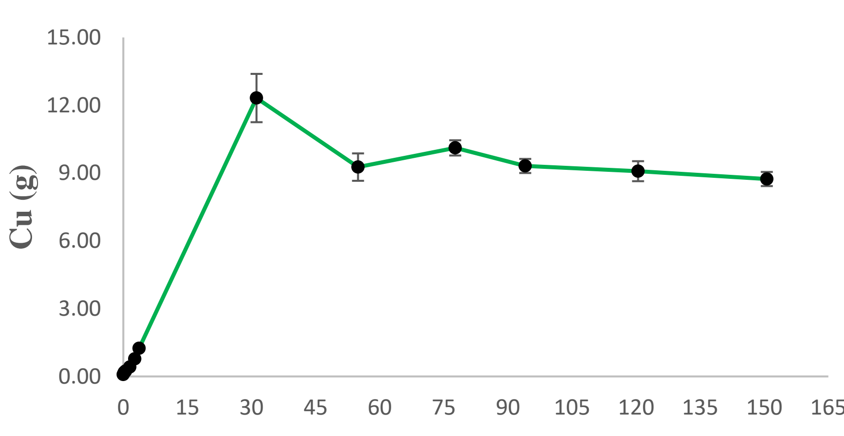
Figure 4.24: PCB Before Leaching (left) and After Leaching (right)



It is clear from Figure 4.24 that the shiny copper that was visible before leaching is no longer on the leached residue. The brown that can still be seen, however, is the inner copper layers that are showing through the FR4.

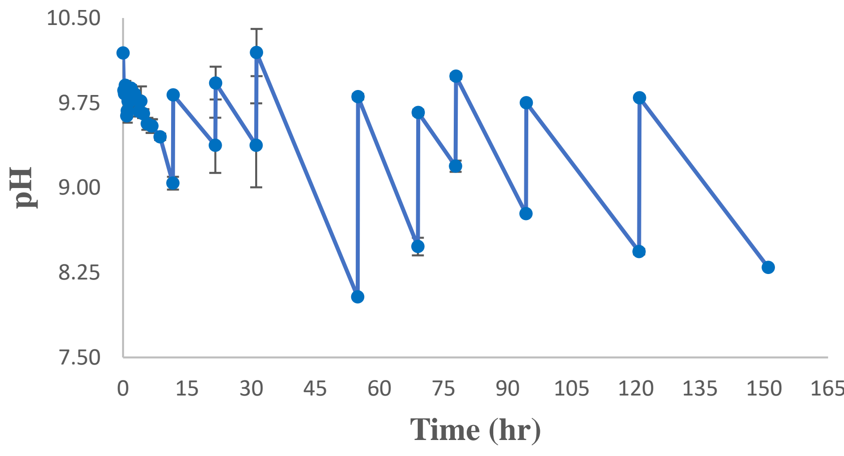
Pre-treatment Method 5

Figure 4.25: Leach Curve for Method 5



The pH profile is as follows in figure 4.26

Figure 4.26: pH Profile for Method 5



In method 5, further size reduction was done by shredding the PCBs. The recovery was about 12.32 g after 31 hours; which is about 44% of the copper which is on the PCB. After that, the pH sharply decreased resulting in precipitation of more than 2g of copper. There were severe material losses during the shredding of the PCBs. Tuncuk et al (2012) report that size reduction techniques can result in losses up to about 35%. This proved to be true because each PCB lost an average of about 19.5 g which is 39% of the board. Only 61% of the PCB was available for leaching which is 30.51 g of PCB.

The severe losses did not happen in proportion to the PCB composition. Due to the different densities of the materials on the PCBs, lighter materials contributed more to the loses thereby affecting the head grade. An aqua regia test was done to check if the PCB composition changed.

Below is a table showing the composition of the shredded PCB (top) and the table for the head grade of the normal PCB (bottom)

Table 4.4: Shredded PCB Composition (top row) Normal PCB Composition (bottom row)

%	**Al**	**Au**	**B**	**Ba**	**Ca**	**Co**	**Cu**	**Fe**	**K**	**Mg**	**Mo**	**Na**	**Ni**	**Pb**	**Si**	**Sr**	**Zn**	**P**
S	9.11	0.08	2.04	0.49	14.84	0	63.6	0	0.21	0.52	0	0.22	0.86	5.28	1.92	0.15	0.16	0.18
N	7.37	0.11	1.19	0.31	27.11	1.44	55.45	3.37	0.24	0.36	0.01	0.23	1.57	0.39	0.21	0.10	0.52	0

The composition changed, and the percentage of copper is more on the shredded PCB. Copper is 55.45% of the normal PCB but it is 63.6% of the shredded PCB. It is worth noting that elements like calcium that form the non-metallic parts such as the mask and the FR4 decreased from 27.11% to 14.84%. On the contrary, most of the heavy elements like lead went from 0.39% in the normal PCB to 5.28%.

The head grade therefore shows that the material losses were mostly non-metals. This is probably due to their low density which caused them to become airborne or be blown off during shredding. The shredded PCBs have an average mass of 30.5 g and in shredded PCBs, the copper that was available for leaching accounted for only 63.6% of that. That translates to 19.4g of copper being available for leaching. Since 12.3 g of copper got leached, that equates to 63.5% copper recovery of the available copper. This is similar to the 64.31% recovery that Bari et al (2009) got for the copper recovery in an ammonia – ammonium sulphate solution.

The above is summarised in Table 4.5

Table 4.5: Summary of Method 5 Results

Parameter	**Normal (whole) PCB**	**Shredded PCB**
Mass	50 g	30.5 g
Copper Grade	55.45%	63.6%
Copper Mass	27.725 g	19.4 g
Copper Recovery	44%	63.5 %

These loses have a significant impact on the recovery. As discussed throughout the literature review, most researchers do not take into account these severe losses and only report the recovery of the available copper after shredding.

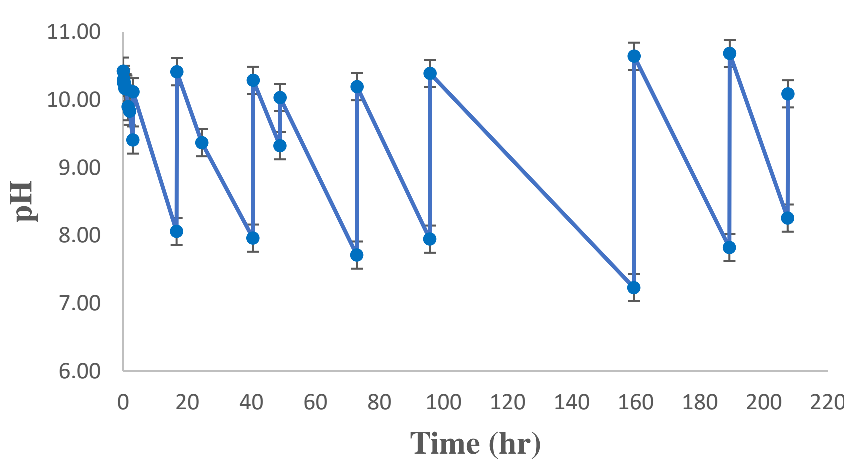
Pre-treatment Method 6

Figure 4.27: Leach Curve for Method 6

Cu (g)
9.00
7.50
6.00
4.50
3.00
1.50
0.00
-5 10 25 40 55 70 85 100 115 130 145 160
Time (hr)

Below is the pH profile

Figure 4.28: pH Profile for Method 6



The pulverised PCBs have a similar composition to that of the shredded PCBs. For this method, 7.03 g of copper got leached and that is 25.36% of the copper on the whole PCB.

During the pulverisation process, a further 0.523 g was lost. This is not as significant but if taken into account, that leaves 29.98g of pulverised PCB to be leached. Since on this PCB the copper is 63.6% that means there is 19.07 g of copper available for leaching. Of the available copper 36.86% got leached. Although the pulverised PCBs have a smaller size distribution that the shredded PCBs, the copper recovery was lower. This may be because the non-metal particles formed a layer on the copper inhibiting diffusion of the lixiviant thereby making dissolution less effective.

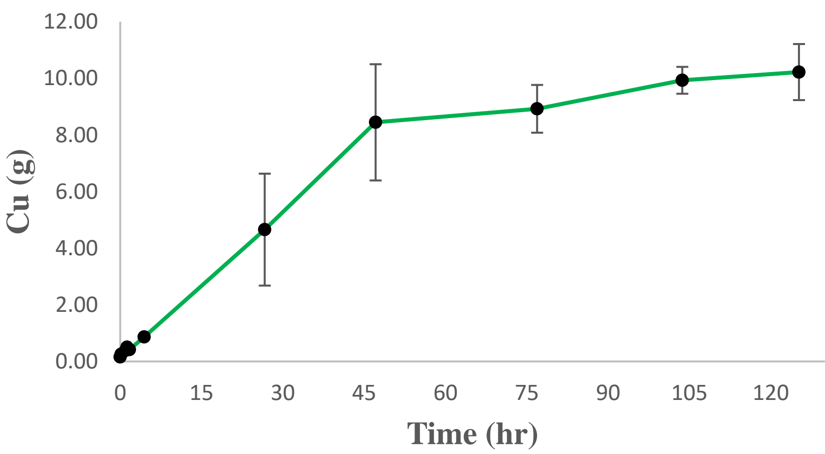
The summary is as follows:

Figure 4.29: Summary of Results for Method 6

Parameter	Normal (whole) PCB	Pulverised PCB
Mass	50 g	28.98 g
Copper Grade	55.45%	63.6%
Copper Mass	27.725 g	19.07 g
Copper Recovery	25.36%	36.86 %

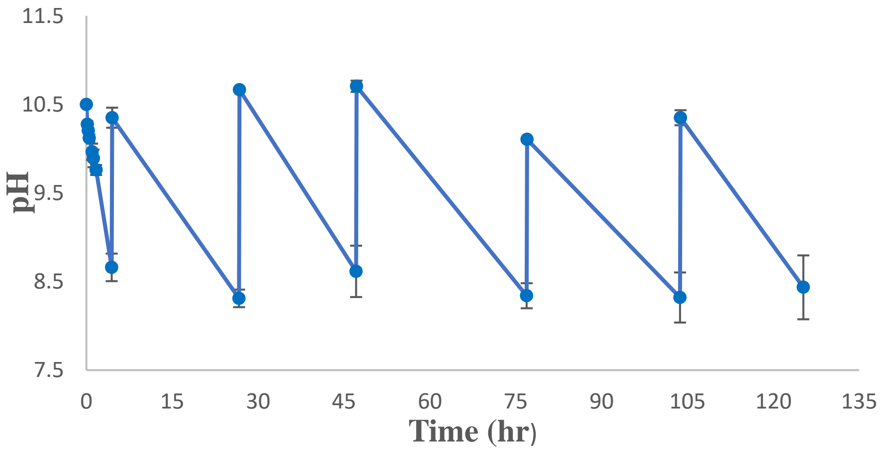
Pre-treatment Method 7

Figure 4.30: Leach Curve for Method 7



The pH profile is shown below.

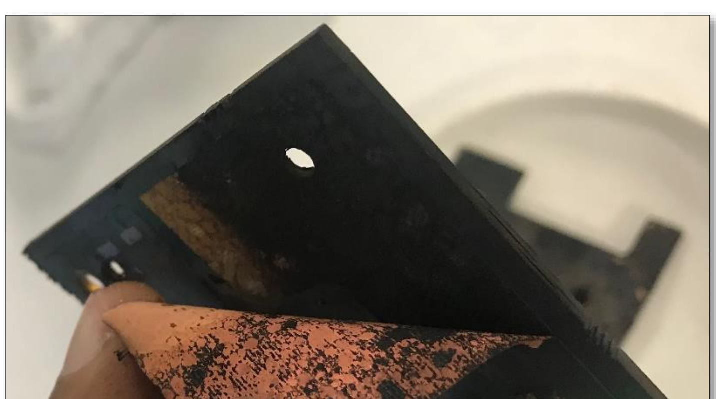
Figure 4.31: pH Profile for Method 7



A different approach was taken in method 7. Since the bond between the copper and the FR4 is a physical one, burning the PCBs was meant to delaminate the FR4 that sandwiches the inner copper layers. This was done to determine how effective delamination of the PCB layers is.

Figure 4.32 shows how some copper layers detached from the FR4 due to the heat that was applied.

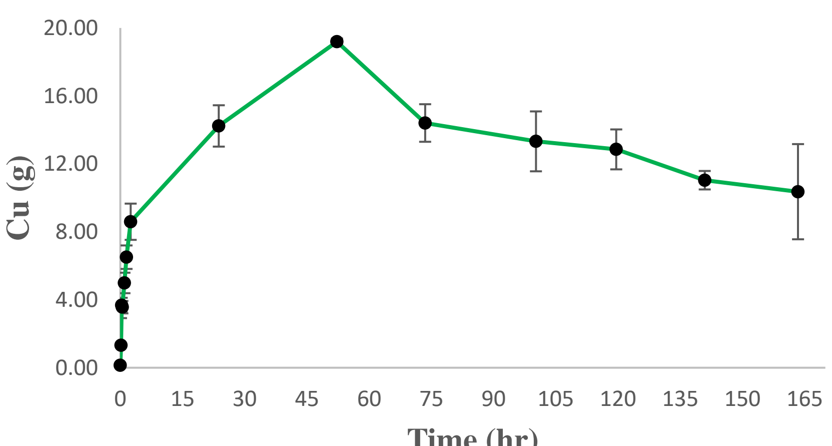
Figure 4.32: Copper Layers Detaching from FR4



The detachment allows for more copper to be exposed so that it is accessible to the lixiviant during leaching. The method resulted in 10.22 g being leached in 125.23 hours. The mask that was on the PCB was not removed prior to burning and that caused a lot of potentially harmful fumes to be produced during the process. The PCBs also caught flames which had to be extinguished after the pre-treatment was done. The copper that was leached is only about 36.9% of the total copper on the PCB which suggests that the bulk of the inner copper still remained inaccessible. Some copper could have re-adsorbed onto the char.

