Sustainable Recovery of Noble Metals from Electronic Wastes (e-waste) Using New Ionic Liquids

MSc RESEARCH

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DECLARATION

I declare that this is my own work. It is being submitted for the degree of Master of Science to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination to any other University.

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(Signature of Supervisor)

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ABSTRACT

Only a minute amount e-waste is being officially recycled of the vast amounts being generated globally. A selective process using ionic liquids was investigated in this research because they have the potential of reducing the gaseous and aqueous emissions with solvent recovery. The objectives of this project was to experimentally determine the best conditions for the selective leaching of the noble metals from e-waste through the use the imidazolium based ionic liquids from e-waste however poor recoveries of gold, silver and palladium of 1%, 0.4% and 1% in the $BmimHSO_4$ respectively showed the ionic liquids were not very selective for the noble metals. Copper leaching in the ionic liquids did give higher recoveries of over 46% in the chloride based ionic liquid BmimCl whilst the other base metals also gave high recoveries to as high 98% for iron. Different factors like sample sizes, pre-treatment of the waste sample and lixiviant concentration were also considered with the aim increasing the leaching ability of the system. It was determined that the leaching of the waste was highly dependent on the pH and oxidation potential of the system and that the presence of base metals hindered the leaching ability of the system. The acid pre-treatment of the sample did give high gold recoveries in the $BmimHSO_4$ ionic liquid at 65%. The overall leaching process did not produce high recoveries of the noble metals or display selectivity for noble metals of the ionic liquids without some pre-treatment process done.

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ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
Bmim	1-butly-3-methylimidazolium
EEE	Electronic and Electrical Equipment
Emim	1-ethly-3-methylimidazolium
e-Waste	Elecronic waste
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectroscopy
PCB	Printed Circuit Boards
SEM	Scanning Electron Microscope
WEEE	Waste Elecronic and Electrical Equipment
WPCB	Waste printed curcuit boards
MSW	Municipal solid waste

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1. INTRODUCTION

1.1 Background of Research

One of the major challenges of sustainable development is promoting an industry which is both ecologically durable and economically viable. This requires processes that are not only raw material and energy efficient but are also able to limit the generation of wastes and toxic effluents through effective methods of process synthesis and intensification. Research has been done to come up with strategies which work towards enhancing resource efficiency and achieving a circular economy with zero waste generation (Hagelüken, Lee-Shin, Carpentier & Heron, 2016) and according to Bangs, Meskers, and Van Kerckhoven (2016) a huge improvement has occurred in the past 10 years. Another way of promoting sustainability is through the use of circular economies in industries and this is only possible through promoting 100% end of life waste recovery, recycling and reuse Hagelüken et al. (2016). There are a few industries if any which would not benefit from a circular economy (Huang, Guo & Xu, 2008). End of life waste from electronic and electrical gargets or the technological world known as electronic waste (e-waste) or waste from electrical and electronic equipment (WEEE) is one of the many industries which could benefit greatly from the circular economy and has generated a high degree of interest in recent years. The e-waste recycling process is popularly known as a form of urban mining because of the rich harvest of minerals which can be recovered (Hagelüken & Meskers, 2009).

There are numerous definitions of e-waste depending on continent, region, politics, regulations, decrees and environmental guidelines. In general, e-waste is said to be waste from electrical and electronic components that are no longer in use or wanted by the user. Some definitions of e-waste do not include the electrical phase or are restricted to electricals of a certain size. To add to the different definitions of e-waste in use, further categories have also been done which are regional, political, regulatory to mention a few and can include the white goods, small/large household appliances, electrical and electronic tools to mention a few. For example in the US, white goods are not considered to be e-waste statistically, whereas they are included in the categories of e-waste legislation of the European Union (EU) and Japan (Goodship & Stevels, 2016). The vastness of the array of equipment covered as e-waste is however common everywhere with the list growing daily. The numerous definitions of the waste mean that the recorded actual amounts of the waste vary vastly across the world. An undisputed fact in South Africa and globally is that miniaturization and technological advances have increased substantially the amount of electronic wastes (e-waste) generated annually with the waste concentration increasing at an estimated rate of approximately 3-8% annually. A range of about 20 to 50 million tonnes of e-waste was generated worldwide each year whilst an approximate 41.8 million tonnes was found for the global waste in the year 2014 with less than 15% of the figure being collected by official take-back systems (Balde et al. 2014; STEP 2014). The rest will be disposed of in the Municipal Solid Waste (MSW) for landfilling or incineration, collected unofficially or just stored in closets, basements, cellars or garages (Goodship & Stevels, 2016).

In addition to various gadgets electronic waste also covers a number of components which includes electric cables, LEDs, plastic covers, printed circuit boards and metal casings making a complex mix of components made up of complex materials. The complex heterogeneous mixture of materials found in e-waste includes metals, ceramics and plastics which may be valuable and/or hazardous and are generally difficult to recycle. The materials are of varying compositions, sizes and shapes because of the differing dynamic technologies and manufacturers, hence coming up with a standard or average composition has proven to be difficult. However according to the European Topic Centre on Resource and Waste Management the approximate weight percentages of the materials are: 61% for metals (ferrous and non-ferrous metals), 21% for plastics, 5% for glass and 10% for “other” (which includes ceramics, glass and wood) (Widmer et al., 2005). The recovery of the larger metal fraction like copper, steel and aluminum is much easier and being done successfully and at a much higher rate. Plastics though difficult to recycle because of their different properties are also being recovered at an increasing rate (Bangs et al., 2016). The smaller components like the PCB, which is arguably the most valuable component in WEEE regardless of the fact that they make up only 3% by weight of the e-waste generated offer a bigger challenge because of the complexity of the materiel mixture, some having over 40 different elements. Hence a lot of research has had to be done to develop formal state of the art recycling plants, which have been able to achieve high recovery rates in most cases for some of the metals in this component including the precious metals. Copper and precious metals which include gold, silver and palladium have the highest value in e-waste and make up about 80% of the overall component value (Letcher & Vallero, 2011). According to research done by Chehade et al. (2012) and Bangs et al in 2016 gold, silver, palladium and copper cover about 90% of the gross metal value found in PCBs. Hence, they shall be the area of interest in this research. With the main objective being to achieve a high recovery of these precious metals in an environmentally sustainable method that is cost effective. In previous research the recovery of precious/noble metals usually ranges at a percentage which is greater than 95 if no metal loses are incurred (Bangs et al., 2016; Hagelüken et al., 2016; Reuter et al., 2013;). The percentage recovery is however highly dependent on the efficiency of the processing technique used and can be as low as 15-20% for gold and silver whilst palladium recovery is in the range of 5-10% (Reuter et al., 2013). It has hence become imperative that sustainable strategies be developed for the recovery of noble metals from e-waste which takes into account all the possible changes in technologies. All these factors will also be taken into account in this research in order to develop a competitive hydrometallurgical method though a lot of research has gone into the recovery of metals from e-waste using all the metallurgical processes (Cui & Zhang, 2008).

Coming up with a plant which can recycle and recover all the material from all components of the e-waste on-site might be not only very expensive but also impossible. Preprocessing the waste into different components (which usually means material constituent) for distribution to various treatment centers has proven to be much more helpful and effective and is being done in many countries including South Africa. The plastics are sent for further processing at a plastic recycling plant whilst the iron casing is sent for processing at a steel company and the rest of the components go to their respective centers. The larger the components of e-waste the easier the separation and recycling process done, however as the components get smaller it becomes more difficult and complicated. The complexity of elements in some of smaller WEEE components like the Printed Circuit Board (PCB) make the recycling procedure almost economically unattainable and at times the physics, chemistry, metallurgy and thermodynamics make it impossible (Reuter et al., 2013). Successful recovery of some of the materials found on PCBs has been done in Switzerland at SWICO and SENS (Sinha-Khetriwal, Kraeuchi, & Schwaninger, 2005) and in South Africa at SA precious metals. The incorporation of the waste into functional ore smelters is usually unfeasible not only because of the vastness of the elemental constituents but also because of the inconsistencies in the waste which would affect the feed and production stream. The technological advancement which are constantly changing the material composition of the waste also adds to problem of incorporating the waste into an already functional system especially as it might eventually be non-profitable (Hagelüken et al., 2016). Though the recovery of the smaller contained metals is possible, some industries which focus on one type of material are reluctant to invest on the smaller quantities of some of the valuable metals found in the e-waste (Reuter et al., 2013).

The passion for electronic devices cannot ignore the scarcity, cost and environmental impacts of noble metal mining which contribute significantly to the manufacture and functioning of these devises (Hagelüken, 2011). Separation technics, physical and mechanical need to be used to separate the different components. After the initial splitting of the waste various into its components both mechanical and chemical separation technics need to be used to achieve further separation of the materials and elements. Each treatment method can cumulate in metal loss and this is an area of interest in this research with an analysis done on the effects of magnetic separation and size reduction which are mechanical treatment processes on the final recovery. Pyro-metallurgical processes have been developed industrially and are in use in some European countries like Belgium which incorporated the use of the copper smelter furnace with a high percentage recovery (Hageluken & Na, 2006). Pyrometallurgical recycling processes usually work together with hydro and electro-metallurgy to achieve high purities which makes the process expensive for a small startup plant especially in Africa. One drawback of these processes is that they require a high capital input, are relatively expensive to run, with a high waste generation in slag as well as loss of metals and production of hazardous gases (Jadhav & Hocheng, 2015; Khaliq, Rhamdhani, Brooks, & Masood, 2014; Seongjun & Cui, 2012).

Recovery of metals by biotechnology has been another promising technology though only a few studies have been carried out for this route (Khaliq et al., 2014). Bio-metallurgy has the potential for a major technology breakthrough for the materials and minerals industry due to the great interest shown by major international companies for this new technology in other similar mineral processes such as recovery of metals from gold ores (Cui & Zhang, 2008). Research has also been focusing on the hydrometallurgical processes because they are relatively cheaper with Kumar, Lee, Kim, Jeong and Yoo (2014) conducting research using sulphuric acid and nitric acid for base metal leaching with 96% recovery for copper; whilst precious metal leaching was researched by Zhou, Zheng and Tie (2005) with the use of hydrochloric acid, sodium chlorate and nitric acid; and patented by Kogan (2006) with the use of a halogenic acid and bromide ions with average high percentage recoveries of 92% and 93% (Cui & Zhang, 2008). However, the use of these acids generates large quantities of hazardous liquid and gaseous wastes. Hence there has also been a lot of research done with the use of alternative solvents like ionic liquids which are greener for copper leaching, thiourea in sulphuric acid for gold and silver leaching, thiousulphate for gold leaching and numerous other methods (Calgaro, Bertuol, Silvas, Romano, & Tenorio, 2009). This research will be investigating the use of hydrometallurgy in the recovery of metals as already stated above using a group of alternative solvents which have been shown to be greener in most studies. These solvents are called ionic liquids and are generally inorganic salts which have a large cation head and a relatively smaller anion tail and can exist as liquids at room temperature in some cases. The advantages of using these solvents is the fact that they are thermally stable, less volatile and exhibit various chemical properties which enable them to be used as metal solvents. The ionic liquids which will be used in this research include 1-butyl-3-methylimmidazolium chloride (BmimCl), 1-butyl-3-methylimmidazolium hydrogen sulphate ($BmimHSO_4$) and 1-ethyl-3-metylimmidazolium chloride EmimCl.

1.2 Problem Statement

This research will be looking into the recovery of the valuable metals from e-waste namely the printed circuit boards (PCBs) using hydrometallurgical processes because they are relatively cheaper, easier to run and start-up, and can operate on a smaller scale. The PCBs which make up only a small fraction of the overall waste and are found deep in the core of the system and need careful pre-processing in order to ensure that the material recovery is high as stated above (Bangs et al., 2016). A process that is selective for specific metals at every turn is crucial. Though not all the metals will be successfully recovered because of the thermodynamic properties of the metals the residues can find other uses like secondary building material (Bangs et al., 2016; Hagelüken et al., 2016).

A lot of research has been conducted on the use of different lixiviants as stated above. However, the use of these acids in hydrometallurgy generates large quantities of hazardous liquid and gaseous wastes. Hence the focus of this research will be on the use of the alternative solvent ionic liquids which are greener (Calgaro et al., 2009). The ionic liquids are non-volatile and non-toxic which makes them both environmentally friendly and healthy. There has also been a lot of study into the use of these solvents in hydrometallurgy of different metals including metal beneficiation technology. Depending on how they are done hydrometallurgical processes can offer a degree of selectivity which is required for such a process. The selectivity offered by the use of ionic liquids is required to make the process feasible and economically viable in industry. Hence the use of the ionic liquids, I-ethyl-3-imidazolium chloride, 1-butyl-3-imidazolium chloride and 1-butyl-3-methyl imidazolium hydrogen sulphate will be investigated. The aim is to leach copper, gold, silver and palladium, some of the valuable metals found on e-waste printed circuit boards. The use of ionic liquids has the potential to reduce the gaseous emissions and aqueous waste generation associated with existing technologies (thermal treatment/

cyanide medium) while maintaining the economy of the overall recycling scheme through recovery of the solvents. Hence this research investigates how well the already mentioned ionic liquids can compare to traditional solvents like water and sulphuric acid when it comes to the leaching gold, silver, palladium and copper using thiourea as the complexing agent. It will also be investigated how well these solvents can complex with our said metals for better recovery and how they are affected by the presence of the base metal iron. Different ionic liquids with different cation carbon lengths will be invested in the research because they have the potential leach the metals differently since they have different properties. Two types of anions will also be investigated that is the HSO_4^- and the Cl^- anion. The effect of the size of the sample and how pre-treatment of the sample affects the ability to leach the value metals will also be investigated because previous studies have shown that there are optimum sizes which exist and that pre-treatments usually results in metal loss.

1.3 Aims

The aim of this project is to come up with a comprehensive study of the various techniques used in the recycling of e-waste using both mechanical and hydrometallurgical methods. A comparison will be conducted on the effect of using mechanical pretreatment of the e-waste in the form of size reduction and magnetic separation processes which are both energy and cost intensive processes against direct hydrometallurgical treatment in ionic liquids. To the best of our knowledge ionic liquids have yet to be investigated for the recovery of gold, silver and palladium from e-waste. The project aims to investigate the success of using ionic liquids in the hydrometallurgical recovery of gold, silver and palladium from e-waste, whilst also studying the recoveries of the process. The second aim is to compare recoveries which result from the use of the environmentally more benign ionic liquid in comparison to the aqueous acids. The project also aims to study the effect of using different ionic liquids 1-ethyl-3-methyl imidazolium chloride, 1-butyl-3-methyl imidazolium chloride and 1-butyl-3-methyl imidazolium hydrogen sulphate on the leaching of gold, silver and palladium. Hence the effect of varying the carbon chain in the in cation and changing the anion head will be compared. The effect of reducing iron and other base metal concentration as a result of pretreatment using magnetic separation and pre-leaching on the ability to leach gold, silver and palladium will also be investigated with ionic liquid as the lixiviant and how this affects copper. Factors like pH, time, particle size and temperature will also be studied in the work. The solid, liquid and gaseous by-products of the process will also be studied to ensure that the final product is less hazardous components and can be safely landfilled.

1.4 Research Objective

- To assess the use of ionic liquids 1-ethyl-3-methyl imidazolium chloride, 1-butyl-3-methyl imidazolium chloride and 1-butyl-3-methy imidazolium hydrogen sulphate in the extraction of gold, silver and palladium under conditions which include:
    - the impact of mechanical pre-processing through size reduction using milling of the waste sample and removing the iron matter prior to the leaching of metals from e-waste will be invested
    - To investigate the ability of the ionic liquids to selectively leach the value metals over the base metals found in e-waste
    - To investigate the effect of thiourea and $Fe_2(SO_4)_3$ on the recovery of gold, silver and palladium from e-waste
    - To investigate the ability of ionic liquids to complex with gold and silver in the absence of a complexing agent
    - To investigate the metal recovery achieved from the system
- To assess the effect of the cation and anion ionic liquid chain in the leaching of metals from e-waste
- To assess the environmental footprint of the implemented metals recovery scheme using the ionic liquids 1-ethyl-3-methyl imidazolium chloride, 1-butyl-3-methy imidazolium hydrogen sulphate and I-butyl-3-methyl imidazolium chloride

1.5 Hypothesis

The hypothesis is that ionic liquids can be successfully used as protic acids in the leaching of gold, silver and palladium from e-waste.

1.6 Report Layout

This dissertation comprises of five chapters. Chapter 1 describes the background and motivation of the research, as well as the problem statement, aims and the objectives. Chapter 2 is literature review which encapsulates key details regarding the e-waste problem and how it has been addressed globally. The initial focus is directed towards understanding the pros and cons of conventional metal recovery techniques and in the latter sections it examines the properties of ionic liquids which make them favorable for the leaching of gold and silver from electronic waste. Chapter 3 provides a detailed description of the materials used, a description of the experimental apparatus/set-up, and experimental procedures and methods applied to achieve the research objectives. Chapters 4 presents the experimental results, coupled with discussions. In Chapter 5 the conclusions and recommendations of the study is given.

2. LITERATURE REVIEW

2.1 e-Waste

The production of e-waste is rapidly increasing annually and cannot be stopped because electronic and electrical equipment (EEE) are necessary for use in everyday life. In spite of the economic difficulties and crunches being encountered globally which have resulted in a reduction in the rate of consumerisms; the buying and selling of EEE is still quite rife and the projections predict an increase by the year for some gargets like tablets, laptops and notebooks whilst other gargets like desktop computers will decrease by approximately 28% 2020 (Bangs et al., 2016). The advance in technology has also had an impact on the life span of most EEE which turns them into waste at a faster rate for example a CPU lifespan is now at 2 years in 2017 from 4–6 years in 1997. Deliberate marketing strategies like planned obsolescence have had a drastic effect on the lifespan of the electronics There is therefore inevitably need to replace or dispose of the EEE over a shorter time and age than previously resulting in the generation ofe-waste which has been given various definitions depending on location, legislation and everyday use (STEP, 2014). But in general e-waste can be said to refer to EEE which are no longer in use or are unwanted by the initial owner. It can also refer to obsolete, broken or irreparable electronic and electrical appliances (Luther, 2010; Maczulak, 2010). The STEP initiative global definition states “E-Waste is a term used to cover items of all types of electrical and electronic equipment and its parts that have been discarded by the owner as waste without the intention of re-use” (STEP, 2014). These components are also known as waste from electrical and electronic equipment and the terms have been used interchangeably in some studies (Maczulak, 2010) which is what we will do. EEE covers a very wide range of appliances found in almost every sector from industrial, hospital, household, offices or schools to mention a few which explains the diversity of WEEE. The European Parliament and Council defined WEEE as having ten categories which were then widely accepted by other communities (Widmer, Oswald-Krapf, Sinha-Khetriwal, Schnellmann, & Böni, 2005). The objective is having a uniform nomenclature which would assist in the identification and data collection of the waste. Of the ten categories identified the heaviest equipment fall under the white goods, referring to equipment normally found in homes for domestic use like refrigerators, microwave ovens, cooking stoves and straightening irons. Small household electrical equipment which includes irons, hairdryers etc which can be in a category of their own. Consumer electronics are another common category which includes servers, printers, scanners, radios, CD and DVD players etc. Information technology is a common category of e-waste which is increasing rapidly in number because of the new age development era. It mainly includes computers, mobile phones, monitors, digital cameras and video games etc. This is the fastest growing category and contributes the highest number though probably the lightest weight entities in e-waste. There is no global agreed upon nomenclature of e-waste yet in use though. From the above information it can be seen why and how vast the EEE industry and why the generation of e-waste is a cause of concern globally (Osibanjo & Nnorom, 2007). Large volumes are being generated on a daily basis because of the advancement in technology which has resulted in the rapid evolution and demand of most of the above mentioned devices which then become obsolete at a faster rate (Balde et al., 2014).

Large volumes of solid waste are collected on a daily basis by most local municipalities. With e-waste comprising of 5-8% of the municipal solid waste (MSW) and is one of the fastest growing waste fractions (Maczulak 2010; Widmer et al. 2005; STEP, 2014). It is an example of waste which has very high value (Namias, 2013). A report by The World Bank in 2012 showed that with the increase in urban population there was doubling in size of uncategorized municipal solid waste (MSW) generation. The report stated that ten years ago there were 2.9 billion urban residents generating about 0.64 kg of MSW per person per day (0.68 billion tonnes per year) these numbers increased to about 3 billion residents generating 1.2 kg per person per day (1.3 billion tonnes per year) in the year 2012 (European Commission, 2010). Estimating that by 2025 this will likely increase to 4.3 billion urban residents generating about 1.42 kg/capita/day of municipal solid waste (2.2 billion tonnes per year) (European Commission, 2010; The worldbank, 2012). The MSW is either incinerated which can generate hazardous fumes or ends up in the landfills which results in the production of harmful leachates and acid rains if not done accordingly, and e-waste contributes significantly to this because of the presence of heavy metals and flame retarded plastics. This e-waste being disposed of also consists of valuable matter which can be recovered or reused. Hence there is need for policies and strict legislature insisting on recycling of any value matter before final disposal. With the increase in waste generation there is a subsequent increase in the cost of dealing with the waste from $205 billion (3 127 billion rand) a year to $375 billion (5 720 billion rand) in the year 2025 with the sharpest increase being in developing countries (The worldbank, 2012).

Focusing on electronics in the communication and information technology, in the year 2004 there were barely over 20 million mobile phones subscribers in South Africa but by the year

2014 the number had extrapolated to over 78 million (The World Bank, 2016). Internet usage has increased from over 3 million in 2004 to over 25.9 million just ten years later (The World Bank, 2016). Assuming the rapid increase in these services correlates with an increase in equipment use hence it can be safely assumed that computer and mobile phone usage has more than tripled in a space of ten years.

2.1.1 Electronic Waste in South and Southern Africa

As a result of the ongoing technological advancement there has been a huge increase in the use of electrical and electronic equipment in South Africa. For example, almost every household has a wide range of white goods and they are constantly being upgraded or changed to measure up to the most recent trends. In the telecommunication department electronic equipment is very common, with almost every adult and most children owning or having owned one at some point in their lifetime a mobile phone. For a mobile phone the life span is approximately 3 years because of the technological advancement with an average weight of 0.1kgs (Bangs et al., 2016; Finlay & Liechti, 2008). The information technology and telecommunications industries have experienced a rapid growth that has led to an improvement in the capacity and specifications of the equipment but simultaneously to a decrease in the products lifetime. Most manufacturers are designing products that last for a couple of years only known as planned obsolescence because of the economic advantage this has on the manufacturers which is not beneficial to either the consumer or the environment. The estimated quantities of white goods, consumer electronics and information technology equipment amount to between one to two million tons in South Africa which will enter the waste stream in the next 5-10 years according to research done to Finlay in 2008 (Finlay & Liechti, 2008).

According to the census carried out in 2011 South Africa had a human population of at least 51.8 million. There has been noted a direct correlation between the population of a country and the amount of e-waste generated. The stage of development of the country also has an influence. South Africa is ranked as one of the highest developed countries in Africa hence will produce a significantly high amount of waste. However few municipalities have accurate data collection systems in place (CSIR, 2011) hence determining the exact amounts of waste generated is rather difficult. “The UNEP study of 2009 warns that by 2020, electronic waste in South Africa and China will have soared by approximately 200-400 percent from the 2007 levels, and by 500 percent in India” (Olowu, 2012). Hence extrapolated increases in the quantities of e-waste are expected and have been predicted. eWASA (e-Waste Association of

South Africa) puts the figure of e-waste production in South Africa at 322 000 tonnes per annum and Table 2.1 shows the total waste classifications and percentage content.

Table 2.1 e-Waste Classifications and the Tonnes Generated
Adapted from Greencape, 2017

e-Waste Classification	Tonnes	Percentage Yield
Large appliances (stoves, fridges)	125 000	39%
Consumer Equipment	78 000	24%
Information technology (IT) equipment	77 000	24%
Small household appliances (toasters, kettles, etc)	40 000	13%

The high number of e-waste recycling companies only recycle 45 000 tonnes which account for only 12% of the waste hence there is a lot of room for growth in the field which would have a lot of positive implications in job creation and on the environment (Greencape, 2017).

In 2004 South Africa, together with India and China became part of a global e-waste knowledge sharing program initiated by the Swiss State Secretariat for Economic Affairs (SECO) and implemented by the Federal Laboratories for Materials Testing and Research which translated from Eidgenössische Materialprüfungs- und ForschungsAnstalt in Swiss (EMPA) (Finlay & Liechti, 2008). eWASA was formed as a result in 2008. A report conducted in South Africa classified e-waste as hazardous hence though there isn’t yet a direct legislature applying to e-waste it can fall under the bill of rights which stipulates that everyone has the right to the following (Department of Environmental Affairs, 2012):

a. an environment that is not harmful to their health or well-being; and
b. have the environment protected, for the benefit of present and future generations, through reasonable legislative and other measures that –
    I. prevent pollution and ecological degradation;
    II. promote conservation; and
    III. secure ecologically sustainable development and use of natural resources while promoting justifiable economic and social development (Finlay & Liechti, 2008).

Other policies and laws which can also cover e-waste include policies which cover water, air, waste, hazardous substances as well as health and safety (Finlay & Liechti, 2008; Schuelp et al., 2009). However this can also have the downside of confusing issues because they each cover the e-waste from different perspectives (Schuelp et al., 2009). In addition to this there are the different governments departments and bills which want to enforce different approaches in dealing with the waste these include the National Environmental Management Waste Bill, Second-hand Goods Bill and the Constitution (Finlay & Liechti, 2008).

The e-Waste Association of South Africa has many members who are actively involved in the collection and disposal of the e-waste. This has resulted in the formation of a number of recycling companies which deal with the waste in variable ways (Finlay & Liechti, 2008; Schuelp et al., 2009). The two largest recycling companied in South Africa are DESCO recyclers and Universal Recyclers which often win tenders from large institutes and the government departments and they process approximately 9000 tonnes per annum (Greencape, 2017). Other smaller recyclers are more involved in the day to day collection of the waste from smaller sources like households, from smaller collectors and from the MSW. Some are only involved in the collection and dismantling of the waste before transport elsewhere for further processing. The product is then sold locally, exported, stockpiled or sent to a registered landfill. The country is also involved in the direct metal recovery of precious metals from the e-waste by the use of hydrometallurgical processes by SA Precious metals another company involved with e-waste recycling.

One of the major challenges faced by South Africa like other countries is with the collection techniques and lack of knowledge exhibited by most consumers. The four common forms of collection techniques have been exhibited in South Africa, the formal recyclers' process approximately 12% of the waste but the target is to get as high as 20% in the next 5 years or less (Snyman & Vorster, 2010). As already stated above about 5-8% of e-waste has reported to the municipal waste where if not collected by scavengers will end up in landfills or incinerated, but studies have shown this is usually for IT scrap, TVs and telecommunications (Lawhon, 2013). In addition to this is usually the fate of shredded plastics (Finlay & Liechti, 2008). The rest of the waste will be stored by the owner in basements and garages, recycled informally, added to the domestic waste stream (mainly batteries and lamps) or dumped illegally/legally at curbsides (Hagelüken & Corti, 2010). The formal take back system is having the least impact because of the reluctance of the manufactures to take responsibility of the End of Life (EoL) of their product (Osibanjo & Nnorom, 2007). South Africa as a country has been a bit more pro-active with trying to control the flow of e-waste and has been looking into engaging major white goods and electronic companies into being involved in EoL (Finlay & Liechti, 2008).

The countries in the Southern Africa region are very diverse ranging from the least developed too some which are very developed. As stated earlier the development and population of a country will affect the amount of electronic waste generated in that country. Municipal solid waste collection, management, disposal and reuse are a very big challenge in most of the countries and they do not have working systems in place. Hence e-waste collection is an even bigger milestone. Data collection is also very difficult in most countries because of the lack of viable statistics and data collection methods where e-waste is concerned. Estimates are therefore made though they do not consider cultural diversities; hence major discrepancies in the estimated and actual values can be expected. Table 2.2 shows the estimated quantities of e-waste generated up to April 2015 in the Southern Africa region. This data was compiled by an organization called STEP (Solving the E-waste Problem) which was formed as a UN initiative in response to the alarming increase in e-waste generation on a global scale (STEP, 2014).