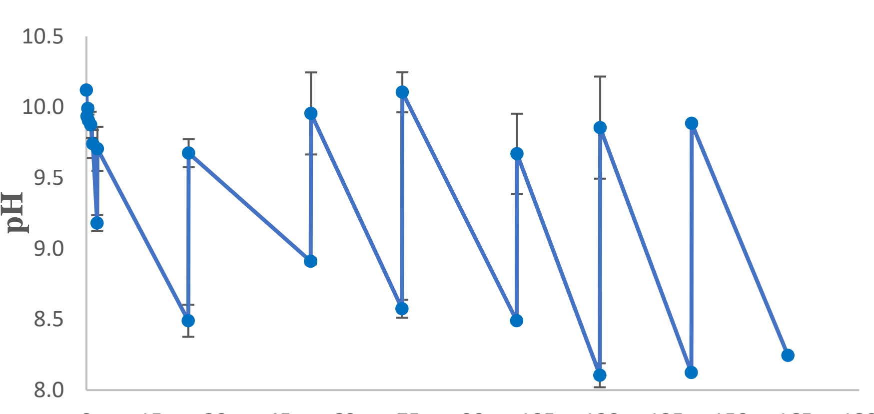
Pre-treatment Method 8

Figure 4.33: Leach Curve for Method 8



The pH profile is as below

Figure 4.34: pH Profile for Method 8



Burning the PCBs in a furnace resulted in highest copper recovery of all the methods. About 69.21% of copper got leached which is 19.19 g after around 52 hours. This is because the layers of the PCBs fully delaminated. The downside is that this method is energy intensive and just like method 7 it produces harmful gaseous substances. There may have been adsorption of copper ammine onto the char which acts like activated carbon. The residue of the PCB after leaching is shown in Figure 4.35.

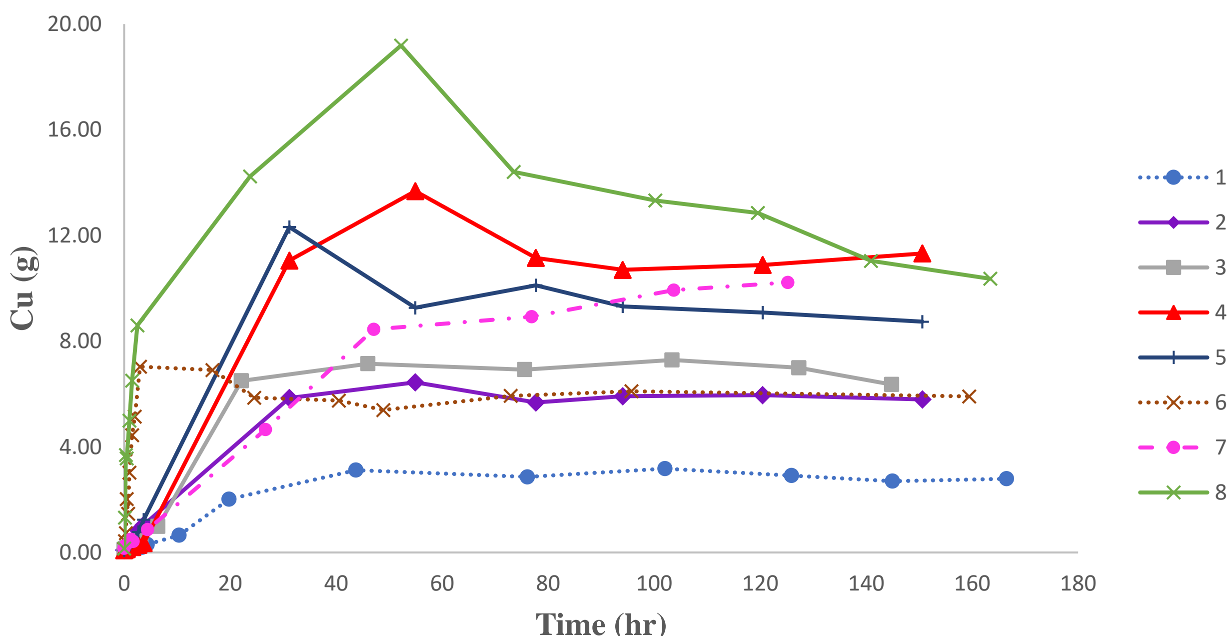
Before Drying (left) and after drying and milling (right)

Figure 4.35: Residue of PCB after Pre-treatment Method 8 and Leaching

The figure above shows that some of the PCB parts were oxidised. The PCB lost its structure due to delamination.

Pre-treatment Methods Combined

Figure 4.36: Diagnostic Leach Curves for All Pre-treatment Methods



Summary of Diagnostic Leach Test

Table showing the copper recovery from the diagnostic leach

Table 4.6: Copper Recovery Summary

Pre-treatment Method	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Available Cu (g)	27.7	27.7	23.0	27.7	19.4	19.1	27.7	27.7
Leached Cu (g)	3.17	6.44	7.29	13.7	12.3	7.03	10.2	19.2
Recovery Available Cu (%)	11.4	23.2	31.7	49.3	63.5	36.86	44.4	69.2
Overall Recovery of Cu (%)	11.4	23.2	26.3	49.3	36.9	25.36	44.4	69.2

As reported in Table 4.6 above, the highest overall recovery was with method 8 thus burning PCBs in the furnace. 69.2% of copper got leached from the PCBs. This is then followed by Method 4 which was done by cutting the PCBs into small pieces of 2 cm x 1.5 cm. The copper that was leached using that method is 49.3%. The method with the lowest copper recovery is method 1 where the PCBs were cut into 5 cm x 5 cm pieces and went straight for leaching.

Choosing the Optimal Pre-treatment Method.

The comparison of the different pre-treatment methods is a multifaceted problem as there is many factors to be considered. The recoveries have been discussed and there is need to come up with the optimal method by also looking at other factors. In addition to recovery these

include the time taken for maximum recovery to be achieved, the associated material losses, health, safety and the practicality of the method in an industrial setting. These factors are not going to be analysed in detail but are going to be summarised for each pre-treatment method qualitatively compared for simple comparison.

Time taken for copper recovery

Time is an important aspect to consider when choosing the optimal method for pre-treating the PCBs. The longer it takes for maximum recovery to be reached, the more the operating costs and the less the production capacity and revenue per unit time. For all the methods, the bulk of the leaching happens in the first 50 hours. By the 130th hour, the maximum copper recovery would have been reached already thus; 130hr is going to be used as a basis since it is the time all the experiments ran for. The methods are going to be compared based on the difference of 130 hours and the time it took for maximum copper recovery.

The following equation is going to be used for comparison:

$$\frac{130\ -\ Hours\ taken\ to\ reach\ highest\ Cu\ recovery}{130} \times 100 = \%\ Time\ Saved$$

The higher the percentage time saved, the better the pre-treatment method.

Table 4.7 shows the percentage time saved for each method.

Table 4.7: Time saved for Each Pre-treatment Method

Method	**Time (hr)**	**Time saved %**
1 5cm x 5cm	102.05	22%
2 NaOH	54.93	58%
3 NaOH & Drilled	103.4	20%
4 2cm x 2cm NaOH	54.93	58%
5 Shredded	31.18	76%
6 Pulverised	3	98%
7 Open Flame	125.23	4%
8 Furnace	52.25	60%

The method that took the least time to reach maximum recovery is method 6 where the PCBs were pulverised. This is expected as the PCBs have the highest surface area exposed due to their small size. Following after it is the shredded PCBs which are also really small. Just like the PCBs in method 6, they have a high surface area exposed.

Method 2 and 4 took around the same time but Method 4 leached more copper in that time than method 2. For method 1, the leaching took long because the mask was a barrier that was preventing diffusion of the lixiviant to the copper.

The PCBs treated in open flames reach their maximum slower probably because the top and bottom mask were still on the board even though it delaminated. Additionally, the soot that was on the PCBs possibly acted as a barrier for the diffusion of the lixiviant to the copper. For

Method 8, the soot did not have a significant effect because the PCBs delaminated better than in method 7.

For Method 3, taking long to reach maximum recovery might be due the fact that a small part of the inner layers was reached slowly through the holes over time. That could have slowly increased the copper in solution until the lixiviant could not reach the inner copper layers any longer. By 46 hours, 7.15 g had been leached already but the reason why maximum recovery took long is because the recovery only increased by 0.14g over the following 11 hours. This suggests that the experiments did not necessarily have to run for that long seeing that significant leaching happens in the first 50 hours.

It should be noted that the leaching rates achieved for the various tests do not necessarily need to be quantified since the speed of reaction is not a huge factor in choosing the best method.

Material Losses

Losing some of the material from the board during pre-treatment poses a health hazard and high capital and operational costs are required to install infrastructure that captures the dust.

For six out of all eight of the methods, the material losses are less than 10% and therefore negligible since most of the lost material is not metal. However, for the shredded and pulverised boards the losses were very significant. Below is a table that shows the material losses incurred with each method of pre-treatment.

Table 4.8: Material Losses Associated with Each Method

Loss of Material		
Method	**Mass Loss (g)**	**Mass Retained %**
1 5cm x 5cm	0	100
2 NaOH	0	100
3 NaOH & Drilled	2.7	94.6
4 2cm x 2cm NaOH	0	100
5 Shredded	19.497	61.01
6 Pulverised	20.02	59.96
7 Open Flame	2.15	95.7
8 Furnace	4.8	90.4

The PCBs burnt in the furnace and open flames only lost a few grams due to the oxidation of some materials that formed lighter oxidants. For method 3 where the PCBs got drilled, the loss is due to the holes that were on the PCBs. For method 5 and 6, there was dust generation during size reduction.

Practicality

Practicality encompasses factors that affect industrial application such as energy intensity or stages required for pre-treatment. Since the machinery or chemicals used for each pre-treatment method contribute to the capital and operating costs, it is favourable to have a method that uses minimal energy and requires a few stages. Below is the table showing the requirements for each pre-treatment method.

Table 4.9: Summary of the Equipment Required for each Method

Required	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Saw	✓	✓	✓	✓	✓	✓	✓	✓
NaOH		✓	✓	✓				
Drill			✓					
Shredder					✓	✓		
Mill						✓		
Furnace								✓
Open Flames							✓	✓
Dust Capture					✓	✓		

Some methods require a lot of machinery and some use extremely energy intensive infrastructure. Method 3, 6 and 8 require 3 stages each to be completed whereas some methods like method 1 only have one stage. For method 8, open flames are a requirement because before they were put in a furnace, they had to be burnt in a crucible over a flame to avoid explosions in the furnace.

Based on the discussion and table above the following equation is going to be used to score the practicality for each method.

$$Practicality = 100 - (number\ of\ requirements\ \times 10)$$

Using the equation above, the methods with a lot of requirements score lower and are therefore deemed less practical than the methods which score higher.

The table below shows the scores for practicality for the different methods.

Table 4.10: Practicality Score for Each Method

Method	**Score**
1	90
2	80
3	70
4	80
5	70
6	60
7	80
8	70

Environmental Impact and Safety of the Pre-treatment Methods

Considering the environmental and health effects of the pre-treatment methods is of utter importance. However, for this study, the comparison of the health and safety is purely qualitative.

Due to the fact that the aim of this study is to come up with an environmentally friendly process to recycle copper from waste PCBs, method 8 is not the most suitable pre-treatment method. Although it has the highest recovery of all the methods it is not eco-friendly. As mentioned in chapter 1 and 2, incinerating e-waste is part of the problem and therefore cannot be incorporated

in the solution. The emissions that would result from burning PCBs are toxic to humans and the environment and should be avoided. The same also applies to method 7 where an open flame is used to delaminate the PCBs (Tuncuk et al, 2012). Integrated pyrometallurgical operations are designed to capture off-gas stream in e-waste recycling unlike in most hydrometallurgical processes. However, the upside is that PCBs that have already been incinerated offer a much higher copper yield because of the liberation of metals.

Method 5 and 6 have significant material losses and this may pose health and environmental hazards. This is due to the production of a dust particles during shredding which may cause respiratory issues and air pollution.

Method 1 is the safest method of all as there is not much dust, gaseous emissions or chemicals used. However, it is not the optimal method as the copper recovery is really low.

From a health and safety standpoint, method 2, 3 and 4 have a more or less similar impact as they all involve cutting by a saw and NaOH treatment. Method 3 undergoes drilling but that is not a significant cause for concern when it comes to health and safety. The NaOH used can be neutralised before it is disposed. These 3 methods do not seem to have a significant negative impact on the environment.

Combining and Comparing all factors

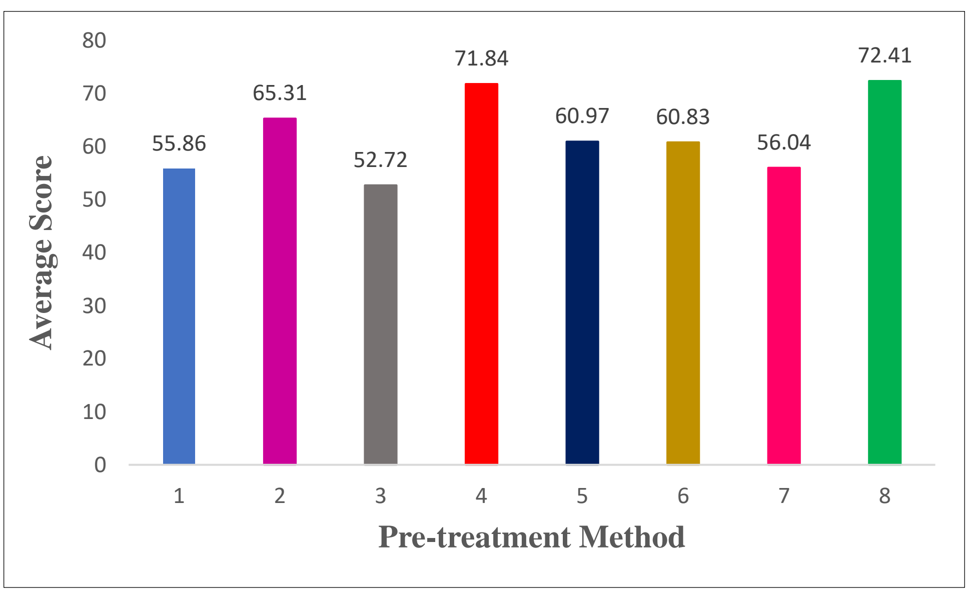
The table below shows the recovery, time saved, practicability score, materials retained and the sum of the scores of all these factors.

Table 4.11: Summary of Scores for All Factors for All Methods

Method	Recovery	Time	Practicability	Mass	HSE	Total
1	11.43	22	90	100	✓	223.43
2	23.23	58	80	100	✓	261.23
3	26.29	20	70	94.6	✓	210.89
4	49.34	58	80	100	✓	287.34
5	36.86	76	70	61.01	x	243.87
6	25.36	98	60	59.96	x	243.32
7	44.44	4	80	95.7	x	224.14
8	69.22	60	70	90.4	x	289.62

The graph in figure 4.37 shows the average score which is the total score divided by the 4 factors which were added together.

Figure 4.37: Average Scores for All Methods



Method 8 overall has the best score but since it is not environmentally friendly, it cannot be the optimal method based on the scores. The method with the second highest score is method 4 and it is eco-friendly. It is therefore the optimal pre-treatment method whereby PCBs are cut into small pieces of 2cm x 1.5cm. The method is relatively safe, takes reasonable amount of time to leach, and has high recoveries of copper. The pre-treatment method is going to be used to test out different leaching parameters for objective 3.