Table 2.2 Different Statistics of e-Waste

Adapted from

**data from recent country census.*

***calculated in the year 2012*

****calculated in 2014*

Country	**Population(million) ***	**EEE put on Market (metric kilotons) ****	**E-waste generated (metric kilotons) *****
South Africa	51.8 (2011)	473	346
Botswana	2.0 (2011)	19	16
Lesotho	1.9 (2006)	3	2
Mozambique	22.3 (2012)	30	16
Namibia	2.1 (2011)	17	11
Swaziland	1.3 (2014)	6.1	4
Zimbabwe	12.9 (2014)	4	4

From Table 2.2, the high quantities of e-waste which are being generated in the Southern African region are visible. One of the major causes of the high increase of e-waste is the illegal import of e-waste into African countries from the developed (European/Western) countries

(Osibanjo & Nnorom, 2007). The amount of waste is also greatly influenced by the influx of second hand or old electrical and electronic equipment from the developed countries which are using developing countries as dumping sites because of the high cost of recycling (Osibanjo & Nnorom, 2007). The developed countries can repair the equipment for temporary use before shipping them out though the product lifespan will be greatly reduced. Countries like Botswana and Namibia have conducted detailed research into the effects of e-waste. However, it is only South Africa which has made any strides in the recycling of this waste by forming responsible associations. Hence a viable recycling industry would receive raw material from a number of countries regionally. With the less developed countries it would be very beneficial for them to have a central disposal site which can handle the waste because these countries do not have the technologies or the resources needed to deal with this waste individually and are many years behind reaching that point.

2.1.2 Financial Impacts of e-Waste

The total number of computers and e-waste production have been directly correlated with the GDP growth in most countries mainly due to the fact that EEE are essential for the functioning most economies. Figure 2.1 shows the direct correlation between the numbers of computers per country in relation to that country's GDP as determined by Robinson (Robinson, 2009a). These projected growths in the electronics sector clearly paint the grim picture and raise apprehension of unmanaged and unprocessed e-wastes, unless appropriate recycling measures are undertaken. The financial impacts of e-waste are both negative and positive. E-waste financial gain varies depending on whether it is being recycled or not and on the type of materials being recovered. It also varies depending on whether the recycling is done formally or informally. Exporting e-waste is much cheaper than recycling the waste for countries like the USA to the less developed countries which might be the downside of end of product responsibility. Therefore, e-waste mostly ends up dumped in countries where environmental standards are low or non-existent and working conditions are poor and entry of the waste is relatively easy. This is common mainly because of the strict environmental regulations which often exist. With recycling the worst-case scenario arises when the cost of the process exceeds the revenue recovered from the materials especially in cases where there are high material losses inefficiency.

In countries which allow the informal recycling of e-waste this can become a source of income to the recyclers with no benefit to the country or the environment though. In countries which have high rates of unemployment this could be an advantage however hazard monitoring and raising awareness is required. Considering the financial burden of recycling e-waste formally assistance for the recyclers could come from product manufacturers through programs like EPR which would ensure that the manufacturer and user can afford to pay partially for the recycling process. The drive however should be to ensure that everyone is willing to participate in the process and play their part whether there are financial benefits or not.

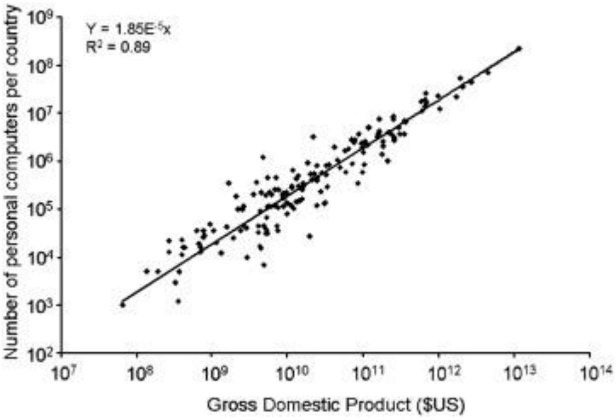


Figure 2.1 Number of personal computers per country as a function of GDP for 161 countries (Robinson, 2009b).

2.1.3 Electronic Waste in Africa and Globally

In Africa as a continent there is generally still a lack of uniform or strict government legislature which governs the movement of e-waste within the countries (Nnorom & Osibanjo, 2008). Some West African countries like Nigeria and Ghana have very active ports for the import of old electrical and electronic equipment most of which is no longer working and ready for disposal (Mccann & Wittmann, 2015). The demand and need for inexpensive EEE and secondary materials make stopping this practice very challenging especially since dumping waste in Africa has proven to be have cheaper cost implications as compared to the waste treatment which has stricter standards in the developed countries. The Northern, Eastern and Southern African countries have better legislature for restricting the import of EEE which has reduced greatly the amount of e-waste imported. However, there is still a lack of a systematic well-defined method of recording the quantities of e-waste generated as a whole. Most of the recycling activities of e-waste in Africa are usually carried out on an informal basis, often involving open burning and leaching in unmonitored dumpsites or landfills. This has had a very negative impact on the environment and the health of people. The lack of formal recycling in Africa is mostly due to the absence of strict legislature again concerning the disposal of e-waste and high rate of poverty. Table 2.3 shows the projected quantities of the waste generated globally from the year 2010 with current projections to the year 2018. Only estimates however are given because of as stated earlier countries still lack a uniform measurement system for e-waste (Widmer, Schluep, & Denzler, 2008).

On a global perspective most, European countries have developed some very strict legislature governing the treatment of e-waste. The vast development of the European countries makes them one of the biggest producers of e-waste. Switzerland has done a lot of research on the recycling of e-waste and has been a pioneer in legislating e-waste management even in less developed countries (Widmer et al., 2008). Belgium also has a very large recycling company UMICORE Precious Metals Refining which operates as one of the world's largest precious metals recycling facilities there are numerous other functional industrial companies. These companies therefore get raw material from the surrounding countries. In the USA one of the largest producers of e-waste is yet to develop strict legislature governing the disposal of the waste and relies mainly on waste exports. This is mainly because the recycling of the waste has proven to be more expensive than cargo export. Table 2.3 shows the annual global waste generation, the figures for the year 2015.

Table 2.3 Global Annual Generation of e-Waste

Adapted from The World Bank, (2012)

Year	E-waste generated (Mt)	Population (billion)	E-waste generated (kg/inh.)
2010	33.8	6.8	5.0
2011	35.8	6.9	5.2
2012	37.8	6.9	5.4
2013	39.8	7.0	5.7
2014	41.8	7.1	5.9
2015	43.8	7.2	6.1
2016	45.7	7.3	6.3
2017	47.8	7.4	6.5
2018	49.8	7.4	6.7

Hence the recycling of e-waste economically and socially seems to be a lucrative business adventure not only because of the environmental and health benefits but also because of the vast source of raw material available regionally, continently and globally as well. With adequate education people in the world would be willing to dispose of their waste appropriately for a small fee.

2.2 Impacts of e-Waste

With the large fractions of EEE being manufactured annually and eventually ending up as e-waste it is inevitable for the waste to have an impact globally. As already mentioned above 5-8% of the MSW in some countries is made up of e-waste with little chances of recovery and there is an estimated annual generation of over 50 million tons. Both the EEE and the e-waste have numerous impacts environmentally, socially and financially.

2.2.1 Social Impacts of E-Waste

The social and cultural implications of ICT are profound, little understood but are obviously playing a big role in the rapid evolution of technologies, yet are almost never addressed in environmental critiques of the sector (Allenby, 2004). The social impacts of e-waste should not be allowed to delay implementation of the environmental and e-waste initiatives though it does affect the forecasting of the sustainability of the sector. E-waste is also an indication of the degree of social development in the country with the developed countries generating a higher percentage of waste. Some treatment methods like reuse and remanufacturing will be easier to implement in certain environments more than others because of factors like social statuses unless it can be made to be “cool”. For example, personal computers are important for social and economic development and the most likely to be transported from one country to another in transboundary trade. The following definition is usually given for social impacts:

> “…the consequences to human populations of any public or private actions that alter the ways in which people live, work, play, relate to one another, organize to meet their needs and generally cope as members of society. The term also includes cultural impacts involving changes to the norms, values, and beliefs that guide and rationalize their cognition of themselves and their society.” (Huisman et al., 2007)

The social and cultural implications of e-waste therefore vary widely from country to country depending on the stage of development and level of involvement with recycling the country is involved in. South Africa is a country which has a developed a strong culture of recycling plastic containers, glass and paper, and this has been a form of informal employment for over

40,000 recyclers (Finlay & Liechti, 2008). Of the 40,000 plus informal recyclers estimated to be working in South Africa, it is likely that most of them, at some time or another, have dealt with e-waste. While this informal/formal waste recycling sector in South Africa offers critical income generating opportunities for people, there are still negative social impacts when it comes to e-waste which includes (ATE, 2012; DST, 2014; Finlay & Liechti, 2008):

- Open burning of plastics, both to extract value from metals such as copper, and for warmth;
- Smashing of computer and television monitors to extract copper;
- Exposure to hazardous substances generally;
- A lack of basic safety equipment;
- A lack of basic safety information about e-waste;
- Vulnerability to e-waste traders (e.g. collectors do not have much leverage or bargaining power when negotiating with scrap metal merchants on prices)

There have also been numerous philosophies that have been developed which address the impacts of the social aspect of e-waste to some extent one of them being the best of two worlds' philosophy which splits the e-waste processing between the developed and the developing countries (Wang et al., 2012). The developing countries because of absence of state of the art recovery machinery can be involved in the pre-processing of the e-waste which includes the manual dismantling of the e-waste before transport to the developed countries for end-processing (Lawhon, 2013). The objective of this endeavor is to try and cut out the need for mechanical processing which has been shown to result in the loss of valuable material. As well as trying to rectify the major concern of informal recycling. Socially this philosophy increases the divide between the developed and developing countries, and the developing countries will be left to take care of the material which is unrecyclable (Doefnaes & Kuehr, 2014; Wang et al., 2012).

2.2.2 Legal Impacts

Policies and laws concerning the proper management of electronic devices are evolving. Groups (of different communities and or countries) have set up committees which look into specific issues such as the formulation of policies and legislation, the creation of a national e-waste baseline, the restructuring of the e-waste recycling sector, the implementation of end of producer responsibility (EPR) and the creation of public awareness among other things

(Mccann & Wittmann, 2015; US EPA, 2000). Different countries have come up with drafts of legislature which address the e-waste concern. However, for now, the leaders on WEEE legislation are mainly driven by certain EU countries and their directives. Most developing nations in the world are lagging behind in the development of similar regulations, more so the enforcement (Bilbao, Dutta, & Lanvin, 2013; Unep, 2011). In the US a nominal fee is now being collected at the point of sale for all CRTs which will be used for CRT recycling activities as a result of legislature which was put into play (Babu, Parande, & Basha, 2007). In addition to this a recycling act which includes provision for reducing the amount of hazardous substances used in electronic products sold in California with a directive to state agencies for what is acceptable to purchase and what is not was implemented (Schuelp et al., 2009). Globally an international initiative which had over 164 signatories is the Basel Convention which was developed in 1989 (Babu et al., 2007; Kahhat et al., 2008; Lundgren, 2012). The developed initiative was put into force in 1992 to try and come up with controls and develop a framework for the transboundary movement of e-waste which had been identified as a hazardous material across national borders because the hazardous chemicals in some parts often ended up going to developing countries. Globally, it is estimated that 80% of e-waste is shipped to Asia and the rest goes to some African countries like Ghana and Nigeria either legally or illegally (Lundgren, 2012; Olowu, 2012; Seongjun & Cui, 2012; Sthiannopkao & Wong, 2013). South Africa and India have set up WEEE strategy groups which consist of delegates from key stakeholders like government agencies, EEE producers and importer associations, recyclers and NGOs to try and come up with a comprehensive WEEE management system (Widmer et al., 2005).

2.2.3 Environmental Impacts

The environmental impacts from the disposal of e-waste are mitigated by recycling more of the material used in equipment as opposed to landfilling or incineration. This also reduces the need to extract more raw materials from the ground which has other numerous environmental repercussions like the depreciation of the land. Alternative disposals of the e-waste which are not recycling or reuse mean the loss of minerals which could have been easily channeled to other uses. With the current debate on the need for sustainability of the supply of finite minerals this is a huge waste which could be easily countered by the recycling of the material (Preisler & Berger, 1947). In addition to this the recycling of the waste does not always have favorable outcomes because it can be done either formally or informally using unscrupulous methods which result in various dangers. The recycling can cause severe environmental and human health effects that need to be addressed and controlled.

Performing recycling procedures and disposal methods can directly results in environmental degradation and negative ecosystem effects. These toxic chemicals can stay in the environment for very long periods of time and will continue to grow in concentration if the amount of e-waste continues to increase as it is now. In South Africa the main type of recycling done is in the manual dismantling and sorting of the e-waste with some involved in metal recovery through either hydro or pyrometallurgical means, whilst this is done on a very large scale informally in countries like China and India (Widmer et al., 2005). Guiyi China employs over 150,000 people who do not always have proper protective equipment and expose themselves to toxins by burning, burying and dumping (Park, Hoerning, Watry, Burgett, & Matthias, 2017). In addition to wasting resources e-waste is also a source of hazardous material which affects both the health and the environment. The environmental hazards of e-waste come in 3 different categories which include (Goodship & Stevels, 2016):

- Primary emissions: these are from hazardous substances used in the production of EEE for example lead (a heavy metal) which then contaminate the environment
- Secondary emissions: these are the hazardous substances which result from the improper treatment of e-waste like incineration or improper smelting of plastics which have halogenated flame retardants which forms dioxins or furans
- Tertiary emissions: these result from the hazardous substances used during the informal recycling of e-waste like cyanide and mercury used in gold recovery that is then released into the environment.

Each of these waste products is equally harmful to the environment and there is need for ways of reducing the waste production by each of these medium if the e-waste threat is to be rectified. A short list given tries to summarize some of the common directives and bodies which have been put in place concerning e-waste over the years in different countries and continents.

Basel Convention and Basel Ban

A global agreement regulating movements of hazardous wastes, including WEEE, between countries, in force since 1992 and its amendment which prohibits exports from OECD (Organization for Economic Co-operation and Development) to non-OECD (Nartey, 2016).

StEP initiative (solving the e-waste problem)

A UN-led international platform started in 2004 in Berlin for exchanging and developing knowledge on WEEE systems among countries (STEP, 2014).

Silicon Valley Toxics Coalition (SVTC)

A network of diverse non-governmental organizations (NGOs) in the US engaged in research, advocacy and grassroots organizing national solutions for hazardous waste management in response to the rapid growth of technology (Huang, Guo, & Xu, 2009; Widmer et al., 2005).

WEEE Forum

Founded in 2002, the WEEE Forum is a group of about 39 representatives of voluntary collective WEEE take-back systems in Europe, taking care of individual producers' responsibility in Europe (Widmer et al., 2005).