Summary of Results for Objective 2

1) The factors considered were recovery of copper, time taken for maximum recovery, practicability, material losses, health and safety.
2) The method with the overall best score for all the factors including health and safety is method 4 where the PCBs were cut into 2 cm x 1.5 cm pieces and treated with 2 M NaOH at 25 °C for 24 hours to remove the mask.

Objective 3: Optimising Leaching Process

The diagnostic leach conditions were as follows:

Table 4.12: Summary of Diagnostic Leach Conditions

Parameter	**Condition**
25% Ammonia Solution (Merk) Concentration	4 M
Ammonium Sulphate (Merk) Concentration	2 M
Copper Sulphate (Merk) Concentration	~100 ppm
Temperature	25 °C
pH	8 - 11
Agitation	500 rpm
Volume	1000 ml
Liquid: Solid Ratio	1000 ml per PCB (~50 g) 20:1
Time	120 hrs+

Parameters Tested
There is need to vary certain parameters to come up with the optimal leaching conditions.

The following parameters were varied:

1) Type of ammonium salt
2) Concentration of the ammonia
3) Liquid to Solid Ration (LTSR)

The following table shows the specifications of the variables

Table 4.13: Parameters Varied

Type of ammonia salt	Ammonium Carbonate		
NH_3 Concentration	4 M	5.5 M	7 M
LTSR	1000 ml: 50 g	750 ml: 50 g	500 ml: 50 g
	20:1	15:1	10:1

The time for the experiments was cut short to be about 60 hours since the bulk of the leaching occurred in the first 50 hours for the diagnostic leach tests (See Appendix D).

Effect of type of Ammonium Salt

4M NH_3 System with Ammonium Carbonate

Figure 4.38: Leach Curve with 4 M system with Ammonia Carbonate

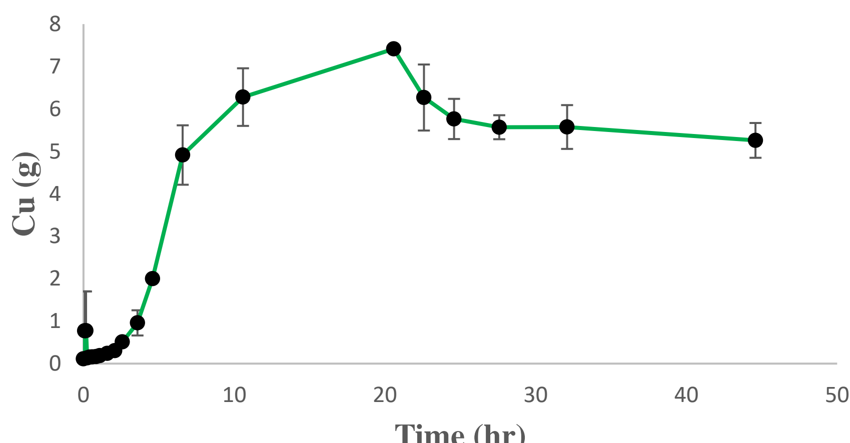


Figure 4.38 shows that the maximum copper extraction is 7.415 g. This is equivalent to 26.74% extraction and this is achieved in 20.58 hours. The extraction of copper for this system is less than that with ammonium sulphate which was 49.34%. However, the leaching rate for the system with ammonium carbonate is faster as it reaches its maximum copper recovery in less than half the time. The extraction is very low but also shows that very little or none of the inner layers were reached by the lixiviant.

The pH profile is in figure 4.39 below:

Figure 4.39: pH Profile for 4 M system with Ammonia Carbonate

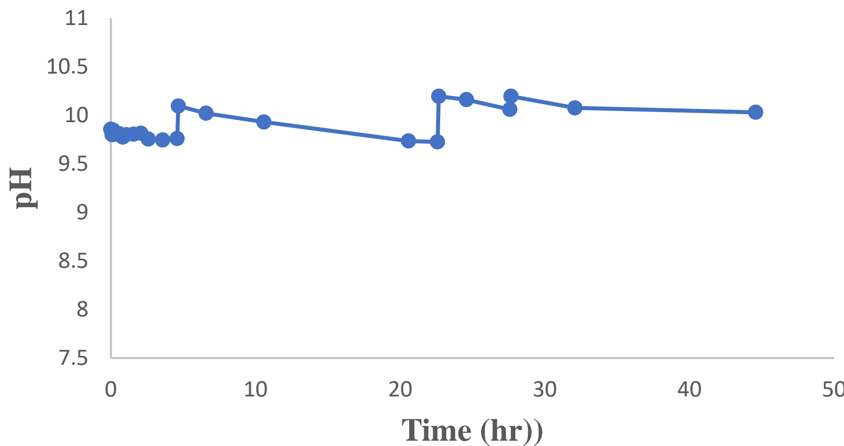
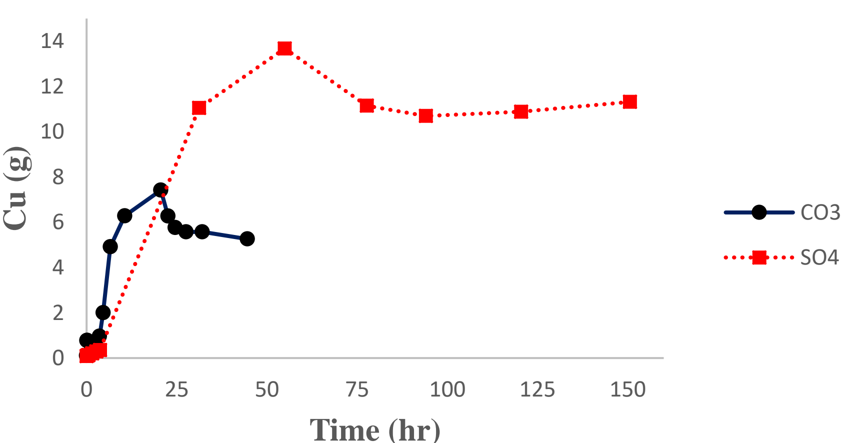


Figure 4.39 shows that there was good control of the pH and it was maintained on the higher bound of the recommended range of 8 – 11 in order to keep the solution alkaline. There is less fluctuations in pH which shows that the carbonate salt is a better buffer than sulphate.

Comparing Sulphate to Carbonate

Figure 4.40: Leach Curve of Sulphate and Carbonate System



In Figure 4.40, the profile for both ammonium salts follow a very similar trend. They both start off with a sharp increase in copper, followed by a slight decrease. The drop is due to copper precipitating out as $CuOH_2$ due to a decrease in pH. After this the copper levels remain nearly constant. It is clear from the graphs that the rate of reaction for the carbonate is faster than that of the sulphate in the first 25 hours. It is also clear that the carbonate system reaches its maximum recovery much sooner than the sulphate system. However, the system with ammonium sulphate has the highest copper that is dissolved in the system. Since they both plateau, longer reaction times will not make a significant difference.

Effect of Ammonia Concentration

Increasing ammonia in the system is expected to increase the copper recovery. This is because increasing the ammonia favours the complexing reaction with copper.

Figure 4.41: Leach Curves for Systems with different Ammonia Concentrations

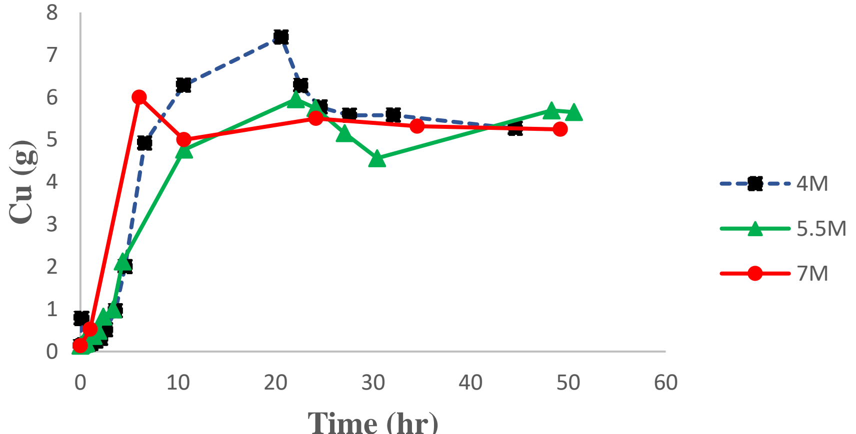
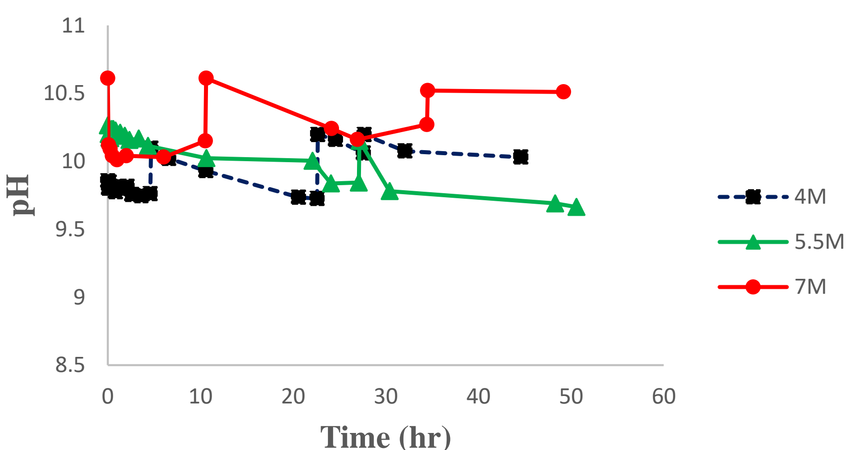


Figure 4.42 pH profiles for different ammonia concentrations



The copper that was extracted in the system with 5.5 M ammonia is 5.95 g which is 21.46% extraction. This was achieved in 22 hours and the concentration remained roughly constant for the 29 hours that the experiment continued. At around 27 hours during the leaching, there was a slight decrease of copper in the solution. This may be due to the low pH at 24 hours and the instant increase in pH at 27 hours. The pH was kept in the bounds of 8 – 11 to minimise the precipitation of copper.

In figure 4.41, the maximum copper that was dissolved from the PCBs averages to be 6.00 g for the 7 M system. There is only small increase of 0.05 g of copper extracted with the system that has 5.5 M ammonia. This is considered to be an insignificant increase seeing that it is only 0.18% of the copper on the PCBs since only 21.64% of the copper got dissolved. Furthermore, the copper that was recovered for this method is less than the copper extracted with 4 M ammonia system by 5.10%. The difference in the copper extracted at different ammonia concentrations is not too pronounced. However, it can be said that the highest copper recovery was achieved by the 4 M solutions. Increasing the ammonia concentration overall decreased the copper recovery. The pH was kept above 10 but below 11 which is still in the set range as shown in figure 4.42.

As aforementioned, increasing the ammonia concentration does not have a significant impact on the recovery but slightly reduces the copper that is recovered. Since using less concentrated ammonia will reduce operating costs as less chemicals are required, the 4 M ammonia solution is the optimal concentration to work with in this case.

Effect of Liquid to Solid Ratio

Figure 4.43: Comparing the Effect of Liquid to Solid Ratio

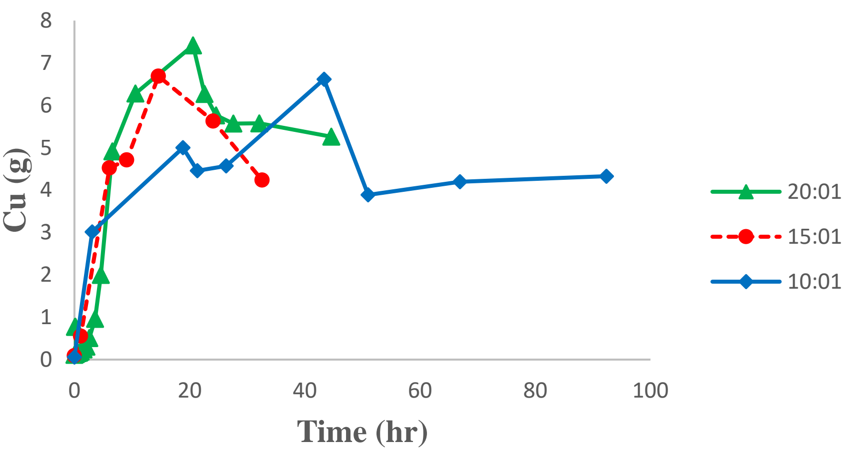
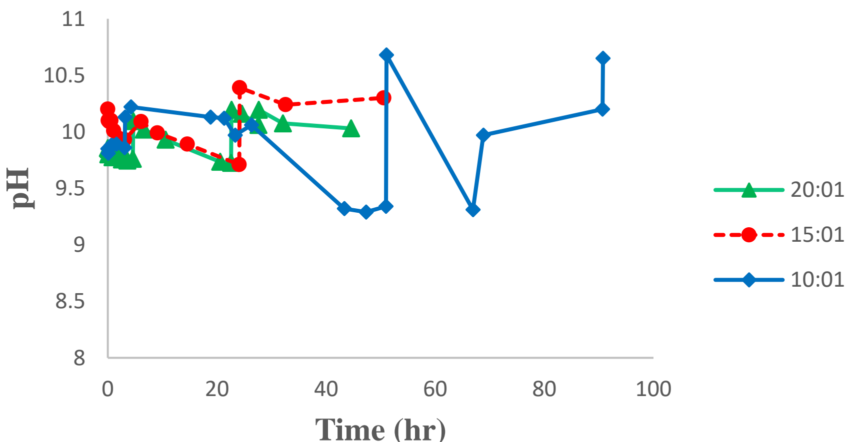


Figure 4.44: pH profiles for different liquid to solid ratios



The liquid to solid ratio does not affect the copper recovery significantly. There are challenges of saturation in all cases and they all dissolve similar amounts of copper. As can be seen in figure 4.43, the profile for the 10:1 (500 ml lixiviant) lagged behind the other two showing that there are slower interactions between the copper and lixiviant. There is not much difference between the 15:1 (750 ml lixiviant) and the 20:1(1000 ml lixiviant) except the 2.61% decrease in copper extraction with the 750 ml. The difference in copper extraction between the 500ml and the 750 ml systems is only a slight decrease of 0.25% copper recovery. This therefore means that halving the lixiviant volume only lessens the copper recovery by 2.86%. It however almost doubles the time required for maximum extraction.

Decreasing the lixiviant volume decreased the kinetics of the copper dissolution reaction. Having a low lixiviant volume reduces the availability of the lixiviant molecules that dissolve the copper on the PCBs. A low LTSR also means that some of the copper may not get exposed to the lixiviant.

Since the reaction time for the 15:1 system is almost similar to that of the 20:1 system, it makes the 15:1 the optimal volume. The 2.61% copper recovery decrease caused by the decrease in volume is not noteworthy.

Discussion of the Carbonate System and Sulphate System Comparison

The carbonate system achieved faster leaching kinetics possibly because the kinematic viscosity of the carbonate system is less than that of the sulphate system which makes ion diffusion much easier in the carbonate system. As stated before, this is what Konishi et al (2014) discovered when the chloride and the sulphate systems were compared.