National Electronics Product Stewardship Initiative (NEPSI)

A multi-stakeholder dialogue in the USA that aims to ensure everyone is responsible for reducing the waste impacts. The dialogue includes representatives from electronics manufacturers, retailers, state and local governments, recyclers, environmental groups, and others who should all share the overall financial responsibility (Widmer et al., 2005).

Electronics Product Stewardship Canada (EPS Canada)

EPS Canada was created to work with both industry and government to develop a flexible, workable Canadian solution. An industry-led organization, the founding members are 16 leading electronics manufacturers (Widmer et al., 2005).

ERP (European Recycling Platform)

Set up at the end of 2002 by Hewlett Packard, Sony, Braun and Electrolux to enable the producers to comply with the WEEE directive. It aims to evaluate, plan and operate a pan-European platform for recycling and waste management services (Widmer et al., 2005).

Seco/Empa e-waste program

A project set up in 2003 by SECO (Swiss State Secretariat for Economic Affairs) and implemented by Empa (Swiss Federal Laboratories for Materials Testing and Research) in cooperation with a number of local partners and authorities, to assess and improve WEEE knowledge partnerships and recycling systems in different parts of the world by analyzing the systems and by exchanging knowledge on recycling techniques and frameworks (Widmer et al., 2008).

Restriction of hazardous substances (RoHS)

This directive restricts the use of hazardous substances and has been in force since 2003. It was begun for the purpose of restricting the use of hazardous substances in EEE whilst protecting the human health and the environment through sound recovery and disposal of e-waste (Reuter, 2013).

2.3 e-Waste Constituents

According to UMICORE e-waste can contain over 60 different elements from the periodic table (Schuelp et al., 2009) and these have in some cases been broadly categorised as ferrous metals, non-ferrous metals (base metals, precious metals and rare earth metals), glass, plastics and “others” which includes ceramics, wood, rubber etc. The mix of materials in the equipment varies with the manufacturer and the period of manufacture. Some of the elements are hazardous whilst some are valuable, some are both (Schuelp et al., 2009). Equipment like the mobile phone can be made up of up to 23% metals. The highest percentages of elements found are usually:

Metals: copper, iron, aluminium, nickel, zinc, gold silver, palladium, tin, lead, mercury, beryllium, cadmium, chromium, selenium (Cui & Zhang, 2008; Robinson, 2009a).

Non-metals: halogens like bromine, chlorine, polybrominated flame retardants; organics like plastics; glass and ceramic (Cui & Zhang, 2008; Namias, 2013).

As already stated above the generalisation of the e-waste constituent distribution is somewhat difficult because of the many differences in the year of manufacture, legislature and cost of product. Figure 2.2 shows an average distribution of the material constituents in e-waste whilst Table 2.4 shows the estimated distribution of constituents found in a television set and the estimated respective mineral values. Each of the material used in the equipment has a specific function which is specialized because of its different properties like non-conductance, conductance, ductility, malleability to mention a few. This explains the need for the wide range of materials because of the complicated way the EEE function.

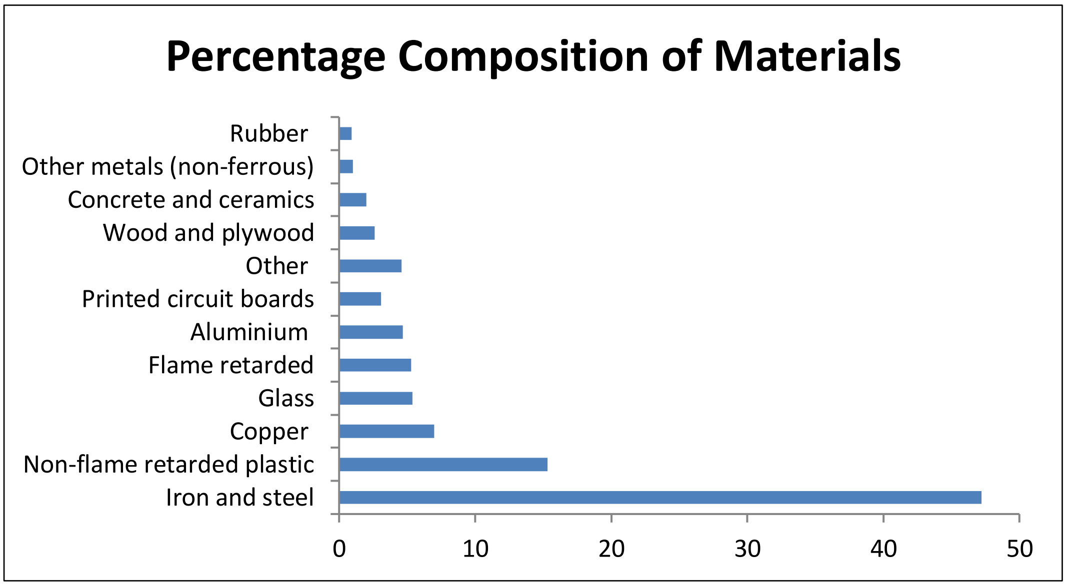


Figure 2.2 Average percentage compositions of materials found in e-waste according to European topic centre on resource and waste management.

Table 2.4 Estimated Distributions of Some Key Constituents Found in a Television Set Adapted from

* *(Microelectronics and Computer Technology Corporation (MCC), 2009)*

***(Schuelp et al., 2009)*

****(Marsden & House, 2006)*

Component	Percentage*	Weight in a unit ≈27kgs**	Weight in a tonne (kg)	Value ($/tonne waste)
Plastics	22.9907	6.207489	229.907	
Copper	6.9287	1.870749	69.287	532.10
Gold	0.0016	0.000432	0.016	631.45
Silver	0.0189	0.005103	0.189	122.75
Palladium	0.0003	0.000081	0.003	51.22
Indium	0.0016	0.000432	0.016	9.03

The complex mix of the elements differs with equipment and specifically the different components in the equipment for example wiring boards, element and the outer covering. The following components can be ranked based on the relative value of the elements they contain high value components containing the highest quantities of valuable elements:

- High Value: circuit boards from mainframes, mobile phones, capacitors
- Medium Value: PC-boards, laptop-and handheld-computer circuit boards
- Low Value: TV-boards, monitor boards, printer boards, cordless phones, calculators, to mention a few.(Namias, 2013).

It is of note that only 3% of the waste is made up of PCBs which usually have the most complex mix of substances (Schuelp et al., 2009). PCBs are high value because together with connectors they contain most of the valuable and noble metals. Iron and some base metals like aluminium and copper metal are still found in the highest percentages. In spite of the low concentration of gold on a weight percentage basis in e-waste it is still higher than the gold that is found in the ore. E-waste can contain 200-350 g/t of gold depending on the scrap in question and 110 g/t palladium whilst the ores contain 5-10 g/t (Hagelüken & Corti, 2010). Table 2.5 shows the general material percentage composition in e-waste and the percentage metal value constituents of the PCBs in some common equipment.

Table 2.5 Material Compositions Found in e-Waste PCBs

Adapted from (Goosey & Keller, 2003)

Materiel	**Percentage**
Non-metals	> 70%
Copper	≈ 16%
Iron	≈ 3 %
Gold	≈ 0.03%
Silver	≈ 0.05%

The properties that make the use of the mentioned metals favourable in most PCBs include the electric conductivity, corrosion resistance, ductility and the malleability. Copper and silver are both used because of their high conductivity; however, copper is much cheaper than sliver and will be favourable in some instances. Silver will be used in sensitive parts were there need to have a high conductance over a small distance compared to the copper which can be used in areas that are not as sensitive, and need to be corrosion resistant. Gold is used at contact points because it is an efficient conductor that can carry currents at contact points without corroding or tarnishing. The speed required in the transmission of the current requires a metal which excellent transmission properties as well as durability. Gold is used in edge connectors, switch and relay contacts, soldered joints, connecting wires, and connection strips. To minimise cost the gold is usually electroplated onto the surfaces of these components with small amount of nickel and cobalt for durability. Iron or steel has numerous uses in electronics mainly because of its magnetic properties and also its affordability which mean it can be used for outer casing housing among other things. The non-metals are used mainly to add body to the gadget, for insulation and for covering among other uses.

2.3.1 e-Waste Harmful Components

Electronic devices contain a plethora of components and parts, many that house portions of toxic chemicals that are harmful to humans. The hazardous metals found in the e-waste can include lead, cadmium, arsenic, barium, mercury, selenium and hexavalent chromium which can be found in relay, switches and batteries, though environmental restrictions have been made in recent years preventing the use of some of the hazardous metals (Chehade et al., 2012). Some of the large household appliances like refrigerators, washers, and dryers contain chemicals which are non-hazardous though they can lead to global warming like (chlorofluorocarbons) CFCs, (Hydrochlorofluorocarbons) HCFC, (Hydrofluorocarbons) HFC and HCs. Consumer equipment is also a large portion of electronic waste and includes TVs, cell phones, computers, monitors, and even sporting equipment. Some of these components that contribute to the toxic waste include batteries, circuit boards, cathode-ray tubes, and lead capacitors. Information technology is key contributor to the production of hazardous chemicals coming from a variety of components, for example the computer. Hence there is need for wise handling and disposal. In addition to this there is also the presence of plastics. 12% of plastics used in EEE contain flame retardants like brominated flame retardants (BFRs) used for television housing and computer monitor cases mainly because they prevent or delay fires in electronic equipment (Letcher & Vallero, 2011). Plastics also contain polybrominated dioxins and furans (PBDD/F). A study conducted in India estimated that over 30,000 computers were decommissioned in Bangalore alone each year which cultivated more than 1,000 tonnes of plastics and 300 tonnes of lead, 0.23 tonnes of mercury and 43 tonnes of nickel (Needhidasan, Samuel, & Chidambaram, 2014) whilst in European community it accounted for the production over 36 tonnes of mercury and 16 tonnes of cadmium per year (Zhang, Zuo, Kers, Peetsalu, & Goljandin, 2008). This percentage of the hazardous metals has a negative impact on the human health and the environment. Organophosphate flame retardants and plasticizers have been found in urine samples of the people living in an e-waste dismantling sites, mostly in developing countries. If landfilled or released to the environment these heavy metals end up in the landfill leachate. Lead, Cadmium, Nickel, and Lithium alone are found in used batteries, much like the ones being mass produced in electric vehicles. A US study showed that 70% of the heavy metals in their landfills came from the electronics, and that 40% of lead in landfills is also from e-waste (Awasthi, Zeng, & Li, 2016; Musee & Oelofse, 2008). Lead is the fifth highest contained metal in e-waste coming after base metals like steel, carbon, aluminium and zinc in spite of the fact that in 2002 it was included under the ROHS directive (Kolias, Hahladakis, & Gidarakos, 2014). It is used for soldering, lead-acid batteries, cable sheathing and in glass CRTs but has however been restricted from use in other countries. The effects of the heavy metals on the health can be seen in the Table 2.6. Many of the chemicals found in electronic components can easily leach out into local water sources, find their way in food, and can easily be blown away by the wind and transported into the air. Table 2.6 shows the environmental and health effects of some of the key metals found in e-waste. In addition to landfilling and other formal disposal methods, informal recycling is another key avenue which results in the intoxication by heavy metals. At a site of informal recycling site in the Philippines a recent study showed that Au, Pb, Ag, and Sb were found in the soil with figures that are 28 times lower than those found Guiyu China (Sepúlveda et al., 2017). Hence the victims of the hazardous chemicals are often in developing countries that are exposed to hazardous chemicals in a variety of ways. Victims of electronic waste can be affected by direct exposure as well as indirect exposure. Direct exposure can occur when the toxic chemicals are inhaled, touched by skin contact, or ingestion of the chemicals directly or indirectly through foodstuffs like plants or fish. This clearly shows how significantly e-waste contributes to the generation of hazardous materials into the environment over time if not treated accordingly.

Table 2.6 Hazardous Materials Found in e-Waste and the Health Effects

Material	**Uses**	**Health and Environmental Effect**
ABS	Housings and casing of phones, small household appliances, microwave ovens, flat screens, certain monitors, enclosures and internal parts of ICT equipment	
As	Doping material for Si	Skin diseases, decrease in nerve conduction, lung cancer
Ba	Getters in cathode ray tubes (CRTs)	Forms poisonous oxides when exposed to air, brain swelling, muscle weakness, damage to the heart, liver and spleen
Be	Motherboards, Silicon-controlled rectifiers	Is a carcinogen (for skin and lungs), skin diseases.
Cd	Semiconductors, batteries, toners, plastics	Affects the liver, can cause poisoning, flue-like symptoms of headache, weakness, muscular pain, lung cancer and kidney damage. Absorbed by plants
Cr	Floppy disks, data tapes	Eye, skin and mucous membrane irritation, permanent eye injury
HIPS	TV housings and computer monitors and some small household appliances and components of TV, computer, printers and copiers	
Pd	Batteries, computer monitors, as soldering	Vomiting, diarrhoea, convulsions, coma, death, appetite loss, pain, constipation, fatigue, sleeplessness, irritability and headache and affects kidneys
Hg	Thermostats, position sensors, sensors, relays and switches	Brain and liver damage, contaminates fish to toxic levels where little consumption can be very harmful to human health. Forms

	Fluorescent lamps, batteries, switches	methylated mercury in water which bio-accumulates in living organisms and concentrates through the food
PBDes	Flame retardants plastic housing of electronic equipment's and circuit boards to reduce flammability	lipophilic, resulting in their bioaccumulation in organisms and biomagnification in food chains. thermal energy release of bromine radicals
PP	Components inside washing machines, dishwashers and electronics, castings of small household appliances	
PVC	Cabling and computer housing plastics	causes reproductive and developmental problems, immune system damage and interferes with regulatory hormones
Se	Rectifiers	Selenosis which has symptoms of hair loss, nail brittleness and neurological abnormalities

The trend in recent years has shown a significant decrease in the use of heavy metals and other hazardous chemicals in EEE because of the different legislature and policies which are trying to limit the environmental impacts in most developed countries. Hence there is a lot of pressure on many manufacturers to be greener. The changes in design also has an effect on the change in e-waste material now being used for example the change from CRT to LCD resulted in the decrease in the use of lead with an increase in the use of mercury. Hence there is a need to determine whether the pros of one outweigh the cons and to come up with ways of eventually completely getting rid of the impacts being felt. The heavy metals need to be treated carefully whether it is in landfilling, incineration or recycling because none of these diminish the threat of these metals unless carefully considered prior to the treatment.

2.3.2 e-Waste Metal Constituents

All e-waste can be seen to as containing a mixture of various metals attached to, covered with or mixed with various types of plastics and ceramics (Letcher & Vallero, 2011). Mobile phones as already mentioned can contain up to 40 different types of elements from the periodic table including base metals, special metals, and precious metals (Meskers, Hagelüken, & Damme, 2009) and they can represent an average of 23% of the weight of a phone with the remainder being made up of plastic and ceramic materials. Some of the metals are in Table 2.7. While the amount of precious and special metals used in an individual cell phone is very small, the total amount contained in the nearly one billion cell phones sold globally is significant. For general e-waste the weight of metals figure is at 63.2% for both ferrous and no-ferrous metals as seem in the graph above. In addition to base and heavy metals e-waste also contains precious metals like gold, silver, palladium and platinum these constitute the lowest percentage. However with the technological advancement the concentration of precious metal used in EEE is being reduced for example early generation computers used to have 4g of gold but now the figure has been reduced to 1g which does not diminish the fact that these metals still add the highest value on a material basis to the equipment. They also contain in low concentrations rare earth metals like indium. The highest percentage will be of the base metals however that is copper, aluminium, iron and zinc. Table 2.8 shows the quantities of precious metals found in some EEE, whilst Table 2.9 shows how different pre-treatment methods affect the extraction of precious metals from mobile phones during recycling:

Table 2.7 Metals Found in e-Waste

Type of Metal	
Base	Fe, Cu, Pb, Zn, Mg
Precious	Au,Ag,Pd, Pt, Ir
Rare earth	Co, In, Sb,

Table 2.8 Percentages of Value of Some Metals Found in Electronic Equipment Adapted from Namias (2013)

Electronic	**Copper**	**Silver**	**Gold**	**Palladium**
TV Board	50%	7%	22%	7%
Pc Board	18%	5%	61%	15%
Mobile Phone	9%	13%	64%	14%
DVD-player	42%	5%	32%	5%

Table 2.9 Metal Constituents of a Mobile Phone
Adapted from Namias (2013)

Electronic	Copper (%)	Silver (grams/metric ton)	Gold (grams/metric ton)	Palladium (grams/metric ton)
Mobile Phone Handset	12.8%	3630	347	151
Shredded Mobile Phones	13.4%	2273	354	113
Mobile Phone Circuit Boards	25.1%	5541	982	287

The combined unit sales of mobile phones and personal computers only used up to 3% of the world's mine supply of gold, 34% of total primary silver production, 15% of cobalt and 13% of palladium (ATE, 2012). Another study showed that roughly 300 tonnes of gold were used in EEE manufacture which constituted about 11% of the total gold production in mines in 2013 (Balde et al., 2014) This is a relatively substantial percentage which is most likely increasing annually with an increase in the metal demand. Metals like energy can neither be destroyed or created, but can only be transformed from one form to another. They start as ores underground which are then processed to a pure metal for use in equipment and other uses before they end up underground again in landfills. The amount of energy and work which goes into the primary production of precious metals is substantial not forgetting the environmental footprint which is left by the generation of gaseous emissions, CO_2 and SO_2, water pollution and land degradation. This could be considered to be serious waste of non-renewable resources which has a potential of running out in the following years (Hagelüken, 2011). The metals are also becoming unreasonably expensive to mine and extract as the ore bodies become deeper underground which cascades down to the overall cost of the manufactured equipment. In addition to the waste in resources associated with mine landfilling there is also a generation of harmful leachates because of the presence of the hazardous components.

2.3.3 e-Waste Plastic Constituents

E-waste contains different types of plastics some are hazardous whilst others are not. 500 million PCs contain approximately 3 million t of plastics according to Widmer hence they cannot be ignored, making up about 15.3% of e-waste. Generally, plastics used in EEE are thermosets and thermoplastics. The thermosets cannot be re-melted into new products hence are shredded. The thermoplastics which make up about 12% of plastics used in EEE and are flame retardants like brominated flame retardants (BFRs) used for television housing, computer monitors and cases mainly because they prevent or delay fires in electronic equipment can be re-melted and formed into new products (Letcher & Vallero, 2011). Plastics also contain polybrominated dioxins and furans (PBDD/F). These generally have halogens added to the plastic resin, making the plastics difficult to recycle. Research has been conducted to find alternative recycling of the plastic matter. One application which has been found of this polymer stream is in the extrusion casting and use as a filler in building materials (Muniyandi, Sohaili, Hassan, & Mohamad, 2013). These downstream applications for separated plastic fractions have recently been superseded by Fuba's own development of their combined use in chemical resistant polymer-based pallets (Li, Shrivastava, Gao, & Zhang, 2004).

2.4 Disposal Methods

Numerous disposal methods of e-waste are being carried out both illegally, legally, informally and formally. The grey area will mostly arise in cases where there is no awareness and the disposal is being done for gain. The available options for e-waste disposal include reuse, recycling, landfilling, incineration, open burning and export to less developed countries. The range of treatment options is broad and some countries have realised there is a problem that needs to be addressed and have tried to put in motion systems that will protect them, for example a country like Germany can easily enforce EPR on to their manufacturers which should obviously force them to come up with viable recycling techniques unlike a third world country which is not involved in industry manufacture (Balde et al., 2014). However there are often no laws which stipulate how the producers who collect their product should dispose of it and they can sometimes export the waste to less developed country in the guise of a second hand product or equipment (Herat et al., 2007). The disposal and recycling of the waste is being done informally or not at all. When it is not being done the old equipment occupies otherwise useful storage space is just randomly piled up in make shift disposal sites which usually results in the generation of harmful leachates or hazardous harmful gases. These leachates end up in underground water bodies as well (de Jager, 2015). The 5-8% of the MSW which is made up of e-waste has very low chances of recovery. With most developing countries poor economies and governmental legislature have had a negative impact on the handling of waste in general with vast amounts of pollution occurring. The governments in African countries have no immediate urgency when it comes to the production and disposal of waste due to the rife economic and political crisis's they have to face. This has hence resulted in a lack of knowledge and disregard concerning proper e-waste disposal (Balde et al., 2014). This has also created an open gold field for some industrious people who can then undergo crude recycling which might be profitable to them individually but at what cost to people or the environment in the long run. Illegal recycling of metals from the e-waste is being done in most under developed countries which is hazardous both for the environment and to the health of people affected which could affect future generations even more. In South Africa electronic waste (e-waste) is said to comprise of 8% of the MSW and is one of the fastest growing waste fractions (Maczulak 2010; Widmer et al., 2005). The government is actively funding the establishment of research into the recycling of e-waste to curb the growing concern. The e-Waste Association of South Africa was formed as a result in 2008 as a result (Finlay & Liechti, 2008). eWASA is concerned with the development of a sustainable environmentally sound management of the e-waste problem in South Africa through the support of small business start-ups and informal recyclers, and support for the investment into new recycling technology through incentives (Finlay & Liechti, 2008). The association has many members who are actively involved in the collection and disposal of the e-waste (de Jager, 2015). This has resulted in the formation of a number of reputable as well as non-reputable recycling companies which deal with the waste in variable ways. Some are only involved in the collection and dismantling of the waste before they transport it elsewhere for further processing (eWasa, 2016). The recycling companies separate the waste into different categories for example Universal Recyclers will separate aluminum, copper wires, zinc, ferrous metals and PC boards (Universal Recycling Company, 2015). The product is then sold locally, exported, stockpiled or sent to a registered landfill. Mintek has been involved in the research focusing on the pyro-metallurgical e-waste recovery for variable feeds hence having flexible process chemistry for the recovery of metals (Mintek, 2015). With the problematic plastics they were used to produce secondary products such as roof tiles, fence poles and benches. The Urban Mining project also started recording notable outputs during 2014/2015 year. An estimated 1.2 tons of e-waste, including computer waste was treated (Mintek, 2015). The main intention of the project is to develop appropriate technologies to process e-wastes in various forms. If successful, Mintek could be a "business incubator" and assist start-ups in the early stages of their business cycles (Mintek, 2015).

Although pyro-metallurgical recycling has achieved some positive results for some countries and is already in industrial use (Cui & Zhang, 2008; Hageluken, 2007) there are some concerns with the generation hazardous gases and the type of slag which is produced. Recovery of the metals from e-waste has been studied and is traditionally carried out using leaching with some very strong solvents like NaCN, strong halides and H_2SO_4 (Castro & Martins, 2009; Cui & Zhang, 2008) which generates hazardous fumes, gaseous emissions, liquids and solids waste whilst being uneconomical because the solvents cannot be recovered (Hageluken, 2007). This project therefore aims to look at the possible use of some leachates which are more environmentally friendly and how they would impact the people using them through the use an alternative ionic liquid solvent which is possibly recyclable. Generation and disposal of waste is an area which needs monitoring if the set goal of waste reduction is to be achieved.

People are generally unaware of the proper e-waste disposal methods or of the negative impacts associated with the matter for example loss or the wanted and unwanted destruction of valuable information. Another issue of concern with e-waste is the use of very precious, rare and base metals which were once very abundant in the world but are currently somewhat scarce. There is also a high case of reluctance by most people to dispose of their e-waste because of a perceived value it might still retain because of the possibility of reuse or repair. A number of methods for the e-waste collection which are presently in use include:

1. Official take back systems

   This is the system whereby manufacturers are forced to adopt the cradle to the grave concept. They are held responsible for their product at whatever stage of its life cycle. Hence the consumer can actually return the equipment back to the source. This forces the manufacturer to find a suitable solution to the problem of disposal and take this into consideration when designing and selecting material.

2. Disposal of e-waste in mixed residual systems

   With this type of disposal, the e-waste will usually end up in the MSW stream. The waste will have been disposed of in the refuse bins and will either be incinerated or landfilled. It is commonly done for small equipment like batteries or lamps. Landfilling of e-waste can lead to the leaching of hazardous substances which have been traditionally used in the manufacture of electronic equipment like cadmium mercury or lead to underground water systems or soil contamination. The incineration of the waste not only has an impact on the carbon footprint but can also generate fumes which are harmful to the environment and to people.

3. Formal collection of e-waste

   The private sector realized the need for e-waste recycling and the opportunity for businesses. There are now numerous private collectors in existence. These collectors have different pick up points and methods of disposal for the waste. The end use is also variable and some perform the role of primary collectors who will dismantle the waste before transporting it or further processing.

4. Informal collection and recycling

   This is done by the informal recyclers who are at a high risk because they do not take the necessary precautions when dismantling the equipment. These recyclers are only interested in the valuable material which they can extract from the waste; the rest will either be disposed of in anyway or left lying around. They also participate in recycling which produces hazardous fumes and air contamination (Balde et al., 2014).

With such a varied range of collection and disposal methods in use it is clear why coming up with an exact figure of the amount of e-waste generated is difficult. Most of the mediums collecting the waste do so informally and do not keep any records of the processes they are carrying out. With the formal collectors there is usually no known database recording the overall movement of the waste. The lack of strict legislature in the countries also allows for this variable collection and disposal to occur and does not restrict any area.

2.4.1 Reduce, Reuse and Remanufacture

In the recent years the drive is to reduce, reuse, remanufacture or recycle. The reuse of EEE has become very common as it reduces the cost of acquiring equipment for those who cannot afford and has greatly increased the trans-boundary movement of equipment from the developed countries to the less developed countries. Reducing is an initiative to try and lower the buying of new EEE if the old gadget is still functional and this can only be promoted by raising awareness with consumers. Reduction can also only be achieved by increase in the lifespan of the equipment by manufacturers and public awareness of the negative impacts of the e-waste which would help prolong the use equipment. Reduction can be also be done by the limiting of the number of gargets one uses. It also involves buying less, as long as equipment is still functional and in an acceptable condition it is better to not change it. On a corporate level reduction can also be done through sharing of office equipment like printers and scanners or using equipment for more than one function. Reducing can also be achieved by smart procurement as well as good maintenance. Reusing is achieved by donating or selling still functional EEE to someone who can still use it (SATA, 2010). With this comes the urgency to not keep functional equipment lying idle. Remanufacture can result in saving as much as 3 times more energy than manufacturing from scratch. This involves the disassembly of used electronics to make new products at a lower cost with waste generation minimisation (US EPA, 2000). There is however the high risk that remanufacture may prolong the lifespan of obsolete material which no longer meets up with the required technology. Up to 80% of energy saving can be made in remanufacturing an old computer as opposed to making a new one.

2.4.2 Open Burning and Incineration

Open burning is done mainly as a precious metal recovery process which is done unofficially in some countries using various methods mainly acid digestion (Schuelp et al., 2009). Whether this is legal or is illegal is debatable depending on the country in question at times because of the lack of legislature defining the acceptable e-waste treatment methods. This can be used for copper recovery as well were the plastic insulators are just burnt off and flotation is done to recover the metal. The open burning process can result in incomplete combustion of the plastics and whatever else is present. The diversity of plastics used in e-waste, polybrominated dioxins and furans (PBDD/F) or brominated flame retardants (BFRs) to mention a few, can result in the formation of toxic brominated dioxins or furans by-products of the burning process (Schlummer, Gruber, & Schlummer, 2017). This causes a lot of air pollution as well as the production of ash which contains toxic elements.

With incineration as a means of municipal waste disposal there is need to instill state of the art air purification vessels or afterburners (Zhang et al., 2008). Consideration has to be given to the fact that copper is a catalyst for dioxin formation when flame retardants are incinerated especially at low temperature and that in the EU it was estimated that waste incineration accounted for the emission of 36 tonnes of mercury and 16 tonnes of cadmium into the air per year (Cui & Zhang, 2008). There are advantages in the use of incineration which can include heat recovery and it is also necessary at times for the treatment of downstream scrap which has remained after treatment as it results in size reduction with little loss of valuables. There will still be loss of resources, hence the disadvantages far outweigh the advantages.

2.4.3 Open Dumping and Landfilling

Due to the ignorance of most communities in the developing countries of the appropriate e-waste dumping systems available some of the e-waste is just randomly dumped in open dumps or even on curbsides. This can also be done on the dismantled e-waste components which have had the valuable matter taken from them (Mccann & Wittmann, 2015). Ash contents are also disposed of in this way. Though landfills are a better option because of the ground lining there are dangers when they leak and the runoff mixes with underground water. The runoff often contains heavy metals and other toxic substances (Memon, 2016). Another problem which arises from landfills is the fact that they do not have a top covering and hence have no way of preventing the formation of acid rains or the evaporation of harmful chemical emissions which form (Scharnhorst, Althaus, Classen, Jolliet, & Hilty, 2005). Volatile substances like mercury and its compounds like dimethyl mercury can be released into the atmosphere as a result of this. Uncontrolled fires which often occur in landfills also result in the formation of toxic fumes because of the low temperatures. Informal recycling can also result in the haphazard disposal of acids onto the land which pollutes the soil, water bodies and the air (Osibanjo & Nnorom, 2008). The acids can also mix with rain and spread out generously forming acid rain for one.