Most leach tests were performed with ammonium sulphate achieved a greater copper recovery than ammonium carbonate. However, the carbonate buffer system was more effective at controlling the pH within the desired range, which minimized precipitation. A combination of ammonium sulphate and ammonium carbonate could potentially be used to achieve optimal leach conditions as it is a mixture of a good buffer and a good lixiviant.

The effect of temperature on the leach rates was not investigated because the aim was to test a system that can operate at room temperature. Operating at room temperature lowers the operating costs of the processes.

Summary of Results for Objective 3

1) Ammonium sulphate is a better ammonium salt for leaching than the ammonium carbonate
2) The optimal ammonia solution concentration is 4 M
3) The optimal Liquid to Solid ratio is 15:1 LTSR

5. CONCLUSIONS AND RECOMMENDATIONS

Conclusions

Recycling PCBs not only mitigates the negative environmental and health impacts that result from dumping and incinerating e-waste, but it also provides a secondary source of metals. The process of recovering metals from PCBs is complex because PCBs are composed of a mixture of a wide variety of materials. The materials on PCBs include base, heavy and precious metals, ceramics, glass, plastic to mention a few. The most abundant material on most PCBs is copper. The PCBs used for this study has 55.45% copper and 69% of that copper is located on the inner layers.

It has proven difficult to access the inner copper layers which is where most of the copper lies using methods that are not energy intensive. The structure of the PCBs is such that the inner layers are underneath the FR4 in the form of a laminate. The lixiviant is thereby hindered from reaching the desired metal. Pre-treatment methods were used in a bid to make the copper more accessible. Some of the methods such as drilling holes on the PCBs created areas of weakness on the FR4 but still did not allow the copper underneath it to be exposed to the lixiviant. This may be due to the strong physical bonds between the PCB layers. The bonds get weakened by pre-treatment methods that delaminate the PCBs such as burning the PCBs in a furnace or open flame. Although burning the PCBs may produce rich products, it also produces a lot of hazardous fumes and is therefore not ideal. The alternative is to mill the PCBs until they are pulverised. This type of pre-treatment, however, poses a health risk as a lot of dust is generated and a lot of valuable material is lost. Additionally, it is an energy intensive process. The method whereby the top coating is chemically removed with NaOH is not energy intensive, but it is only effective with single sided boards where there are no inner layers. Leaching gets even more complex with populated PCBs as there may be hinderance to the outer layers which would otherwise be accessible on unpopulated PCBs.

Leaching large PCB pieces is more energy efficient than leaching pulverised PCBs. In addition, there is potential to recycle the non-metallic parts if the PCBs are leached in large pieces. Although pulverised PCBs result in faster reactions due to larger exposed surface area, overall recovery or metal is relatively low due to the losses incurred during pulverisation. Wet milling might reduce material losses possibly by minimising dust formation. size reduction would still require more energy than using composite boards.

The diagnostic leach test was a comparison tool for pre-treatment methods, but it had its downsides. There was a lot of precipitation that occurred with the ammoniacal systems that were used in this study. This was as a result of the decrease in ammonia in the system. The ammonia mainly reduced when more copper dissolved into solution and complexed with it. To a small degree, there was evaporation of the ammonia, but this was minimised because the reactors were covered. Adjusting pH using ammonia minimised the precipitation reaction but it did not stop it entirely.

The copper recovery in ammoniacal systems is affected by liquid to solid ratio and type of salt. The concentration of ammonia did not have a significant effect on the leaching of copper from the PCBs. This is because 4M ammonia is adequate to form tetraamines with all the accessible copper and any additional ammonia did not affect the complexing reaction.

Recommendations

There is need to do more investigations on how to pre-treat the PCBs to make copper more accessible. Instead of only removing the mask, the FR4 may need to be removed from the PCBs to allow the exposure of the inner copper layers. This is normally done by pyrolysis which is a very energy intensive process.

There is need to find a way to completely stop the precipitation that occurs in the ammoniacal systems in order to keep all the copper dissolved. Ammonia was added in the system to keep the pH high but there is need to keep the same pH in the system to avoid any decrease in free ammonia as more copper is produced.

Tuncuk et al (2012) puts across the idea that precious metals contribute significantly to the value of WEEE and their extraction is of prime importance. It will therefore be of benefit to focus on the recovery of precious metals. Though they are in small quantities, their value still may exceed that of base metals that are abundant on the PCBs. In doing so, sequential leaching should be employed where base metals are leached first. Leaching the precious metals requires strong lixiviants that could potentially leach out the base metals thereby complicating downstream processes.

There is need to look at more parameters to determine the optimal leaching conditions. The parameters that could be investigated include temperature, agitation, air flowrate, type of salt and pH. There should be further investigation on how to completely stop precipitation from occurring in the ammoniacal system. Different chemical systems can also be studied and used as tools to compare the effectiveness of pre-treatment methods. Leaching populated PCBs should also be evaluated since the waste PCBs are populated in most cases.

PCBs have more than 10 species of chemicals and their chemical interactions should be closely looked at. Some may act as catalysts or inhibitors in certain reactions and it would be helpful to know what each chemical species' role is in the chemistry.

As seen in the study, the way in which a PCB is manufactured directly impacts the recycling process. PCB manufactures therefore play a significant role and any changes in the manufacturing process could potentially simplify recycling. Some of the changes that could be implemented could be using material that easily delaminates to liberate metals. Additionally, manufacturers could look into reusing recycled materials to make PCBs. Recycling PCBs gets more complex when the PCBs have solders and if feasible, manufacturers can make PCBs which have easily detachable solders.

The findings of this study are also significant to the semiformal hydrometallurgical recycling businesses which are mostly in developing countries. The majority of the businesses use wet or dry comminution operations before chemical leaching which has been shown to result in significant material losses. Additionally, it can be a very energy intensive process compared to leaching composite boards. It may be beneficial to use composite boards as this has been shown to not only preserve the non-metallic parts in a reusable form but also results in a higher metal recovery.

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7. Appendix A - 3D X-ray CT Scan Settings

The following tables show the settings that were used to scan the pieces of PCBs.

X-ray Settings

Table 7.1: X-ray Settings

Parameter	Value
X-ray kV	140
X-ray µA	100

X Tek CT Settings in X, Y and Z

Table 7.2: X Tek CT Settings in X, Y and Z

Parameter	X	Y	Z
Voxels	2237	325	2273
Voxel Size	0.0238472055643797	0.0238472055643797	0.0238472055643797
Offset	-0.447135076011854	-0.286166448647585	0
Detector Pixels	1900	1516	-
Detector Pixels Size	0.127	0.127	-
Detector Offset	0	0	-
Region Start	0	0	-
Region Pixels	1900	1516	-
Slice Area Start	237	237	-
Slice Area End	1662	1662	-

X Tek CT Settings

Table 7.3: X Tek CT Settings

Parameter	**Value**
Src To Object	220.939876556396
Src To Detector	784.4208
Mask Radius	33.5873035364083
Centre of Rotation Top	0.618284026622772
Centre of Rotation Bottom	0.829387722969055
White Level	60000
Scattering	0
CoefX4	0
CoefX3	0
CoefX2	0
CoefX1	1
CoefX0	0
Scale	1
Projections	2985
Initial Angle	4.9911
Angular Step	0.120602516765628
Filter Type	0
Cut Off Frequency	3.93700787401575
Exponent	1
Normalisation	1
Interpolation Type	1
Median Filter Kernel Size	1
Scaling	1000
Output Units	/m
Units	mm
Automatic Centre of Rotation	0
Automatic Centre of Rotation Offset Z1	0
Automatic Centre of Rotation Offset Z2	0
Output Type	2
Import Conversion	1
Auto Scaling Type	1
Low Percentile	0.2
High Percentile	99.8
Centre of Rotation	0.723835874795913
Blanking	0
Order FFT	13
Scaling Minimum	0
Scaling Maximum	1
Time Stamp Folder	1

CT Pro settings

Table 7.4: CT Pro settings

Parameter	Value
Filter Pre-set	1
Filter Thickness MM	1
Filter Material	Copper
Shuttling	False
Filter Method	0
Auto COR Num Bands	2
Cor Auto Accuracy	1
Slice Single Height Px	758
Slice Single Region	X= 0, Y= 0, Width = 1, Height = 1
Slice Dual Top Height Px	1137
Slice Dual Top Region	X= 0, Y= 0, Width = 1, Height = 1
Slice Dual Bottom Height Px	379
Slice Dual Bottom Region	X= 0, Y= 0, Width = 1, Height = 1
Angle File Use	False
Angle File Ignore Errors	True

Auto Beam Hardening settings

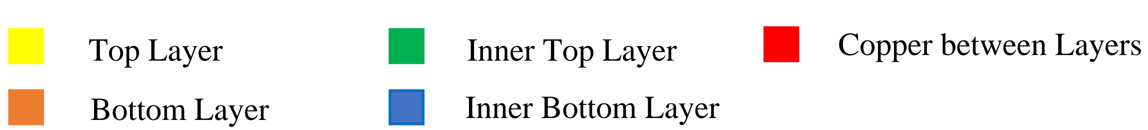
Table 7.5: Auto Beam Hardening settings

Parameter	Value
Stack	0
Slice	0
Sinogram Offset X	0
Sinogram Band Sampling	1
Slice Threshold	0

8. Appendix B - 3D X-ray CT Scan Images of Individual Pieces

3D X-ray CT Scan results are shown below.

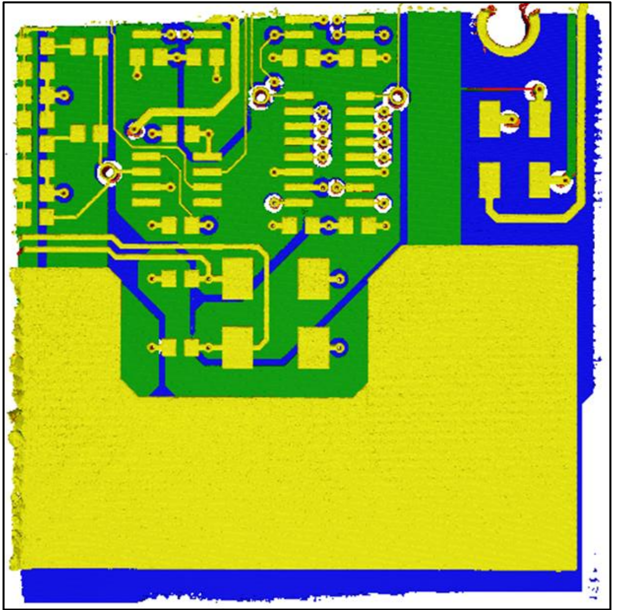
Key



Individual PCB Pieces

Image of PCB Piece 1 Front (left) and Back (right)

Figure 8.1: PCB Piece 1



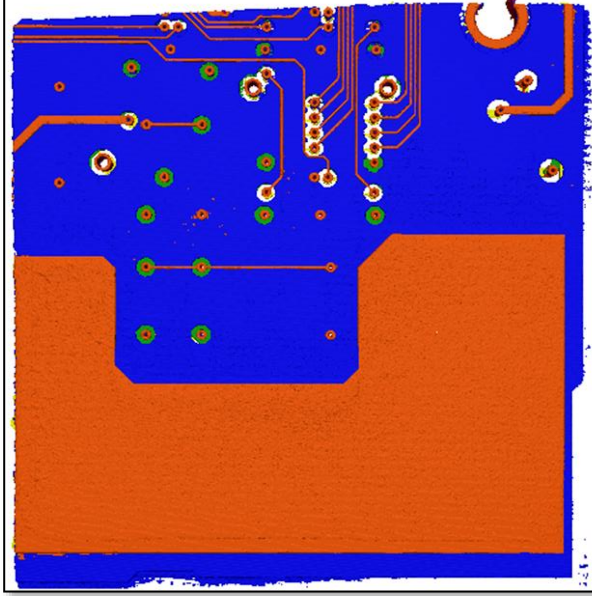
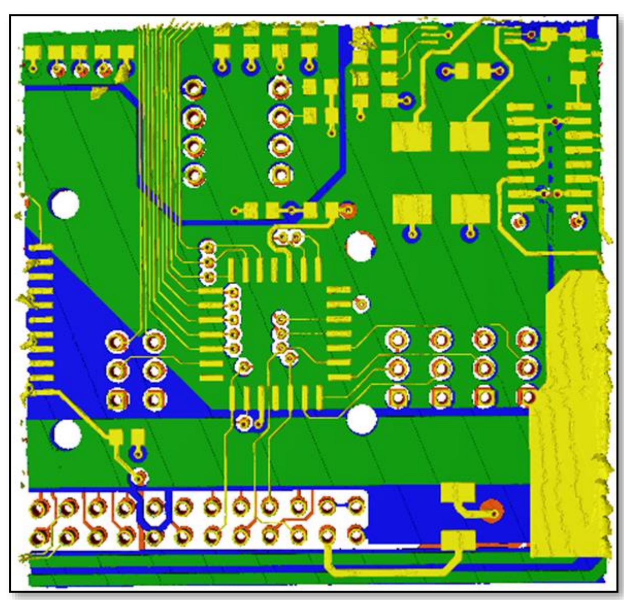


Image of PCB Piece 2 Front (left) and Back (right)

Figure 8.2: PCB Piece 2



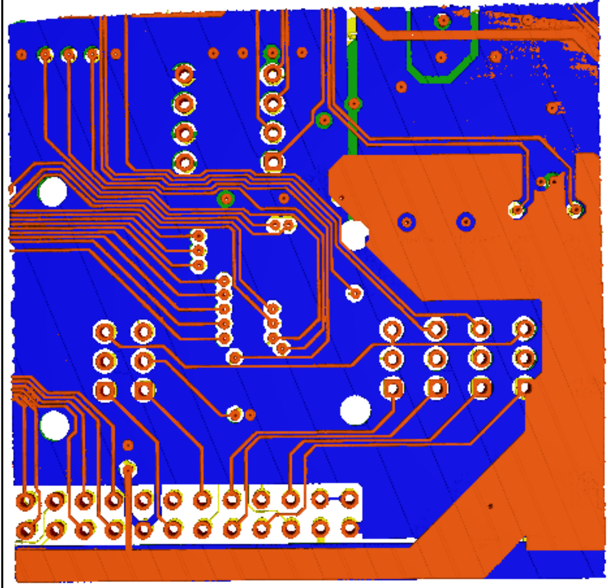
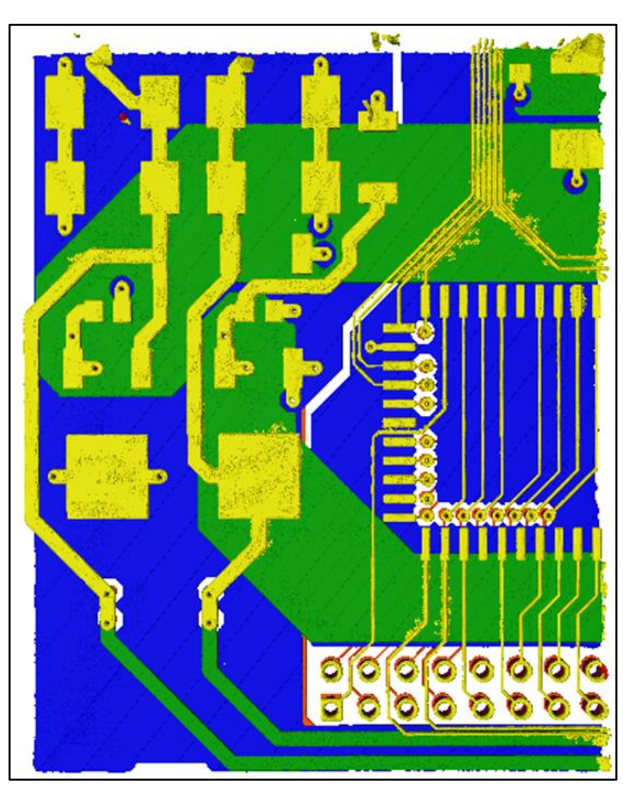