2.4.4 e-Waste Recycling

There is a great need to recycle the electronic and electrical equipment which is now e-waste for a number of reasons some which have already been given above. According to research carried out electrical and electronic equipment are using up high percentages of valuable metals and other rare earth metals. In 2007 the combined unit sales of mobile phones and personal computers only used up to 3% of the world’s mine supply of gold, 34% of total primary silver production, 15% of cobalt and 13% of palladium (ATE, 2012) which is highly significant and has obviously increased with time because of an increase in the manufacture of electronics. The landfilling of the e-waste results in the loss of great amounts of metals which is countered by recycling. Environmentally sustainable recovery of precious metals has economic advantages because of the high value that precious metals amount to. This percentage is at approximately 40% of the total value of TV boards and DVD players and 80% in mobile phones and printed circuit boards for example (Cui & Zhang, 2008). The recycling of gold can reduce energy usage by as much of 65% energy usage compared to primary production whilst energy savings for palladium are up to 14% (Wang & Gaustad, 2012). Some of the advantages are given:

Advantages of e-waste recycling

- It has environmental advantages in that there will be a reduction in disposal of the waste in the municipal solid waste system which means it does not end up in either landfills or incineration (by preventing emissions from discarded products or landfills into soil, water and air: reducing land use for waste deposits etc.) (Hartard & Liebert, 2015).
- It protects the workers that faced chances of exposure to hazardous wastes from the informal recycling of the waste.
- There are economic advantages associated with the recycling of the e-waste. EEE uses many metals some of which are extremely precious and expensive to mine like Indium hence the recycling of the metals is cheaper and provides an alternative source of the metals.
- Mitigates the environmental impacts of mining by a reducing energy need, CO_2 impact, and SO_2 production, as well as land and water use. Whilst also reducing the generation of large amounts of secondary solid and liquid wastes. For example the production of 1 tone off gold produced through mining emits approximately 17000 tonnes of CO_2, while platinum produces approximately 14000 tones and palladium approximately 10000 tonnes (Hartard & Liebert, 2015).
- There is generally a reduction in the amount of energy used in recycling that from primary production.
- Recycling of the e-waste results in the preservation and extension of lifespan of the metal resources which are running out at a very fast rate while also buying time to develop improved extraction techniques, which one day might enable less burdensome mining of poor or deep ore bodies (Hartard & Liebert, 2015).
- Formal recycling of the waste would result in job creation because of the many stages involved in the process. Among which are a number of high tech jobs and infrastructure.
- Formal recycling results in the safe disposal of private data which might otherwise be abused if it got into the wrong hands
- It provides a legal and safe disposal method for the waste which would otherwise occupy useful storage space in organisations and homes.
- Reduces the geopolitical dependence in case of a high concentration of certain critical metals on few mining countries or companies (while creating a significant intra-European metal source) (Hartard & Liebert, 2015).
- Dampens the metal price volatility (by improving the demand–supply balance, and limits speculation, as a broader supply base is less vulnerable to disruptions)

Though the recycling of e-waste might have some disadvantages there seem to be numerous more advantages which have encouraged studies and implementation in this area.

2.4.4.1 Recycling methods

EEE are made up of many different parts or components as already stated above like the cables, the screen, batteries and covers. These components are all made up of a combination of different materials and elements (Huang et al., 2009). A wide spectrum of materials contained in e-waste demands diverse and separate treatment processes which at times demand a considerable investment. Informal recycling of e-waste involves the use of hazardous chemicals in the leaching of the waste after haphazardly dismantling it, which makes the problem even worse than it would otherwise have been (Widmer et al., 2005). The formal recycling of e-waste has to be done in stages to ensure there is minimum loss of material as well as the least amount of danger to the environment only then can the process be really sustainable (Rochat, Hagelüken, Keller, & Widmer, 2007). Hence the first stage of e-waste recycling will be the collection of the waste, followed by sorting/dismantling, then pre-processing and finally end-processing. South Africa has been championing the recycling of e-waste in Southern Africa since earlier than the 1990s with companies like DESCO and Universal recyclers which are now very well established. These two companies however focus mainly on the collection and dismantling of e-waste. However, the actual recovery of some of the metals like the precious metals and some of the plastics is not yet being done on a large scale with most of the pre-processed raw material being exported to Europe although SA Precious Metals does have a fully functional hydro-met plant for precious metal recovery. In metallurgical processes it is required to have a high recovery rate with a low environmental impact for sustainably hence when it comes to e-waste precious metal refinery, there are only a few companies in the world equipped with technical know-how, sophisticated flow sheets and sufficient economy of scale (e.g. Aurubis AG in Germany, Boliden in Sweden, DOWA in Japan, Umicore in Belgium, Xstrata in Canada), to fulfil the technical and environmental requirements (Wang et al., 2012). The high cost input required for the different stages of e-waste recycling and refining poses a challenge for any company that is interested in plant start-up, without back-up from the government especially when taking into account economic and social boundary conditions. In China and South Africa it was shown how the financing of state-of-the-art e-waste recycling plants fails when not supported by a proper collection network and suffers from the competition of informal sector (Schuelp et al., 2009; Yose, 2014). Factors like the amount of e-waste to be processed, social and cultural boundary conditions and role of existing informal sectors will probably hamper and cause such pilot projects to fail hence they need to be carefully considered (Schuelp et al., 2009). The following section looks at the differences in the recycling practices in developed and developing countries. It costs more money to recycle the e-waste properly in a formal facility than to recycle the waste informally. Informal recycling facilities are primarily used in developing nations (Marinelli, Wang, Huisman, Zhang, & Van, 2008; Nartey, 2016). Hence countries like the USA would rather export their e-waste to the developing which is also cheaper for them because of the strict requirements of setting up a recycling plant (UNEP, 2011).

2.4.4.2 Informal Recycling of e-waste

This is done mostly in the undeveloped countries and involves the following stages

i) collection,
ii) crude dismantling,
iii) sorting of the e-waste
iv) recovery of the valuable and required metals (Song & Li, 2014).

The informal e-waste sector consists of sites that extract the valuable parts of the electronics using crude recycling and disposal methods usually without any kind of safety equipment such as goggles or gloves or the assistance of technology (Song & Li, 2014; Widmer et al., 2005). This is done mainly by families and other individual workers in communities that depend on the extraction of the valuable metals from e-waste for their livelihood. The removal of the valuable material is done primitively and the remaining parts of the e-waste are typically burned, buried or discharged haphazardly into waterways for convenient disposal sites. These crude procedures used in the informal sectors are what lead to environmental contamination because the processes emit toxic chemicals from the e-waste into the surrounding environment. The dismantling is done using chisels, hammers, pliers and cutting torches as well as electronic blowers to open solder connections and separation of various complicated components (Awasthi, Zlamparet, Zeng, & Li, 2017). Pollutants from e-waste being dismantled in this way can be exposed to the environment through burying or dumping. Some recyclers use incineration or open-pit burning as a way of burning off the plastics covering the cables of electrical components so that they can recover the copper wires and other components. This improper incineration and burning of cables creates different types of dioxins which are extremely toxic persistent compounds that can be very difficult to remove from the environment and can travel long distances before ending up in the food chain (Kreith & Tchobanoglous, 2002; STEP, 2011). The hazardous recycling of monitors is also done. This results in the release of toxic chemicals such as polycyclic aromatic hydrocarbons (PAHs) and halogenated PAHs into the air and surrounding environment. In addition to incineration chemical methods are also widely used in the informal recycling of e-waste. These include open acid bath procedures where acid is used to strip metals from the electrical components, such as cyanide leaching, hot acid baths used for the chips and PCBs (Awasthi et al., 2017). The used acid from acid treatment procedures is disposed of into the environment in most cases and it can be filled with heavy metals and other toxic chemicals creating an environmental hazard. The burning of the waste is also done on the boards as a way of removing the solder which results in the release of lead into the environment (Memon, 2016). For environmental sustainability and other reasons, all e-waste should be recycled in formal recycling facilities. However, because the formal e-waste facilities are costly to construct and operate, especially in less developed countries, informal recycling sites are prevalent.

2.4.4.3 Formal recycling practices

The formal recycling of e-waste which is mainly done successfully in developed countries, needs to be taken very seriously for a number of reasons which include waste management (Renz et al., 2012). Ideally proper tracking of the processes needs to be done from the collection stage to the final disposal, which would enable proper accounting (Hagelüken & Meskers, 2009). The success of formal recycling depends greatly on the different stages involved in the recycling process and how well each is done. Strict legislature also contributes to how environmentally sustainable the process is done and to the overall recoveries achieved at the end of the process. The following stages could be involved in the successful recycling of e-waste:

e-Waste Collection

The collection of the e-waste presents the biggest challenge in most countries because of lack of awareness, suitable resources and strict legislature governing the collection (Manomaivibool, 2009). The mentioned reasons have either enabled or hindered the collection of e-waste both formally and informally. In South Africa there has been an increase in the number of e-waste recycling companies dramatically which greatly aids in the formal collection of the e-waste. Informal collection is usually carried out at curb sides or at the landfills or other municipal collection points. These informal collectors then distribute the ferrous metals to appropriate dealers and can be involved in crude metal recycling by various methods like burning or acid leaching. Formally as already mentioned South Africa has numerous e-waste recycling companies which have tried to be involved in all types of e-waste collection ranging from large enterprises to that the domestic stuff. Some collectors are even willing to pay a fee for the e-waste to encourage community involvement (Finlay & Liechti, 2008). The collection of the e-waste is also being done by reputable collecting firms like Pick-It-up unlike in most struggling African countries.

One concerned party that has not been as involved as they can or should be in e-waste collection are the EEE manufacturers or vendors (Osibanjo & Nnorom, 2007). They are yet to implement manufacturer EPR which would ensure to a larger extent the collection of most old electronic equipment. However the success of EPR has clearly been shown to lie with the local legislature put in place, which determine whether it will enforce this or not (Finlay, 2005; Kang & Schoenung, 2005). There are a number of recycling companies which deal with the waste in variable ways. Some are only involved in the collection and dismantling of the waste before they transport it elsewhere for further processing.

Dismantling/Disassembly

This area adds significantly to the cost element were e-waste is concerned depending mostly on the geographical location in which it is being conducted and also on the labour laws found in that place either as a continent or as a country. The WEEE directive contributes greatly to the way in which the treatment is carried out, because hazardous components such as batteries can also be removed during this stage of the process whilst classification of low- and high-grade materials is also possible. Various techniques like software tools in developed countries can be used to predict how the disassembly systems can be done.

The recycling companies have to dismantle the waste into different categories for example Universal Recyclers will separate aluminium, copper wires, zinc, ferrous metals and PC boards (Universal Recycling Company, 2015). The separated products are sold locally, exported, stockpiled or sent to a registered landfill. The dismantling of e-waste is done both manually and automated in a relatively environmentally safe way. During the dismantling stage the e-waste is separated into its various components which are generally motherboards, PCBs, screens, batteries, main bodies, etc and in some cases this is grouped into plastics, metals and glass (Sun & Zeng, 2016). The dismantling stage of the waste then becomes very important as it enables the grouping of like elements for better processing. E-waste can have iron, aluminium or plastics as the main body of the system.

Disassembly is considered an integral part of realising intrinsic value on a scrap PCB assembly. As such it is carried out at a number of different levels. Levels of disassembly may also be undertaken as a preparation stage within primary upgrading operations, for example removal of transformer cores (Cui & Forssberg, 2003). Such disassembly operations are all practically carried out manually, which in itself places limits on the operation in respect of the costs involved (Sthiannopkao & Wong, 2013). Manual disassembly of scrap is essentially carried out with the aid of tools such as chisels, screwdrivers, pliers and pincers which may be driven electrically or pneumatically. This is done either formally or informally. It is of significance to note that the extent to which PCBs and electronic equipment is designed facilitates the recycling method done at end of life and significantly influences the dismantling process. Automated low cost disassembly is an area of increasing significance and research in the marketplace (Sheng & Etsell, 2007a). The disassembly may also be considered to have an impact on overall future recycling strategies and recoveries. As already noted the limitations of a purely mechanical process can result in preventing precious metal loss from component structures on populated boards (due to the nature of the metal/non-metal interface) and an effective automated disassembly methodology could well expand the potential for mechanical turnkey approaches for all grades of scrap PCBs (Li et al., 2004). In respect of both cost reduction and the insurance of safety objectives, mechanical dismantling and automated and robotic dismantling techniques have been considered (Li et al., 2004). In Austria, the organisation SAT has developed an automated component disassembly methodology for the dismantling of components from scrap, redundant or malfunctioning PCB assemblies (Hester & Harrison, 2009). Whilst the existing production facility deals with the recovery of relatively expensive components from faulty products and over capacity manufacture from several German, Hungarian and Austrian OEMs, the potential exists to expand the application of this technology to complete component disassembly (Mccann & Wittmann, 2015; Hester & Harrison, 2009). SAT concur that the dismantling of components by any manual approach will be both time and cost intensive and have little future applicability within the overall treatment of scrap PCBs, (which SAT currently estimate quantitatively as 400,000 tonnes per annum within Europe) (Hester & Harrison, 2009). SAT's technology essentially comprises automated component scanning and dual-beam laser desoldering with vacuum removal of selected components. The NEC Group in Japan has also sought to address the automation of disassembly via a mechanical approach using equipment to remove components in a conveyorised mode via heating with infrared and shearing or via crushing with impacting rollers (Hester & Harrison, 2009). The Best of two worlds philosophy however favours the use of mechanical dismantling as a way of job creation in developing countries (Wang et al., 2012).

Recovery of Plastics from E-waste

The plastic component of e-waste can be recovered using various technologies. According to studies carried out there are basically two types of plastics which are found in e-waste these include the thermoplastics and the thermosets. Thermoplastics which are also resin based can be re-melted and formed into new products (Kang & Schoenung, 2005). The thermosets have to be shredded before they are recycled because they cannot be melted to form new products. In general the plastic recycling of e-waste components can be carried in three ways that is chemical recycling, mechanical recycling and thermal recycling (Kang & Schoenung, 2005). Mechanical recycling is done after sorting of the plastics which are then shredded before they are separated, resin identified and eventually pelletized (Yang, Sun, Xiang, Hu, & Su, 2013). In chemical recycling of plastics the matter is depolymerised which enables removal of metals at temperatures of about 350-400^{o}C and dehalogenated before they undergo the hydrogenation and petrochemical processes (Kang & Schoenung, 2005). In thermal recycling the plastics are used as a fuel however would require state of the art off-gas cleaning systems like we scrubbers to prevent environmental pollution (Hagelüken, 2006).

Recovery of Glass from E-waste

The glass found in most electronic waste can be recycled ideally into new glass which can be used for the same function. Glass-to-glass recycling is considered a closed loop recycling process because glass that is collected is used as a raw material for the same component (Ari, 2016; Lee, Song, & Yoo, 2007). However, care must be taken to avoid contamination. The efficient recycling of the glass can improve the quality output, lower energy consumption and reduce emissions from the glass making process. The CRTs which are usually the main source of glass in EEE are sent to a recycler and ground into cullet using the different glasses found on the panel and funnel (Kang & Schoenung, 2005). The cullet is then sent to the CRT manufacturers for use in making new CRTs. Care needs to be taken to avoid contamination of material as this would result in varying of the glass composition which could affect further production leading to company downtime for up to 3-4 days trying to rectify the altered composition (Kang & Schoenung, 2005). Hence in spite of the advantages which come from the glass recycling most manufacturers are reluctant to take recycled CRT glass because of the unknown composition (Ari, 2016). The contamination could potentially alter the properties of the glass. The disadvantages of glass to glass recycling include the difficulty in identifying glass composition which would lead to a high cost of CRT demanufacturing, the cost and complexity of the required collection infrastructure, and insufficient supply of recycled cullet (Kang & Schoenung, 2005).

Recovery of Metals from E-waste

The recovery of metals from electronic waste has in recent years been known as a form of urban mining which should be done in order to preserve our natural resources as stated earlier. There are numerous methods available for the recovery of metals from ores, however the development of highly effective, low-temperature and environmentally benign technologies for metal processing to reduce energy consumption, lower investment costs and greenhouse gas emissions is urgent (Park et al., 2014). To date much research has been carried out on the recovery of metals from the e-waste. Most of these studies have focused mainly on the recovery of base metals found in the waste; examples include different types of mechanical, pyro-metallurgical, bioleaching and hydrometallurgical processes (Cui & Zhang, 2008). Some of these processes are being used successfully scaled industrially. There is need to find a process which is affordable and environmentally friendly so as to not generate future problems.

Mechanical Processes

On e-waste mechanical processes are carried out for several reasons which include the need for homogenisation, characterisation, classification, comminution and liberation of metals from the non-metals, ceramics from plastics etc. These processes are either automated or done manually or use both methods. The type of process used depends greatly on the geographical region, in which it is being done for example in Europe were the cost of labour is much more expensive the processes are more automated unlike in Asia and Africa were the cost of labour is cheaper and there are hence more benefits in using human labour (Unep, 2011; Widmer et al., 2005). There are other pros and cons associated with the choice of process as well which range from efficiency to environmental issues. The type of physical/mechanical separation method used will also affect the degree to which recoveries are achieved and is greatly dependent on the type of size reduction and liberation of the various materials achieved (Li et al., 2012). Liberation methods which can be and are generally used with e-waste include shredding and pulverisation of the material, after successful liberation of the waste the matter can be then be fed into further processes which can be further mechanical, pyro, or hydrometallurgical treatment. In Germany, Fuba Printed Circuit Boards Gmbh has a 21000 tonnes per annum plant able to achieve the generation of 92-95 percent metal stream output from scrap of PCBs using mechanical process route which includes shredding, granulation magnetic separation, classification and electrostatic separation (Goosey & Kellner, 2003). The process deploys three stage liberation and sequential separation route which involves ferromagnetism removal, eddy current techniques and air table techniques for separation of particle fractions in the +5-10 mm, +2-5mm and -2mm ranges (Goosey & Kellner, 2003). High recoveries of copper at 76%, gold at 83% and silver at 91% have been achieved from low grade PCB scrap or general electronic scrap (Goosey & Kellner, 2003). Other products include the polymer stream which has application in extrusion casting and is used as filler in building materials.

Turnkey plants which deploy comminution, magnetic and eddy current separation for ferrous and aluminium fractions have been commercialised using treatments such as classification, electrostatic separation and secondary treatment to generate metallic fractions, non-conductive and ferrous fractions from scrap PCB assemblies (Goosey & Kellner, 2003). The many differences in the physical and chemical properties of the materials and components present in PCBs and electronic scrap as a whole, permit recycling approaches that separate them into their individual fractions (Goosey & Kellner, 2003). These differences in characteristics determine which separation route is most appropriate ultimately with each difference being exploited. It is crucial to carry out an in-depth characterisation of the material so that separation becomes possible. Material properties like magnetism, densities, polyformity, electropositivity and conductivity can be considered (Zhang & Forssberg, 1998). There are also controlled characterisation variables like particle size, shape and degree of liberation which also affect the degree of separation and can the adjusted to suit requirements (Ghosh, Ghosh, Parhi, Mukherjee, & Mishra, 2015; Rossouw, 2015). Particle size distribution and other factors will determine the composition of the material being treated and whether the process will be profitable or not. Mechanical treatment of e-waste can be used to upgrade the e-waste by separating it into different phases in preparation for further processes. In South Africa at one of the biggest e-waste recyclers the mechanical treatment of the e-waste is what is done through processes like shredding, density separation, rotary magnets, extractors, granulation, shears and balers before transport to the refinery when its PC boards. If the hydrometallurgical route is to be used the metallic elements covered with or encapsulated by various plastic or ceramic materials on printed circuit boards, need to a mechanical pre-treatment process allowing their liberation and separation in order to facilitate their efficient extraction with acid or alkali at times (Rossouw, 2015). Therefore, the mechanical processes are usually only used as a pre-treatment method. There are also plants which will only shred the PCBs prior to leaching in South Africa. Numerous separation technics have been studied in research which include shape separation, jigging, density-based separation, two-step crushing and corona electrostatic separation (Xiu, Qi, & Zhang, 2013; Li, Lu, Guo, Xu, & Zhou, 2007). In the mechanical pre-processing of metals magnetic separation can be used for extraction of iron while aluminium can be removed using gravity separation (Yamane, de Moraes, Espinosa, & Tenório, 2011; Cui & Forssberg, 2003).

Magnetic Separation

The magnetic susceptibilities of any materiel are usually the easiest to use for separation of the ferrous material from non-ferrous material. This does not only refer to iron but to the alloys as well depending on the magnetic field intensity, as is shown in Table 2.10. The main type of equipment to use is the magnetic separator which has undergone many advances in design and operation, with the introduction of rare earth alloy permanent magnets which have very high field strengths with high-intensity and gradients (Rossouw, 2015). These magnets can be used in drum separators. An intense field separation can be used for the following group of alloys:

- Copper alloys with relatively high mass susceptibility (Al multi-compound bronze);
- Copper alloys with medium mass susceptibility (Mn multi-compound bronze, special brass);
- Copper alloys with low mass susceptibility and/or diamagnetic material behaviour (Sn and Sn multi-compound bronze, Pb and Pb multi-compound bronze, brass with Fe content) (Cui & Forssberg, 2003).

Table 2.10 Iron Alloys Magnetically Separated from e-Waste

Adapted from Cui and Forssberg (2003)

Material	Fe content (%)	Mass susceptibility, ($x10^{-7}$ m^3kg^{-1})
Aluminium-multi-compound bronze	2-4	6.5-11.5
Manganese-multi-compound bronze	1.5-3	0.7-2.4
Special brass	0.7-1.2	1.3-5.8
Brass	<0.2	<0.1
Tin and lead bronze	<0.2	<0.1

Electric Conductivity Separation

This separation is based on the use of the different electric conductivities or resistivity. There are three main separation techniques which can be used (Chehade et al., 2012):

1. Eddy Current separation

This is based on the use of rare earth permanent magnets. Eddy current separators are almost exclusively used for waste reclamation where they are suited to handling the relatively course sized feeds.

2. Corona electrostatic separation

The corona electrostatic separator separates materiel into conductive and non-conductive fractions using corona charging. The difference in electric conductivity or specific electric resistance between metals and non-metals supplies an excellent condition for the implantation.

3. Triboelectric separation

Triboelectric separation makes it possible to sort plastics depending on the difference in their electric properties. This process has shown many advantages in plastic separation independent of particle shape, low energy consumption and high throughput.

Hence electrostatic separation methods can be used for the separation and recovery of copper and precious metals from printed circuit board scrap as well as recovery of copper or aluminium from chopped wires and cables.

Density Separation

The difference in density is basis for separation of heavier materials from the lighter ones. Gravity concentration separates materials of different specific gravities, using gravity and resistance to motion offered by a fluid like water or air. The specific gravity ranges for some of the metals found in e-waste are given in Table 2.11.

Table 2.11 Specific Gravities of Key Metals Found in e-Waste
Adapted from Goosey and Kellner (2003)

Materials	**Specific gravity range (g/cm3)**
Gold, PGM, Tungsten	19.3-21.4
Lead, Silver, Molybdenum	10.2-11.3
Magnesium, Aluminium, Titanium	1.7-4.5
Copper, Nickel, Iron, Zinc	7-9
GRP	1.8-2

Screening and Shape Separation

There are numerous advantages to using material of a uniform size which include upgrade of metal contents. The particle size and shape properties of metals are different from that of plastics and ceramics hence the advantage of screening. The main instruments for screening that can be used include the rotating screen or trammel (Cui & Forssberg, 2003). This is also affected by size and shape. This unit has resistance to blinding which is important considering the diverse array of particle shapes and sizes encountered in waste. Vibratory screening is also commonly used in particular at non-ferrous recovery sites though wire blinding is a marked problem. Shape separation makes use of the differences in:

- Particle velocity on a tilted solid
- The time the particles take to pass through a mesh aperture
- The cohesive force of the particle to a solid wall
- The settling velocity of particles in a liquid

Shape separation by tilted plate and sieves are the basic methods used in recycling, an inclined conveyor and inclined vibrating plate were used as a particle shape separator to recover copper from electric cable waste, printed circuit boards and e-waste (Cui & Forssberg, 2003).

Mechanical separation processes do have numerous disadvantages as well. According to research done by Jadhav and Hocheng (2015) much care is required when carrying out the mechanical processing of the e-waste to avoid valuable material being lost which can amount to about 10-35% loss resulting from insufficient liberation of metals due to the intimate association of the valuable metals with plastics and the generation of fines which is lost as dust (-75micrometers) during size reduction and inefficiency of separation processes for metal recovery from fine fractions (Tuncuk, Stazi, Akcil, Yazici, & Deveci, 2012). Such processes also do not remove toxic organic matters such as BFR in waste PCBs efficiently neither can they wholly classify the matter and result in the generation of fine hazardous dust particles (Khaliq et al., 2014; Tuncuk et al., 2012; Xiu et al., 2013). Hence losses can occur as the valuable matter adheres to resin powder which usually forms. There is also much noise and harmful gases which are generated because of the strength and tenacity of the feed material. Another area of concern is the high cost required for the complicated equipment applied in the mechanical processes. The use of mechanical separation in e-waste recycling is very effective as an enrichment process which still requires further processing and treatment using pyrometallurgical and hydrometallurgical processes for the extraction (Tuncuk et al., 2012). Hence the initial investment might not always be worth it.

Pyrometallurgical Processes

Pyrometallurgy has been used since the Iron Age as a conventional method for metal extraction with the furnace being used for the recovery of copper from the ore for many years. The pyro-metallurgical process has also been widely used to recover non-ferrous metals as well as precious metals from e-waste in the past decades (Calgaro et al., 2009). Different pyrolytic treatment processes exist, which include incineration, smelting, drossing, sintering, melting and high temperature gas phase reactions which operate at different temperatures (Calgaro et al., 2009; Ramunno, De Moraes, Espinosa, & Tenório, 2014). Though the other pyrometallurgical processes do not require very high temperatures they produce metal alloys which need further processing. One method involves the ignition and melting of ground feedstock in a furnace at approximately 1200^{o}C via air injection (Kellner, 2009; Zhang et al., 2008). The organic constituent is destroyed at this temperature and is a source of energy for the system with the need of afterburners to deal with the toxic emissions. This furnace produces black metal which is rich in copper and can be electro-refined (Kellner, 2009). The precious metals report to the anodic sludge and can be recovered via leaching, melting and precipitative route. The vast majority of scrap or redundant PCB assemblies which enter the recycling route for precious metal content are smelted after an initial primary mechanical treatment. At UMICORE in Belgium the copper furnace has been implored in the recovery of copper, other base metals and precious metals from the 10wt% electronic waste and several other types of wastes, the plastic component becomes a source of energy and the SiO_2 and other components will be found in the slag, state of art the off-gas systems and waste water recycling systems are also used (Na, 2006; Schuelp et al., 2009). This process has recovered copper, gold, silver and some base metals which can later be separated using various technologies like leaching and electrowinning being carried out after conversion (Na, 2006). From the resulting sludge silver, gold, platinum, palladium, rhondium, iridium, and ruthenium can be recovered with 99.9% purity using pyrometallurgy and hydrometallurgy (Schuelp et al., 2009). UMICORE annually has a production of 100 tons of gold, 25 tons of palladium, 25 tons of platinum and 2400 tons of silver from waste electronic, catalysts and others. Of the total UMICORE production of Au and Ag 25% is from e-waste plus catalysts whilst with Pd and Pt the percentage is 65% (Schuelp et al., 2009). Another process in commercial use is the Ronnskar process, which recycles metal rich e-waste along with copper concentrates whilst the poor quality e-waste is recycled along with lead concentrates (Cayumil, Khanna, Rajarao, Mukherjee, & Sahajwalla, 2016). Black copper that is the slag produced in the lead process line is later transferred to copper conversion, the product is refined using electrolysis and the generated slime containing silver, gold and palladium metal is in a granulated form.