Image of PCB Piece 3 Front (left) and Back (right)

Figure 8.3: PCB Piece 3



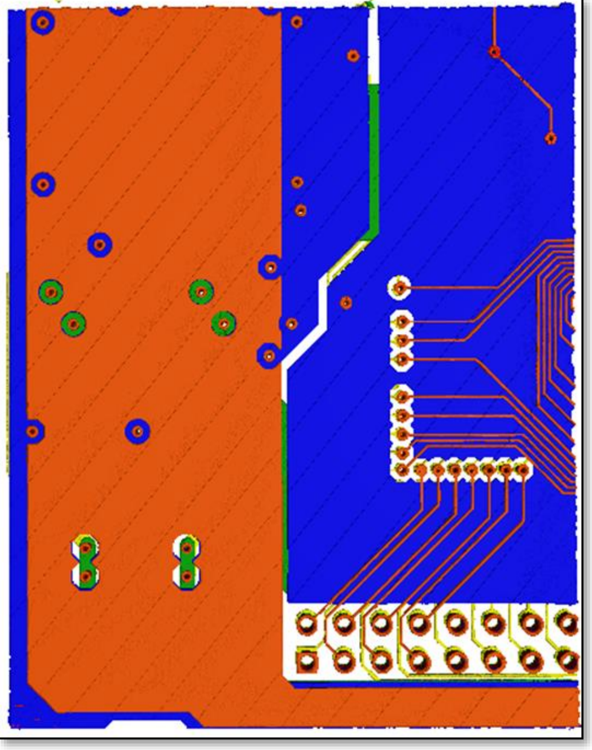
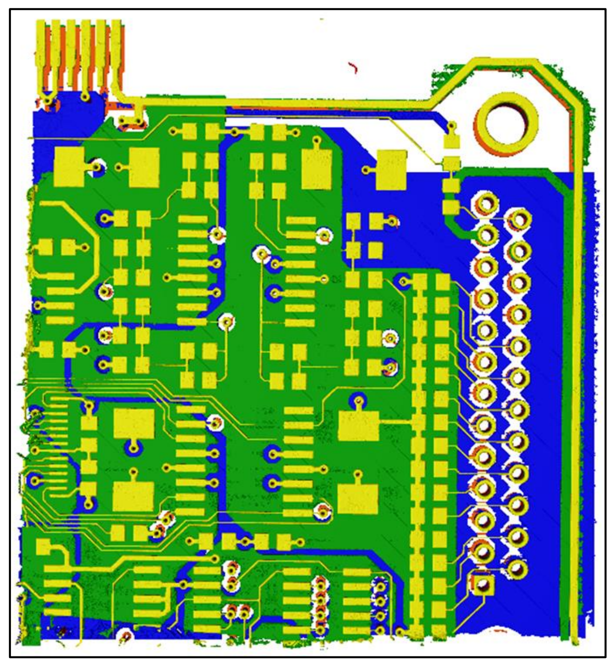
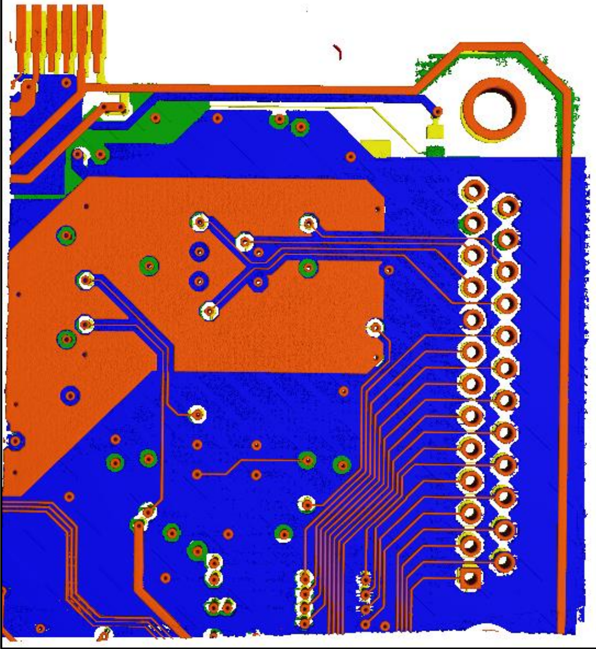


Image of PCB Piece 4 Front (left) and Back (right)

Figure 8.4: PCB Piece 4

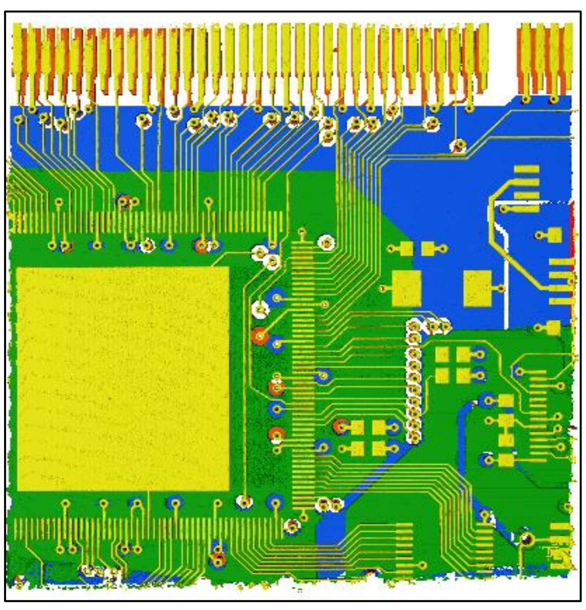




Pre-treated PCB Piece 5

Image of PCB Piece 5 Front (left) and Back (right)

Figure 8.5: PCB Piece 5



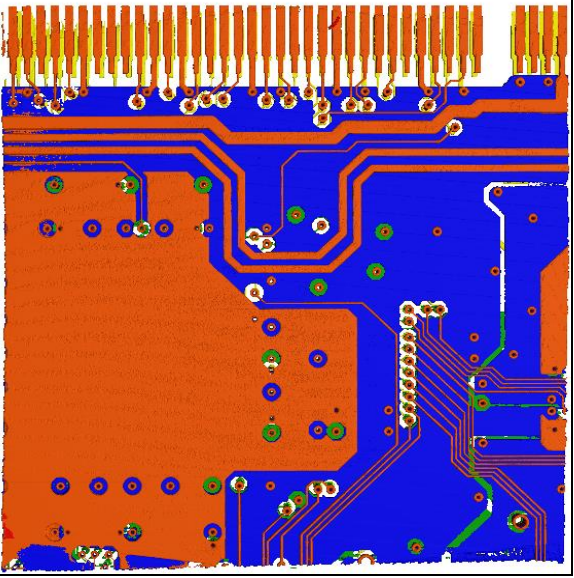
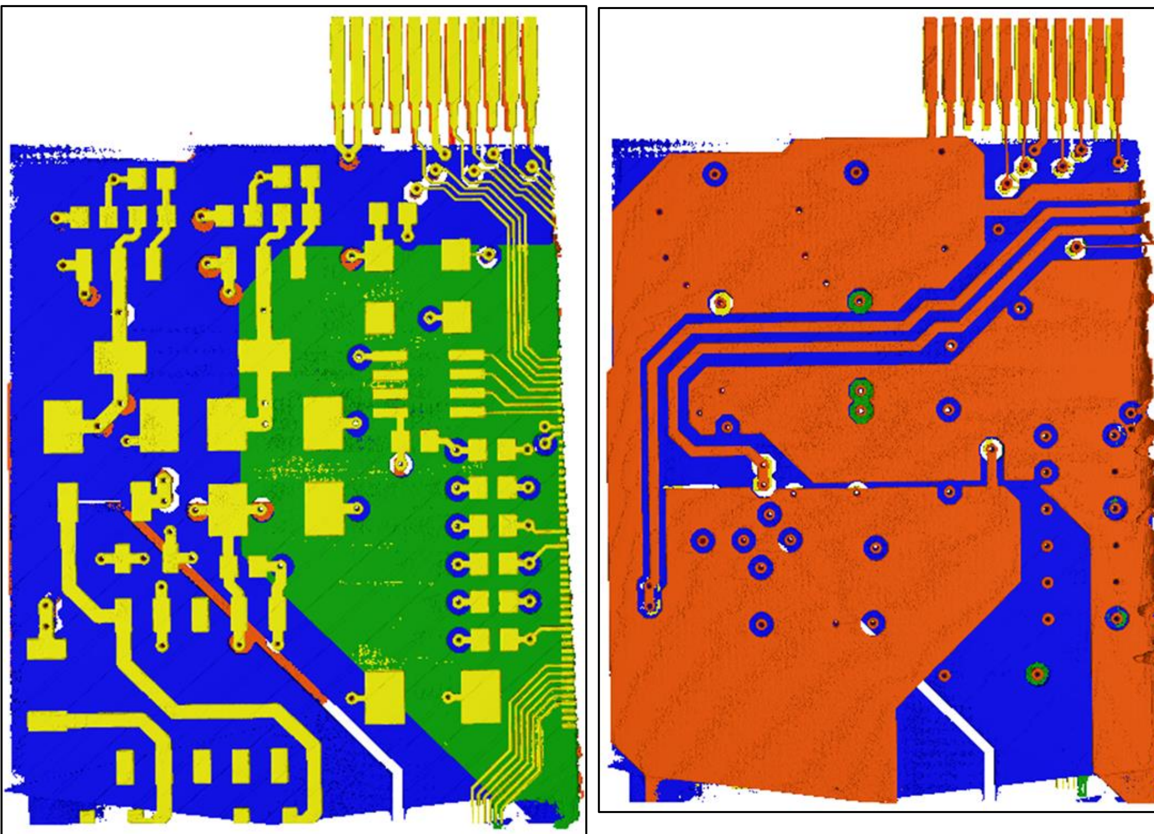


Image of PCB Piece 6 Front (left) and Back (right)

All the coloured parts of the 3D XCT scan images are copper because the artificial colours

Figure 8.6: PCB Piece 6



9. Appendix C – Aqua Regia Test

		Concentration (ppm)				%				
No	Elements	1	2	3	4	1	2	3	4	Average
1	Al	616.8	799.2	359.33	349.5	10.06%	7.97%	5.82%	5.63%	7.37%
2	As	0.2	0.2	0.2	0.2	0.00%	0.00%	0.00%	0.00%	0.00%
3	Au	6.74	8.23	7.57	7.23	0.11%	0.08%	0.12%	0.12%	0.11%
4	B	104.83	121.1	56.4	58.2	1.71%	1.21%	0.91%	0.94%	1.19%
5	Ba	19.68	22.5	22.13	21.81	0.32%	0.22%	0.36%	0.35%	0.31%
6	Ca	1773.75	3695.9	1130.8	1510	28.94%	36.84%	18.33%	24.32%	27.11%
7	Cd	0.2	0.2	0.2	0.2	0.00%	0.00%	0.00%	0.00%	0.00%
8	Co	17.61	240.52	176.98	13.28	0.29%	2.40%	2.87%	0.21%	1.44%
9	Cr	0.2	0.2	0.2	0.2	0.00%	0.00%	0.00%	0.00%	0.00%
10	Cu	3304.75	4197.55	3758.85	4043.9	53.92%	41.84%	60.92%	65.12%	55.45%
11	Fe	59.67	536.25	399.11	42.7	0.97%	5.35%	6.47%	0.69%	3.37%
12	Hg	0	0	0	0	0.00%	0.00%	0.00%	0.00%	0.00%
13	K	16.76	21.51	8.44	21.82	0.27%	0.21%	0.14%	0.35%	0.24%
14	Mg	28.27	34.78	20.03	19.9	0.46%	0.35%	0.32%	0.32%	0.36%
15	Mn	0.2	0.2	0.2	0.2	0.00%	0.00%	0.00%	0.00%	0.00%
16	Mo	1.1	1.47	0.2	0.2	0.02%	0.01%	0.00%	0.00%	0.01%
17	Na	18.61	26.95	10.61	10.15	0.30%	0.27%	0.17%	0.16%	0.23%
18	Ni	61.04	184.14	151.3	62.39	1.00%	1.84%	2.45%	1.00%	1.57%
19	P	0	0	0	0	0.00%	0.00%	0.00%	0.00%	0.00%
20	Pb	52.07	61.91	3.7	1.03	0.85%	0.62%	0.06%	0.02%	0.39%
21	Sb	0.2	0.2	0.2	0.2	0.00%	0.00%	0.00%	0.00%	0.00%
22	Se	0.2	0.2	0.2	0.2	0.00%	0.00%	0.00%	0.00%	0.00%
23	Si	5.19	27.74	22.32	6.34	0.08%	0.28%	0.36%	0.10%	0.21%
24	Sr	8.74	10.33	4.61	4.67	0.14%	0.10%	0.07%	0.08%	0.10%
25	V	0.2	0.2	0.2	0.2	0.00%	0.00%	0.00%	0.00%	0.00%
26	Zn	32.46	40.7	36.15	35.07	0.53%	0.41%	0.59%	0.56%	0.52%

10. Appendix D – Leaching Results

Formulae

SD – Standard Deviation

$$\sqrt{\frac{\sum_{i=1}^{N}(x_i - A)^2}{N-1}}$$

Where:

x = Data points

N = number of points

A= Mean

SE – Standard Error

$$\frac{SD}{\sqrt{N}}$$

Where:

SD = Standard Deviation

N = number of points

RSD – Relative Standard Deviation

$$\frac{SD}{A}$$

Where:

SD – Standard Deviation

A – Mean

CV – Coefficient of Variance

$$RSD \times 100$$

Where:

RSD – Relative Standard Deviation

Method 1

Copper Recovery								
No	Time (hr)	Cu (1) g	Cu (2) g	Average	SD	SE	RSD	CV%
1	0.00	0.11	0.11	0.11	0	0	0	0
2	0.43	0.11	0.13	0.12	0.017	0.012	0.1399	13.989
3	1.07	0.14	0.13	0.14	0.01	0.0071	0.0736	7.3627
4	2.32	0.18	0.17	0.18	0.01	0.0071	0.0564	5.6427
5	3.38	0.20	0.19	0.19	0.0067	0.0048	0.0348	3.4751
6	4.38	0.30	0.31	0.30	0.0013	0.001	0.0044	0.4433
7	10.38	0.65	0.65	0.65	0.0008	0.0006	0.0013	0.1255
8	19.82	2.03	2.01	2.02	0.018	0.0127	0.0089	0.8911
9	43.75	3.13	3.11	3.12	0.011	0.0077	0.0035	0.3513
10	76.12	2.86	2.86	2.86	0.0065	0.0046	0.0023	0.2286
11	102.05	3.18	3.16	3.17	0.0119	0.0084	0.0038	0.3762
12	125.95	2.91	2.91	2.91	0.0013	0.001	0.0005	0.0463
13	145.00	2.70	2.70	2.70	0.0023	0.0016	0.0008	0.0849
14	166.50	2.79	2.79	2.79	0.0067	0.0048	0.0024	0.2417

Ave CV %	2.38

	Cu (g)	**Cu (%)**
Recovery	3.17	11.4%

pH Profiles								
No	**Time (hrs)**	**pH 1**	**pH (2)**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	10.02	9.98	10.00	0.02	0.02	0.00	0.00
2	2.32	10.14	10.12	10.13	0.01	0.01	0.00	0.00
3	3.38	10.03	10.01	10.02	0.01	0.01	0.00	0.00
4	4.38	9.80	9.78	9.79	0.01	0.01	0.00	0.00
5	10.38	9.43	9.39	9.41	0.03	0.02	0.00	0.00
6	19.82	9.10	9.08	9.09	0.02	0.01	0.00	0.00
7	19.83	9.70	9.68	9.69	0.01	0.01	0.00	0.00
8	43.75	9.09	9.07	9.08	0.01	0.01	0.00	0.00
9	43.77	9.81	9.79	9.80	0.02	0.01	0.00	0.00
10	47.08	9.79	9.71	9.75	0.05	0.04	0.01	0.00
11	76.12	8.61	8.47	8.54	0.10	0.07	0.01	0.00
12	76.13	9.93	9.33	9.63	0.42	0.30	0.04	0.00
13	91.80	8.93	8.79	8.86	0.10	0.07	0.01	0.00
14	91.82	9.67	9.59	9.63	0.06	0.04	0.01	0.00
15	96.28	10.16	8.80	9.48	0.96	0.68	0.10	0.00
16	102.05	9.27	9.19	9.23	0.05	0.04	0.01	0.00
17	102.07	9.79	9.63	9.71	0.11	0.08	0.01	0.00
18	125.95	9.04	8.94	8.99	0.07	0.05	0.01	0.00
19	125.97	9.79	9.23	9.51	0.40	0.28	0.04	0.00
20	145.00	9.34	9.24	9.29	0.07	0.05	0.01	0.00
21	145.02	9.47	9.39	9.43	0.06	0.04	0.01	0.00
22	168.50	8.63	8.63	8.63	0.01	0.00	0.00	0.00

Ave CV %	0.00

Method 2

Copper Recovery								
No	**Time (hrs)**	**Cu (1) g**	**Cu (2) g**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	0.09	0.09	0.09	0.00	0.00	0.00	0.00
2	0.20	0.12	0.12	0.12	0.00	0.00	0.02	2.44
3	0.37	0.18	0.17	0.17	0.01	0.00	0.04	4.02
4	0.53	0.21	0.22	0.21	0.01	0.00	0.03	3.24
5	1.53	0.46	0.46	0.46	0.00	0.00	0.00	0.49
6	2.70	0.81	0.86	0.83	0.04	0.03	0.05	4.51
7	3.70	0.91	1.18	1.05	0.19	0.13	0.18	17.96
8	31.18	5.62	6.07	5.85	0.32	0.23	0.06	5.52
9	54.93	6.75	6.13	6.44	0.44	0.31	0.07	6.81
10	77.68	6.09	5.26	5.68	0.59	0.41	0.10	10.32
11	94.07	6.09	5.74	5.91	0.24	0.17	0.04	4.14
12	120.47	6.17	5.75	5.96	0.30	0.21	0.05	4.96
13	150.60	6.14	5.45	5.79	0.49	0.34	0.08	8.40

Ave CV %	5.60

	Cu (g)	**Cu (%)**
Recovery	6.44	23.2%

pH Profiles								
No	**Time (hr)**	**pH (1)**	**pH (2)**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	10.08	10.08	10.08	0.00	0.00	0.00	0.00
2	0.20	9.78	9.81	9.80	0.02	0.02	0.00	0.22
3	0.37	9.77	9.82	9.80	0.04	0.03	0.00	0.36
4	0.53	9.75	9.72	9.74	0.02	0.01	0.00	0.22
5	0.70	9.72	9.79	9.76	0.05	0.03	0.01	0.51
6	0.87	9.59	9.63	9.61	0.03	0.02	0.00	0.29
7	1.00	9.51	9.56	9.54	0.04	0.03	0.00	0.37
8	1.18	9.43	9.44	9.44	0.01	0.00	0.00	0.07
9	1.52	9.55	9.65	9.60	0.07	0.05	0.01	0.74
10	1.85	9.48	9.59	9.54	0.08	0.05	0.01	0.82
11	2.18	9.37	9.46	9.42	0.06	0.05	0.01	0.68
12	2.68	9.23	9.37	9.30	0.10	0.07	0.01	1.06
13	3.18	9.16	9.24	9.20	0.06	0.04	0.01	0.61
14	3.68	9.12	9.19	9.16	0.05	0.04	0.01	0.54
15	4.18	8.90	8.99	8.95	0.06	0.04	0.01	0.71
16	4.68	8.93	9.00	8.97	0.05	0.04	0.01	0.55
17	4.77	9.39	9.36	9.38	0.02	0.02	0.00	0.23
18	5.68	9.32	9.30	9.31	0.01	0.01	0.00	0.15
19	6.68	9.20	9.17	9.19	0.02	0.01	0.00	0.23
20	6.77	9.82	9.78	9.80	0.03	0.02	0.00	0.29
21	8.68	9.75	9.71	9.73	0.03	0.02	0.00	0.29
22	11.68	9.34	9.35	9.35	0.01	0.00	0.00	0.08
23	11.75	9.73	9.75	9.74	0.01	0.01	0.00	0.15
24	21.58	9.34	9.30	9.32	0.03	0.02	0.00	0.30
25	21.67	10.13	9.86	10.00	0.19	0.14	0.02	1.91
26	31.17	9.50	9.69	9.60	0.13	0.09	0.01	1.40
27	31.25	9.50	9.69	9.60	0.13	0.09	0.01	1.40
28	54.92	7.60	7.80	7.70	0.14	0.10	0.02	1.84
29	55.00	9.68	9.68	9.68	0.00	0.00	0.00	0.00
30	69.00	8.26	8.40	8.33	0.10	0.07	0.01	1.19
31	69.08	9.58	9.65	9.62	0.05	0.04	0.01	0.51
32	77.83	9.28	9.14	9.21	0.10	0.07	0.01	1.07
33	77.92	9.88	9.68	9.78	0.14	0.10	0.01	1.45
34	94.30	8.64	8.68	8.66	0.03	0.02	0.00	0.33
35	94.38	9.69	9.39	9.54	0.21	0.15	0.02	2.22
36	120.78	8.12	8.21	8.17	0.06	0.05	0.01	0.78
37	120.87	9.62	9.66	9.64	0.03	0.02	0.00	0.29
38	151.00	8.08	8.54	8.31	0.33	0.23	0.04	3.91

Ave CV %	0.73

Method 3

Copper Recovery								
No	Time (hrs)	Cu (1) g	Cu (2) g	Average	SD	SE	RSD	CV%
1	0.00	0.11	0.12	0.11	0.01	0.01	0.08	7.83
2	0.27	0.15	0.12	0.14	0.02	0.01	0.14	14.16
3	0.50	0.17	0.18	0.17	0.01	0.01	0.07	6.74
4	1.15	0.28	0.19	0.23	0.06	0.05	0.27	27.47
5	2.17	0.37	0.28	0.33	0.07	0.05	0.21	20.77
6	3.20	0.50	0.38	0.44	0.08	0.06	0.18	18.38
7	6.37	1.10	0.87	0.99	0.17	0.12	0.17	16.86
8	22.13	6.08	6.91	6.50	0.59	0.42	0.09	9.06
9	46.01	7.72	6.57	7.15	0.81	0.57	0.11	11.30
10	75.58	7.78	6.06	6.92	1.22	0.86	0.18	17.61
11	103.40	7.33	7.25	7.29	0.06	0.04	0.01	0.80
12	127.32	7.04	6.94	6.99	0.07	0.05	0.01	1.07
13	144.83	6.50	6.21	6.36	0.21	0.15	0.03	3.25

Ave CV %	11.95

	Cu (g)	**Cu (%)**
Recovery	7.29	26.3%

pH Profiles								
No	Time (hr)	pH 1	pH 2	Average	SD	SE	RSD	CV%
1	6.37	9.92	9.77	9.85	0.11	0.08	0.01	1.08
2	22.14	9.46	9.62	9.54	0.11	0.08	0.01	1.19
3	46.01	8.16	9.23	8.70	0.76	0.54	0.09	8.70
4	46.42	9.71	9.82	9.77	0.08	0.05	0.01	0.80
5	52.35	9.29	9.81	9.55	0.37	0.26	0.04	3.85
6	75.58	8.51	8.41	8.46	0.07	0.05	0.01	0.84
7	75.59	9.78	9.67	9.73	0.08	0.05	0.01	0.80
8	103.40	9.05	9.16	9.11	0.08	0.05	0.01	0.85
9	103.42	9.36	9.67	9.52	0.22	0.16	0.02	2.30
10	127.32	9.05	9.01	9.03	0.03	0.02	0.00	0.31
11	127.33	9.33	9.52	9.43	0.13	0.09	0.01	1.43
12	144.83	9.17	9.38	9.28	0.15	0.11	0.02	1.60

Ave CV %	1.98

Method 4

Copper Recovery								
No	Time (hr)	Cu (1) g	Cu (2) g	Average	SD	SE	RSD	CV%
1	0.00	0.10	0.08	0.09	0.01	0.01	0.16	16.44
2	0.20	0.13	0.09	0.11	0.03	0.02	0.24	24.11
3	0.37	0.13	0.11	0.12	0.02	0.01	0.14	14.17
4	0.53	0.15	0.12	0.14	0.02	0.02	0.16	15.57
5	1.53	0.22	0.20	0.21	0.01	0.01	0.07	7.21
6	2.70	0.30	0.28	0.29	0.02	0.01	0.06	5.97
7	3.70	0.30	0.42	0.36	0.08	0.06	0.23	22.84
8	31.18	11.12	10.98	11.05	0.09	0.07	0.01	0.86
9	54.93	14.23	13.13	13.68	0.78	0.55	0.06	5.70
10	77.68	11.17	11.13	11.15	0.03	0.02	0.00	0.31
11	94.07	10.76	10.63	10.70	0.09	0.06	0.01	0.84
12	120.47	10.93	10.83	10.88	0.07	0.05	0.01	0.65
13	150.60	11.33	11.31	11.32	0.02	0.01	0.00	0.14

Ave CV %	8.83

	Cu (g)	Cu (%)
Recovery	13.68	49.3%

pH Profiles								
No	**Time (hr)**	**pH (1)**	**pH (2)**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	10.34	10.04	10.19	0.21	0.15	0.02	2.06
2	0.20	9.73	9.71	9.72	0.01	0.01	0.00	0.14
3	0.37	9.70	9.68	9.69	0.02	0.01	0.00	0.21
4	0.53	9.79	9.55	9.67	0.17	0.12	0.02	1.73
5	0.70	9.65	9.63	9.64	0.01	0.01	0.00	0.08
6	0.87	9.30	9.28	9.29	0.02	0.01	0.00	0.21
7	1.00	9.32	9.30	9.31	0.02	0.01	0.00	0.16
8	1.18	9.60	9.60	9.60	0.00	0.00	0.00	0.04
9	1.52	9.60	9.60	9.60	0.00	0.00	0.00	0.05
10	1.85	9.62	9.62	9.62	0.00	0.00	0.00	0.03
11	2.18	9.60	9.60	9.60	0.01	0.00	0.00	0.06
12	2.68	9.62	9.62	9.62	0.00	0.00	0.00	0.04
13	3.18	9.53	9.53	9.53	0.00	0.00	0.00	0.05
14	3.68	9.49	9.49	9.49	0.00	0.00	0.00	0.03
15	4.18	9.58	9.32	9.45	0.18	0.13	0.02	1.93
16	4.68	9.45	9.27	9.36	0.12	0.09	0.01	1.31
17	4.77	9.45	9.27	9.36	0.12	0.09	0.01	1.30
18	5.68	9.31	9.17	9.24	0.10	0.07	0.01	1.11
19	6.68	9.27	8.93	9.10	0.24	0.17	0.03	2.66
20	6.77	10.19	9.97	10.08	0.16	0.11	0.02	1.57
21	8.68	9.96	9.78	9.87	0.12	0.09	0.01	1.22
22	11.68	9.19	9.05	9.12	0.09	0.07	0.01	1.02
23	11.75	10.03	9.87	9.95	0.11	0.08	0.01	1.08
24	21.58	9.50	9.06	9.28	0.32	0.22	0.03	3.39
25	21.67	10.30	9.40	9.85	0.63	0.45	0.06	6.40
26	31.17	9.79	9.75	9.77	0.03	0.02	0.00	0.27
27	31.25	10.22	9.32	9.77	0.63	0.45	0.06	6.45
28	54.92	9.11	8.59	8.85	0.37	0.26	0.04	4.16
29	55.00	10.03	9.99	10.01	0.02	0.02	0.00	0.22
30	69.00	8.64	8.62	8.63	0.01	0.01	0.00	0.15
31	69.08	9.72	9.70	9.71	0.01	0.01	0.00	0.13
32	77.83	9.43	9.41	9.42	0.01	0.01	0.00	0.12
33	77.92	10.22	10.18	10.20	0.03	0.02	0.00	0.25
34	94.30	8.98	8.96	8.97	0.02	0.01	0.00	0.19
35	94.38	9.82	9.80	9.81	0.01	0.01	0.00	0.13
36	120.78	8.44	8.42	8.43	0.01	0.01	0.00	0.12
37	120.87	9.90	9.88	9.89	0.02	0.01	0.00	0.17
38	151.00	8.16	8.08	8.12	0.05	0.04	0.01	0.62

Ave CV %	1.07

Method 5

Copper Recovery								
No	**Time (hr)**	**Cu (1) g**	**Cu (2) g**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	0.09	0.09	0.09	0.00	0.00	0.00	0.00
2	0.20	0.19	0.17	0.18	0.00	0.00	0.03	2.52
3	0.37	0.21	0.19	0.20	0.01	0.00	0.03	3.33
4	0.53	0.24	0.24	0.24	0.00	0.00	0.00	0.03
5	1.53	0.41	0.43	0.42	0.01	0.01	0.02	2.33
6	2.70	0.82	0.74	0.78	0.03	0.02	0.04	3.60
7	3.70	1.11	1.38	1.24	0.09	0.07	0.08	7.52
8	31.18	13.83	10.81	12.32	1.07	0.76	0.09	8.67
9	54.93	8.41	10.12	9.26	0.61	0.43	0.07	6.54
10	77.68	10.59	9.64	10.11	0.34	0.24	0.03	3.34
11	94.07	9.75	8.87	9.31	0.31	0.22	0.03	3.35
12	120.47	9.71	8.46	9.08	0.44	0.31	0.05	4.87
13	150.60	9.18	8.29	8.74	0.31	0.22	0.04	3.58

Ave CV %	3.82

	Cu (g)	**Cu (%)**
Recovery	12.32	44.4%

pH Profiles								
No	**Time (hr)**	**pH 1**	**pH 2**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	10.19	10.19	10.19	0.00	0.00	0.00	0.00
2	0.20	9.79	9.93	9.86	0.05	0.04	0.01	0.50
3	0.37	9.78	9.88	9.83	0.04	0.03	0.00	0.36
4	0.53	9.85	9.96	9.91	0.04	0.03	0.00	0.39
5	0.70	9.78	9.94	9.86	0.06	0.04	0.01	0.57
6	0.87	9.72	9.55	9.64	0.06	0.04	0.01	0.62
7	1.00	9.69	9.67	9.68	0.01	0.00	0.00	0.07
8	1.18	9.84	9.69	9.77	0.05	0.04	0.01	0.54
9	1.52	9.64	9.88	9.76	0.08	0.06	0.01	0.87
10	1.85	9.84	9.92	9.88	0.03	0.02	0.00	0.29
11	2.18	9.79	9.91	9.85	0.04	0.03	0.00	0.43
12	2.68	9.79	9.87	9.83	0.03	0.02	0.00	0.29
13	3.18	9.73	9.83	9.78	0.04	0.02	0.00	0.36
14	3.68	9.61	9.74	9.68	0.05	0.03	0.00	0.48
15	4.18	9.58	9.95	9.77	0.13	0.09	0.01	1.34
16	4.68	9.60	9.71	9.66	0.04	0.03	0.00	0.40
17	4.77	9.60	9.71	9.66	0.04	0.03	0.00	0.40
18	5.68	9.49	9.64	9.57	0.05	0.04	0.01	0.55
19	6.68	9.46	9.63	9.55	0.06	0.04	0.01	0.63
20	6.77	9.46	9.63	9.55	0.06	0.04	0.01	0.63
21	8.68	9.41	9.49	9.45	0.03	0.02	0.00	0.30
22	11.68	8.96	9.12	9.04	0.06	0.04	0.01	0.63
23	11.75	9.80	9.84	9.82	0.01	0.01	0.00	0.14
24	21.58	9.72	9.03	9.38	0.24	0.17	0.03	2.60
25	21.67	9.72	10.13	9.93	0.14	0.10	0.01	1.46
26	31.17	8.85	9.90	9.38	0.37	0.26	0.04	3.96
27	31.25	10.49	9.90	10.20	0.21	0.15	0.02	2.05
28	54.92	8.05	8.02	8.04	0.01	0.01	0.00	0.13
29	55.00	9.77	9.84	9.81	0.02	0.02	0.00	0.25
30	69.00	8.37	8.59	8.48	0.08	0.05	0.01	0.92
31	69.08	9.63	9.70	9.67	0.02	0.02	0.00	0.26
32	77.83	9.12	9.26	9.19	0.05	0.04	0.01	0.54
33	77.92	9.95	10.02	9.99	0.02	0.02	0.00	0.25
34	94.30	8.78	8.76	8.77	0.01	0.00	0.00	0.08
35	94.38	9.73	9.77	9.75	0.01	0.01	0.00	0.15
36	120.78	8.40	8.47	8.44	0.02	0.02	0.00	0.29
37	120.87	9.82	9.77	9.80	0.02	0.01	0.00	0.18
38	151.00	8.29	8.30	8.30	0.00	0.00	0.00	0.04

Ave CV %	0.70

Method 6

Copper Recovery								
No	**Time (hrs)**	**Cu (1) (g)**	**Cu (2) g**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	0.13	0.13	0.13	0.00	0.00	0.00	0.00
2	0.17	0.42	0.43	0.43	0.01	0.01	0.02	2.36
3	0.33	0.84	0.62	0.73	0.15	0.11	0.21	21.11
4	0.50	2.02	2.19	2.02	0.12	0.09	0.06	5.95
5	0.75	1.24	1.68	1.46	0.31	0.22	0.21	21.15
6	1.00	3.01	3.03	3.02	0.01	0.01	0.00	0.40
7	1.50	4.44	4.54	4.44	0.07	0.05	0.02	1.56
8	2.00	5.89	4.39	5.14	1.06	0.75	0.21	20.70
9	3.00	7.16	6.91	7.03	0.18	0.13	0.03	2.55
10	16.67	6.36	5.99	6.91	0.27	0.19	0.04	3.84
11	24.53	5.99	5.73	5.86	0.18	0.13	0.03	3.14
12	40.50	5.61	5.88	5.75	0.19	0.14	0.03	3.33
13	48.92	5.17	5.61	5.39	0.31	0.22	0.06	5.69
14	72.93	5.24	6.62	5.93	0.98	0.69	0.16	16.46
15	95.73	5.51	6.69	6.10	0.83	0.59	0.14	13.68
16	159.45	5.40	6.42	5.91	0.73	0.51	0.12	12.27

Ave CV %	8.39

	Cu (g)	**Cu (%)**
Recovery	7.03	25.4%

pH Profiles								
No	**Time hr**	**pH 1**	**pH 2**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	10.42	10.42	10.42	0.00	0.00	0.00	0.00
2	0.08	10.32	10.19	10.26	0.09	0.07	0.01	0.90
3	0.17	10.33	10.27	10.30	0.04	0.03	0.00	0.41
4	0.33	10.26	10.25	10.26	0.01	0.00	0.00	0.07
5	0.50	10.14	10.19	10.17	0.04	0.02	0.00	0.35
6	0.75	10.17	10.18	10.18	0.01	0.00	0.00	0.07
7	1.00	10.14	10.17	10.16	0.02	0.01	0.00	0.21
8	1.50	9.91	9.88	9.90	0.02	0.01	0.00	0.21
9	2.00	9.86	9.80	9.83	0.04	0.03	0.00	0.43
10	3.00	9.41	9.40	9.41	0.01	0.00	0.00	0.08
11	3.08	10.06	10.17	10.12	0.08	0.05	0.01	0.77
12	16.67	8.21	7.91	8.06	0.21	0.15	0.03	2.63
13	16.75	10.45	10.37	10.41	0.06	0.04	0.01	0.54
14	24.53	9.48	9.25	9.37	0.16	0.12	0.02	1.74
15	40.50	8.10	7.82	7.96	0.20	0.14	0.02	2.49
16	40.58	10.17	10.40	10.29	0.16	0.12	0.02	1.58
17	48.92	9.45	9.19	9.32	0.18	0.13	0.02	1.97
18	49.00	10.02	10.04	10.03	0.01	0.01	0.00	0.14
19	72.93	7.84	7.58	7.71	0.18	0.13	0.02	2.38
20	73.02	10.04	10.34	10.19	0.21	0.15	0.02	2.08
21	95.73	8.17	7.72	7.95	0.32	0.23	0.04	4.01
22	95.82	10.36	10.41	10.39	0.04	0.03	0.00	0.34
23	159.45	7.35	7.11	7.23	0.17	0.12	0.02	2.35
24	159.53	10.65	10.63	10.64	0.01	0.01	0.00	0.13
25	189.28	8.00	7.64	7.82	0.25	0.18	0.03	3.26
26	189.37	10.66	10.70	10.68	0.03	0.02	0.00	0.26
27	207.47	8.60	7.91	8.26	0.49	0.35	0.06	5.91
28	207.55	10.12	10.05	10.09	0.05	0.03	0.00	0.49

Ave CV %	1.28

Method 7

Copper Recovery								
No	Time (hr)	Cu (1) g	Cu (2) g	Average	SD	SE	RSD	CV%
1	0.00	0.16	0.16	0.16	0.00	0.00	0.00	0.00
2	0.17	0.25	0.26	0.25	0.01	0.01	0.04	4.23
3	1.00	0.37	0.42	0.39	0.03	0.02	0.08	8.24
4	1.25	0.48	0.52	0.50	0.03	0.02	0.06	6.26
5	1.70	0.40	0.44	0.42	0.03	0.02	0.07	7.06
6	4.42	0.86	0.87	0.87	0.01	0.01	0.01	0.86
7	26.67	3.26	6.05	4.66	1.98	1.40	0.42	42.44
8	47.12	6.99	9.90	8.45	2.05	1.45	0.24	24.31
9	76.92	8.33	9.52	8.92	0.84	0.60	0.09	9.45
10	103.70	9.59	10.27	9.93	0.48	0.34	0.05	4.79
11	125.23	10.92	9.52	10.22	0.99	0.70	0.10	9.69

Ave CV %	10.67

	Cu (g)	Cu (%)
Recovery	10.22	36.9%

pH Profiles								
No	Time (hr)	pH 1	pH 2	Average	SD	SE	RSD	CV%
1	0.00	10.50	10.50	10.50	0.00	0.00	0.00	0.00
2	0.17	10.25	10.30	10.28	0.04	0.03	0.00	0.34
3	0.33	10.19	10.22	10.21	0.02	0.02	0.00	0.21
4	0.50	10.15	10.09	10.12	0.04	0.03	0.00	0.42
5	1.00	9.90	10.03	9.97	0.09	0.06	0.01	0.92
6	1.25	9.96	9.82	9.89	0.10	0.07	0.01	1.00
7	1.70	9.72	9.80	9.76	0.06	0.04	0.01	0.58
8	4.42	8.55	8.77	8.66	0.16	0.11	0.02	1.80
9	4.50	10.27	10.43	10.35	0.11	0.08	0.01	1.09
10	26.67	8.24	8.38	8.31	0.10	0.07	0.01	1.19
11	26.75	10.65	10.68	10.67	0.02	0.01	0.00	0.20
12	47.12	8.41	8.82	8.62	0.29	0.21	0.03	3.37
13	47.20	10.66	10.75	10.71	0.06	0.04	0.01	0.59
14	76.92	8.24	8.44	8.34	0.14	0.10	0.02	1.70
15	77.00	10.11	10.10	10.11	0.01	0.00	0.00	0.07
16	103.70	8.12	8.52	8.32	0.28	0.20	0.03	3.40
17	103.78	10.29	10.41	10.35	0.08	0.06	0.01	0.82
18	125.23	8.18	8.69	8.44	0.36	0.26	0.04	4.28

Ave CV %	1.22

Method 8

Cu Recovery								
No	**Time (hr)**	**Cu (1) g**	**Cu (2) g**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	0.15	0.15	0.15	0.00	0.00	0.00	0.00
2	0.17	0.19	2.45	1.32	1.60	1.13	1.21	121.36
3	0.33	3.99	3.38	3.69	0.43	0.30	0.12	11.66
4	0.50	3.82	3.31	3.56	0.37	0.26	0.10	10.26
5	1.00	4.56	5.42	4.99	0.60	0.43	0.12	12.07
6	1.50	6.02	7.00	6.51	0.69	0.49	0.11	10.63
7	2.50	7.84	9.35	8.59	1.07	0.75	0.12	12.41
8	23.75	15.09	13.37	14.23	1.22	0.86	0.09	8.55
9	52.25	19.06	19.33	19.19	0.19	0.14	0.01	1.00
10	73.50	15.19	13.62	14.41	1.11	0.78	0.08	7.67
11	100.22	14.57	12.08	13.33	1.76	1.25	0.13	13.23
12	119.58	13.68	12.02	12.85	1.18	0.83	0.09	9.15
13	140.92	10.65	11.42	11.04	0.54	0.38	0.05	4.92
14	163.42	12.34	8.38	10.36	2.80	1.98	0.27	27.04

Ave CV %	17.85

	Cu (g)	**Cu (%)**
Recovery	19.19	69.2%

pH Profiles								
No	**Time (hr)**	**pH 1**	**pH 2**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	10.12	10.12	10.12	0.00	0.00	0.00	0.00
2	0.17	9.93	9.94	9.94	0.01	0.00	0.00	0.07
3	0.33	10.01	9.97	9.99	0.03	0.02	0.00	0.28
4	0.50	9.90	9.91	9.91	0.01	0.00	0.00	0.07
5	1.00	9.93	9.82	9.88	0.08	0.05	0.01	0.79
6	1.50	9.84	9.64	9.74	0.14	0.10	0.01	1.45
7	2.50	9.28	9.08	9.18	0.14	0.10	0.02	1.54
8	2.58	9.74	9.67	9.71	0.05	0.04	0.01	0.51
9	23.75	8.61	8.37	8.49	0.17	0.12	0.02	2.00
10	23.83	9.81	9.54	9.68	0.19	0.14	0.02	1.97
11	52.25	8.70	9.12	8.91	0.30	0.21	0.03	3.33
12	52.33	9.95	9.96	9.96	0.01	0.01	0.00	0.07
13	73.50	8.58	8.57	8.58	0.01	0.00	0.00	0.08
14	73.58	10.14	10.07	10.11	0.05	0.04	0.00	0.49
15	100.22	8.87	8.11	8.49	0.54	0.38	0.06	6.33
16	100.30	9.76	9.58	9.67	0.13	0.09	0.01	1.32
17	119.58	7.92	8.29	8.11	0.26	0.19	0.03	3.23
18	119.67	9.86	9.85	9.86	0.01	0.00	0.00	0.07
19	140.92	8.11	8.14	8.13	0.02	0.02	0.00	0.26
20	141.00	9.91	9.86	9.89	0.04	0.03	0.00	0.36
21	163.42	8.19	8.30	8.25	0.08	0.06	0.01	0.94

Ave CV %	1.20

4M Ammonia in Carbonate System

Cu Recovery								
No	**Time (hr)**	**Cu (1) g**	**Cu (2) g**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	0.12	0.10	0.11	0.02	0.01	0.14	14.01
2	0.08	1.43	0.12	0.77	0.93	0.66	1.20	120.37
3	0.17	1.43	0.12	0.78	0.92	0.65	1.19	118.85
4	0.25	0.14	0.13	0.13	0.01	0.01	0.06	5.83
5	0.42	0.17	0.14	0.16	0.02	0.01	0.12	11.86
6	0.58	0.16	0.15	0.16	0.01	0.01	0.08	7.73
7	0.83	0.17	0.16	0.17	0.01	0.01	0.06	5.52
8	1.08	0.19	0.18	0.19	0.01	0.01	0.04	3.78
9	1.58	0.25	0.23	0.24	0.01	0.01	0.05	5.00
10	2.08	0.33	0.28	0.31	0.04	0.03	0.12	11.59
11	2.58	0.56	0.46	0.51	0.07	0.05	0.14	13.86
12	3.58	1.17	0.75	0.96	0.30	0.21	0.31	30.94
13	4.58	2.05	1.95	2.00	0.07	0.05	0.04	3.54
14	6.58	3.71	6.12	4.92	0.70	0.49	0.14	14.24
15	10.58	6.76	5.80	6.28	0.68	0.48	0.11	10.81
16	20.58	7.39	7.44	7.42	0.04	0.03	0.00	0.48
17	22.58	6.82	5.72	6.27	0.78	0.55	0.12	12.41
18	24.58	6.10	5.43	5.77	0.47	0.34	0.08	8.22
19	27.58	5.77	5.37	5.57	0.28	0.20	0.05	5.08
20	32.08	5.94	5.21	5.58	0.52	0.37	0.09	9.26
21	44.58	4.97	5.55	5.26	0.41	0.29	0.08	7.80

Ave CV%	20.06

	Cu (g)	**Cu (%)**
Recovery	7.42	14.8%

pH Profiles								
No	Time (hr)	pH 1	pH 2	Average	SD	SE	RSD	CV%
1	0.00	9.78	9.93	9.86	0.11	0.08	0.01	1.08
2	0.08	9.73	9.87	9.80	0.10	0.07	0.01	1.01
3	0.17	9.78	9.91	9.85	0.09	0.07	0.01	0.93
4	0.25	9.74	9.89	9.82	0.11	0.08	0.01	1.08
5	0.42	9.74	9.87	9.81	0.09	0.06	0.01	0.94
6	0.58	9.74	9.88	9.81	0.10	0.07	0.01	1.01
7	0.83	9.70	9.85	9.78	0.11	0.08	0.01	1.09
8	1.08	9.74	9.86	9.80	0.08	0.06	0.01	0.87
9	1.58	9.74	9.87	9.81	0.09	0.06	0.01	0.94
10	2.08	9.75	9.88	9.82	0.09	0.07	0.01	0.94
11	2.58	9.69	9.82	9.76	0.09	0.07	0.01	0.94
12	3.58	9.67	9.82	9.75	0.11	0.08	0.01	1.09
13	4.58	9.66	9.86	9.76	0.14	0.10	0.01	1.45
14	4.67	10.05	10.14	10.10	0.06	0.04	0.01	0.63
15	6.58	9.95	10.09	10.02	0.10	0.07	0.01	0.99
16	10.58	9.82	10.04	9.93	0.16	0.11	0.02	1.57
17	20.58	9.51	9.96	9.74	0.32	0.23	0.03	3.27
18	22.58	9.45	10.00	9.73	0.39	0.28	0.04	4.00
19	22.67	10.09	10.30	10.20	0.15	0.11	0.01	1.46
20	24.58	10.01	10.31	10.16	0.21	0.15	0.02	2.09
21	27.58	9.92	10.20	10.06	0.20	0.14	0.02	1.97
22	27.67	10.10	10.29	10.20	0.13	0.09	0.01	1.32
23	32.08	9.93	10.22	10.08	0.21	0.15	0.02	2.04
24	44.58	9.69	10.37	10.03	0.48	0.34	0.05	4.79

Ave CV %	1.56

5.5M Ammonia in Carbonate System

Cu Recovery									
No	**Time (hr)**	**Cu (1) g**	**Cu (2) g**	**Cu (3) g**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	0.14	0.14	0.14	0.14	0.00	0.00	0.03	2.55
2	0.08	0.15	0.16	0.16	0.16	0.01	0.01	0.05	5.44
3	0.17	0.16	0.17	0.16	0.17	0.00	0.00	0.01	0.93
4	0.25	0.18	0.18	0.19	0.18	0.01	0.00	0.03	3.45
5	0.42	0.17	0.17	0.20	0.18	0.02	0.01	0.09	9.21
6	0.58	0.20	0.18	0.23	0.21	0.02	0.01	0.11	10.95
7	0.83	0.27	0.56	0.34	0.45	0.15	0.09	0.34	33.78
8	1.33	0.36	0.35	0.38	0.37	0.02	0.01	0.05	4.70
9	1.83	0.40	0.42	0.55	0.49	0.08	0.05	0.17	17.10
10	2.33	0.54	0.65	1.00	0.82	0.24	0.14	0.29	29.19
11	3.33	0.78	0.83	1.15	0.99	0.20	0.12	0.21	20.58
12	4.33	1.41	1.62	2.63	2.12	0.65	0.38	0.31	30.76
13	10.63	0.55	3.54	5.98	4.76	0.21	0.12	0.04	4.47
14	22.08	0.55	5.31	6.59	5.95	0.46	0.27	0.08	7.74
15	24.08	5.62	5.76	5.73	5.74	0.07	0.04	0.01	1.25
16	27.08	4.98	4.97	5.33	5.15	0.21	0.12	0.04	4.00
17	30.42	4.73	4.00	5.12	4.56	0.57	0.33	0.12	12.47
18	48.28	5.60	5.64	5.73	5.69	0.07	0.04	0.01	1.19
19	50.58	4.98	5.44	5.85	5.65	0.44	0.25	0.08	7.72

Ave CV%	10.92

	Cu (g)	**Cu (%)**
Recovery	5.95	11.9%

pH Profiles									
No	**Time**	**pH 1**	**pH 2**	**pH 3**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	10.27	10.24	10.28	10.26	0.02	0.01	0.00	0.20
2	0.08	10.18	10.19	10.23	10.20	0.03	0.02	0.00	0.26
3	0.17	10.14	10.17	10.21	10.17	0.04	0.02	0.00	0.35
4	0.25	10.14	10.17	10.20	10.17	0.03	0.02	0.00	0.29
5	0.42	10.21	10.23	10.27	10.24	0.03	0.02	0.00	0.30
6	0.58	10.21	10.23	10.27	10.24	0.03	0.02	0.00	0.30
7	0.83	10.20	10.23	10.25	10.23	0.03	0.01	0.00	0.25
8	1.33	10.18	10.21	10.24	10.21	0.03	0.02	0.00	0.29
9	1.83	10.16	10.18	10.22	10.19	0.03	0.02	0.00	0.30
10	2.33	10.13	10.16	10.18	10.16	0.03	0.01	0.00	0.25
11	3.33	10.15	10.16	10.19	10.17	0.02	0.01	0.00	0.20
12	4.33	10.09	10.10	10.15	10.11	0.03	0.02	0.00	0.32
13	10.63	10.03	9.98	10.06	10.02	0.04	0.02	0.00	0.40
14	22.08	9.99	9.98	10.04	10.00	0.03	0.02	0.00	0.32
15	24.08	9.81	9.81	9.89	9.84	0.05	0.03	0.00	0.47
16	27.08	9.84	9.80	9.89	9.84	0.05	0.03	0.00	0.46
17	27.17	10.15	10.13	10.17	10.15	0.02	0.01	0.00	0.20
18	30.42	9.79	9.76	9.79	9.78	0.02	0.01	0.00	0.18
19	48.28	9.67	9.66	9.74	9.69	0.04	0.03	0.00	0.45
20	50.58	9.63	9.64	9.72	9.66	0.05	0.03	0.01	0.51

Ave CV %	0.31

7M Ammonia in Carbonate System

Cu Recovery								
No	Time (hr)	Cu (1) g	Cu (2) g	Average	SD	SE	RSD	CV%
1	0.00	0.12	0.15	0.14	0.02	0.02	0.16	15.71
2	1.00	0.56	0.49	0.52	0.04	0.03	0.09	8.57
3	6.03	6.17	5.82	6.00	0.25	0.18	0.04	4.14
4	10.62	3.98	6.01	4.99	0.85	0.60	0.17	17.04
5	24.15	5.42	5.57	5.50	0.10	0.07	0.02	1.88
6	34.53	4.92	5.71	5.31	0.56	0.40	0.11	10.53
7	49.20	5.25	5.23	5.24	0.02	0.01	0.00	0.30

Ave CV %	8.31

	Cu (g)	Cu (%)
Recovery	6	21.6%

pH Profiles								
No	Time (hr)	pH 1	pH 2	Average	SD	SE	RSD	CV%
1	0.00	10.59	10.63	10.61	0.03	0.02	0.00	0.27
2	0.08	10.14	10.10	10.12	0.03	0.02	0.00	0.28
3	0.25	10.09	10.09	10.09	0.00	0.00	0.00	0.00
4	0.50	10.00	10.08	10.04	0.06	0.04	0.01	0.56
5	1.00	10.01	10.01	10.01	0.00	0.00	0.00	0.00
6	2.00	10.04	10.04	10.04	0.00	0.00	0.00	0.00
7	6.03	10.03	10.03	10.03	0.00	0.00	0.00	0.00
8	10.53	10.16	10.14	10.15	0.01	0.01	0.00	0.14
9	10.62	10.60	10.62	10.61	0.01	0.01	0.00	0.13
10	24.15	10.23	10.25	10.24	0.01	0.01	0.00	0.14
11	26.95	10.16	10.16	10.16	0.00	0.00	0.00	0.00
12	34.45	10.33	10.21	10.27	0.08	0.06	0.01	0.83
13	34.53	10.52	10.52	10.52	0.00	0.00	0.00	0.00
14	49.20	10.51	10.51	10.51	0.00	0.00	0.00	0.00

Ave CV %	0.17

15 LTSR in Carbonate System

Cu Recovery								
No	**Time (hr)**	**Cu (1) g**	**Cu (2) g**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	0.08	0.10	0.09	0.01	0.01	0.16	15.71
2	1.08	0.56	0.54	0.55	0.01	0.01	0.02	2.16
3	6.08	4.63	4.41	4.52	0.15	0.11	0.03	3.40
4	9.08	4.81	4.61	4.71	0.14	0.10	0.03	3.02
5	14.58	6.20	6.70	6.45	0.35	0.25	0.05	5.47
6	24.08	5.78	5.48	5.63	0.22	0.15	0.04	3.84
7	32.58	4.81	3.66	4.23	0.82	0.58	0.19	19.30

Ave CV%	7.56

	Cu (g)	**Cu (%)**
Recovery	6.45	12.9%

pH Profiles								
No	**Time (hr)**	**pH 1**	**pH 2**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	9.98	10.22	10.20	0.17	0.12	0.02	1.66
2	0.08	10.47	9.73	10.10	0.52	0.37	0.05	5.18
3	0.25	10.23	9.95	10.09	0.20	0.14	0.02	1.96
4	0.58	10.31	9.89	10.10	0.30	0.21	0.03	2.94
5	1.08	10.11	9.91	10.01	0.14	0.10	0.01	1.41
6	2.08	9.95	9.93	9.94	0.01	0.01	0.00	0.14
7	3.08	10.01	9.85	9.93	0.11	0.08	0.01	1.14
8	6.08	10.21	9.97	10.09	0.17	0.12	0.02	1.68
9	9.08	10.17	9.81	9.99	0.25	0.18	0.03	2.55
10	14.58	10.07	9.71	9.89	0.25	0.18	0.03	2.57
11	24.08	9.50	9.92	9.71	0.30	0.21	0.03	3.06
12	24.17	10.62	10.16	10.39	0.33	0.23	0.03	3.13
13	32.58	10.35	10.13	10.24	0.16	0.11	0.02	1.52
14	50.58	10.56	10.04	10.30	0.37	0.26	0.04	3.57

Ave CV %	2.32

10 LTSR in Carbonate System

Cu Recovery								
No	**Time (hr)**	**Cu (1) g**	**Cu (2) g**	**Average**	**SD**	**SE**	**RSD**	**CV%**
1	0.00	0.06	0.06	0.06	0.00	0.00	0.05	5.42
2	3.08	3.10	2.93	3.01	0.12	0.08	0.04	3.91
3	18.83	5.07	4.93	5.00	0.10	0.07	0.02	2.05
4	21.33	4.71	4.20	4.46	0.36	0.26	0.08	8.13
5	26.33	4.73	4.41	4.57	0.22	0.16	0.05	4.86
6	43.33	6.90	6.33	6.62	0.40	0.29	0.06	6.10
7	50.98	4.04	3.74	3.89	0.21	0.15	0.05	5.42
8	66.92	4.58	3.81	4.20	0.54	0.38	0.13	12.89
9	92.33	4.50	4.16	4.33	0.24	0.17	0.06	5.52

Ave CV%	6.04

	Cu (g)	**Cu (%)**
Recovery	6.62	13.2%

pH Profiles								
No	Time (hr)	pH 1	pH 2	Average	SD	SE	RSD	CV%
1	0.00	9.98	9.72	9.85	0.18	0.13	0.02	1.87
2	0.08	9.95	9.67	9.81	0.20	0.14	0.02	2.02
3	0.58	9.65	10.11	9.88	0.33	0.23	0.03	3.29
4	0.83	9.87	9.90	9.88	0.02	0.02	0.00	0.21
5	1.58	10.00	9.78	9.89	0.16	0.11	0.02	1.57
6	3.08	9.91	9.81	9.86	0.07	0.05	0.01	0.72
7	3.17	10.20	10.06	10.13	0.10	0.07	0.01	0.98
8	4.25	10.14	10.30	10.22	0.11	0.08	0.01	1.11
9	18.83	10.23	10.03	10.13	0.14	0.10	0.01	1.40
10	21.33	10.01	10.23	10.12	0.16	0.11	0.02	1.54
11	23.33	9.99	9.95	9.97	0.03	0.02	0.00	0.28
12	26.33	10.22	9.90	10.06	0.23	0.16	0.02	2.25
13	43.33	9.25	9.39	9.32	0.10	0.07	0.01	1.06
14	47.33	9.21	9.38	9.29	0.12	0.09	0.01	1.29
15	50.98	9.37	9.32	9.34	0.04	0.03	0.00	0.38
16	51.07	10.76	10.61	10.68	0.11	0.07	0.01	0.99
17	66.92	9.46	9.17	9.31	0.21	0.15	0.02	2.20
18	68.83	10.04	9.91	9.97	0.09	0.06	0.01	0.92
19	90.67	10.09	10.20	10.20	0.08	0.05	0.01	0.76
20	90.75	10.81	10.65	10.65	0.11	0.08	0.01	1.06

Ave CV %	1.295472