Noranda process copper concentrates and e-waste (up to 14wt%) are melted at 1250^{o}C under oxidising atmosphere, this results in a metallic fraction composed of copper and the precious metals which are then transferred to the conversion process (Cayumil et al., 2016; Namias, 2013). The conversion process produces 99.1% pure blister copper; the remaining constituents include several precious metals which can be recovered in subsequent electro-refining. There are numerous other pyro-metallurgical recovery plants in Europe as described by Khaliq et al. (2014) which have a reasonable recovery rate. However, this process has a number of disadvantages which make implementation difficult for the less developed countries. Pyro-metallurgical processes require a very high heat input for heating the waste to recover the valuable metals which makes the process relatively expensive. This treatment is also not very environmentally friendly and leads to the production of hazardous gases that need to be removed from the air with flue gas and other cleaning systems. The formation of dioxins and furans is unavoidable due to the presence of halogenated flame retardants in the EEE (Jadhav

& Hocheng, 2015; Tuncuk et al., 2012), which presents environmental problems. The cleaning of flue gas is also expensive. Generation of large quantities of slag which contain silicon dioxide and other impurities found in the waste also result from this process. Valuable metals like aluminium and iron have also been found to report to the slag which is a loss in resource (Khaliq et al., 2014). Hence the pyro-metallurgical processes are generally energy intensive, high cost and require high-grade metal feeds to produce a profitable system (Jadhav & Hocheng, 2015). The process can be used successfully on a large scale not for small scale urban mining and it would be difficult for less developed countries to use it.

Biometallurgical Processes

It is believed that biotechnology is one of the most promising upcoming technologies in metallurgical processing which does not require too much capital investment, labor, and energy consumption (Cui & Zhang, 2008; Zhu et al., 2011). Biological approach also has the advantage of being eco-friendly. Bioleaching has been successfully applied in the recovery of metals from metallic sulfides, which make up the majority of mineral bearing ore for many base and precious metals, by the use of bacterially assisted reactions (Morin et al., 2006). Extraction of metals from sulfidic ores by bioleaching is technically feasible however, today only copper and gold are the metals that are industrially produced in significant proportions by this way (Morin et al., 2006). With regards to e-waste a few studies have been carried out on the bio-metallurgical processes. Bioleaching which uses bacteria for metal recovery from electronic waste using room temperature acidophilic Sulphur oxidizing and or iron-oxidizing bacteria (Cui & Zhang, 2008; Morin et al., 2006; Zhu et al., 2011) and bio-sorption which uses algae, bacteria, yeasts and or fungi for the recovery of precious metals from e-waste usually at elevated temperatures has the potential to result in and faster metal dissolution. The use of chitin into the bio-sorption of gold from waste was investigated by Cortes, the leaching solution used composed of 50g/l thiourea and 15g/l aqueous ferric sulphate and had 20g/l chitin at 25^{O}C for 4h and the gold precipitated out while other constituents dissolved in the solution hence the bio-sorption had up to 80% gold recovery (Syed, 2012). Copper recovery and other precious metals have also been investigated with moderate thermophiles in shake flasks, stirred tanks, rotating-drum reactor and lab scale columns with recoveries of 81% of Ni, 89% of Cu, 79% of Al and 83% of Zn (Ilyas, Anwar, Niazi, & Ghauri, 2007). 90% extractions of copper were reported with the mesophilic strains at low solids concentrations of up to 10g/l. simultaneous recovery of gold and copper was also researched using *Bacillus megaterium* which produced cyanide as a leaching agent with simultaneous recoveries of 36.81% gold and 13.26% copper (Arshadi & Mousavi, 2015). Pre-treatment to avoid copper interference was also done using *Acidithiobacillus ferrooxidans* for 100% copper removal followed by *B. megaterium* of gold which increased recovery to 64%. However the downside of the use of bioleaching is the fact that the non-metallic phase poisons the bacteria (Brandl, Bosshard, & Wegmann, 1999) and fine PCB particles inhibit bacterial growth. Further research by Zhu et al. (2011) was more favorable in controlling the toxicity. There is no process which has been implemented industrially however. Further research is needed to optimize the process by reducing time which is usually very high for example and increase the recovery rate of the metals (Awasthi et al., 2017).

Hydrometallurgical Processes

Traditionally hydrometallurgical processes have been a very effective method for the metal recovery especially with low grade ore. A number of investigations have been conducted to check its viability in the recovery of metals from e-waste in the recent years (Khaliq et al., 2014) using various dilute mineral acids. The subsequent metal recovery techniques which depend on the metal concentration and degree of separation such as solvent extraction, ion exchange, adsorption and cementation have also been investigated (Goosey & Kellner, 2003). However, in some of the metal ore processing there is use of very hazardous leachates which are often volatile and environmentally unfriendly. In general solvents like hydrogen cyanide, mercury, hydrochloric acid, nitric acid, sulphuric acid and aqua regia are the most commonly used mineral acids for base metal, silver and gold recovery and have each been investigated for use in e-waste metal recovery (Chehade et al., 2012; Kumar, Lee, Kim, Jeong, & Yoo, 2014; Park & Fray, 2009). These processes can have a relatively low capital cost with a relatively reduced environmental impact (no hazardous gases from oxidation/dusts), potential for high metal recoveries and are suitable for small scale applications when compared to other processes like pyrometallurgy (Havlik, Orac, Berwanger, & Maul, 2014; Pant, Joshi, Upreti, & Kotnala, 2012; Tuncuk et al., 2012).

In the United States A hydrometallurgical approach has even been developed up to pilot plant stage with preliminary cost studies indicating the potential recovery of all materials, with the exception of discrete components, at an operational profit of some $200 per tonne (Goosey & Kellner, 2003). Another method based on solvolsis was also developed in the US which could enable efficient recovery of metals and the recovery of plastic materials such as epoxides with extraction of halogens and brominated hydrocarbon derivatives (Hester & Harrison, 2009). The UK has also been involved in PCBs recycling research, with two potentially significant development projects undertaken which both have demonstrated some viability to a pre-pilot plant stage. The first of these approaches is from a Cambridge University led consortium which deploys a selective dissolution/electrolytic recovery route for discrete metal constituents (Kellner, 2009). On a relatively small scale there have been a number of hydrometallurgical approaches traditionally pursued in the recovery specifically of gold from pins, edge connectors and gold coated assemblies which have been manually separated from the scrap board (Hester & Harrison, 2009). The aim is either liberate gold as metal flake via acidic dissolution of the copper substrates or dissolution of the gold in cyanide or thiourea based leachates followed by electrowinning or chemical displacement/precipitation with powdered zinc (Hester & Harrison, 2009). Another research development was that at the Imperial College, London, consortium which has taken shredded and classified sub-4mm populated PCB scrap through a single leachate route comprising electrogenerated chlorine in an acidic aqueous solution of high chloride ion activity (Hester & Harrison, 2009). This has produced a multi-metal leach electrolyte containing all of the available metal content at generally mass transport-controlled rates with respect to dissolved chlorine. The viability of subsequent metal recovery via electrolytic membrane cells with discrete metal separation has also been demonstrated. The use of non-selective leachates to dissolve the non-precious metal content of scrap PCBs has also received attention. Apart from gold other metals have also been investigated like solder (lead alloy) recovery stage which employs a selective (non-copper etching) leachate based on fluoroboric acid which can be regenerated (Hester & Harrison, 2009). The selectivity enables this process to be a pre-treatment stage before subsequent selective leaching of the more valuable metals is carried out.

In general, the recovery methods of precious metals has undergone a number of creative investigations, some will be given. There is the dissolution of mixed waste PCBs in HNO_3, before the leachate is mixed with lime-sulphur-synthetic-solution ($CaSx/CaS_2O_3$, $CuSO_4$, aqueous ammonia and sodium sulphite with pH of 10) which was conducted in China (Cayumil et al., 2016) with residue concentrates of Au – 92% and Ag - 90%. Another process investigated was the use of HNO_3 which dissolved silver, copper and other base metals (Naseri Joda & Rashchi, 2012) followed by the solution precipitation with NaCl to give silver chloride, followed by leaching in KOH and H_2O_2 to recover 82.65% of silver. These are two processes which have both used HNO_3 for metal recovery. Another acid which has been investigated for the leaching of copper is sulphuric acid; the residue was leached in a chloride solution to recover palladium followed by leaching tests with thiourea and cyanide to recover gold and silver (Quinet, Proost, & Lierde, 2005). The best recoveries were achieved with cyanide and activated carbon for the extraction. This process achieved a recovery of 93% silver, 95% gold and 99% palladium (Quinet et al., 2005). Nitric acid and aqua regia were used for gold recovery which could be precipitated with ferrous sulphate (Sheng & Etsell, 2007b). The use of thiourea was investigated as a substitute for the traditional hydrogen cyanide recovery of gold in e-waste (Tuncuk et al., 2012). Copper, silver, gold and palladium were recovered from PCBs by a three-step process of dissolving the samples in a solution of sulphuric acid and hydrogen peroxide for 99% copper recovery, the residue was then treated in a thiourea and Fe^{3+} solution. The recovery was up to 85.76% for gold and 71.36% for silver (Awasthi et al., 2017). Further treatment was done in a NaClO-HCl- H_2O_2 solution to recover Pd and the remaining gold. There was 100% recovery of gold and palladium at a temperature of 336K for 3hrs with 5M HCl, 1v% H_2O_2 and 10 V% NaClO with a solid to liquid ratio of 1:10. The metals were precipitated with sodium borohydride (Cayumil et al., 2016). Thiourea leaching has also been used to recover gold and silver from the waste with up to 90% gold recovery and 50% of silver were extracted after 2 hours from the solution containing 24g/l thiourea and 0.6% Fe^{3+} at room temperatures (Jing-ying, Xiu-li, & Wen-quan, 2012). Birloaga, De Michelis, Ferella, Buzatu, & Vegliò (2013) used two leaching solutions of 2M sulphuric acid solution in the presence of hydrogen peroxide for 100% copper recovery and a thiourea solution of 20g/l thiourea and 6g/l of Fe^{3+} in 0.5M H_2SO_4. A cross-leaching method was carried out where spent thiourea solution and 5g/l of the reagent were used to leach the samples. The concentration of gold leached doubled after the pre-treatment while the recovery of silver had tripled.

These solvents are highly toxic, volatile and dangerous to the environment and human health and generate large volumes of liquid waste (Joskowska& Hupka 2008). The different hydrometallurgical methods used above have relatively high recoveries however most of the processes generate a significant amount of spent acid and aqueous solutions. There is also production of a residue consisting of plastics and other metals which will not have gone into solution including mercury, lead chloride, the organic phase, ceramics and spent solutions as secondary bi-products. There is also a significant amount of different gases produced for example during the chloride leaching step when HNO_3 was used as an oxidizing agent (Cayumil et al., 2016). Hence there is a need to reduce the environmental impacts of hydrometallurgical treatment of the e-waste or to find end use of the bi-products. The disadvantages associated with the metal leaching are that the process is generally slow when compared to pyro-metallurgical processes and might not be industrially feasible. The mechanical processing which has to be done before efficient recycling of e-waste generates large quantities of air pollution through dust and has been proven to result in the loss of valuable matter (Jadhav& Hocheng 2015). Some of the leachates which have been investigated are generally very corrosive and hence difficult to handle like the halide ions which require acidic environment to be used (Khaliq et al., 2014). The thiourea leachate is expensive and hence the process might not be feasible (Khaliq et al., 2014; Jadhav & Hocheng, 2015). One option available is the use of less volatile solvents which will be investigated. Hence recent studies have focused on finding alternative recovery solvents which are environmentally sustainable (Zhao, Xia, & Ma, 2005).

The research is going to be carried to find out if the ionic liquids can be used for recovery of precious metals from e-waste as opposed to the traditional use of organic solvents with a high recovery. The use of ionic liquids in metallurgy has recently become an area of much research. Whitehead et al. (2006) and other researchers have been able to achieve a high percentage of copper and precious metal recovery with the use of ionic liquids from the ore.

Ionic liquids are salts which have very low melting points and can be liquid at room temperature or at temperatures below 100^{o}C (Thuy Pham, Cho, & Yun, 2010). They are made up of a large organic cations such as imidazolium or pyridinium, with large chain substituents that alter hydrophobicity of the molecule and a relatively smaller anion which can be organic or not (Croll, 2008; Peric et al., 2012; Thuy Pham et al., 2010). The arrangement of the salt varies the arrangement of the ions in the system disturbs the intermolecular forces between the components hence lowering the melting point (Marsh, Boxall, & Lichtenthaler, 2004; Peric et al., 2012). These salts are highly versatile and their properties can be easily altered (Mikkola, Virtanen, & Sjoholm, 2006; Smith, Abbott, & Ryder, 2014). They can also be easily reused in some processes (Tajik, Niknam, & Sarrafan, 2011). Production of ionic liquids has increased drastically in the past years to replace the conventional highly volatile organic solvents that contribute to air pollution (Mikkola et al., 2006; NTP, 2004; Tavares, Rodríguez, & Macedo, 2013). Ionic liquids have the potential to be benign industrial alternatives for most processes because they have low vapor pressures and do not cause air pollution (Docherty & Kulpa, 2005). The properties of ionic liquids make them very attractive because of the industrial benefits which could save billions of dollars in future clean ups and mitigation (Docherty & Kulpa, 2005)

The use of ionic liquids recently became very famous and the liquids have been studied and applied in many areas which include various types of catalysis, to provide improved conditions, better selectivity, faster rates and better enzyme action when compared to organic solvents (Siedlecka et al., 2011). The processes were use of ionic liquids has been done include biology, electrochemical transformation, fuel cells, solar cells, sensors, nano-chemistry, lubricants, modifiers of mobile and stationary phases in the separation sciences to mention only a few (Siedlecka et al., 2011). In hydrometallurgy ionic liquids are considered to be a promising candidate due to their low toxicity and little environmental impact for the recovery of metals (Cui & Zhang, 2008; Whitehead et al., 2006). They are alternative solvents which are more environmentally friendly in the hydrometallurgical process of ore beneficiation (Davris et al., 2014), can be used in metal recovery from waste, electro-chemistry of various metals (Aldous et al., 2006) and solvent extraction of different metals including the platinum group metals (Park et al., 2014). There is a need to come up with new and greener solvents that can be used for the processing of metal oxides under ambient atmosphere and low temperature. A favourable and sustainable process would have low solvent consumption and low energy use, whilst not generating pollution. Metal oxides are insoluble in most molecular solvents and generally require strong aqueous mineral acids for their dissolution (Abbott et al., 2016). Ionic liquids which have the ability to dissolve a wide range of inorganic and organic compounds have hence been considered as a potential greener solvent for metal oxides (Zhu et al., 2012; Wellens, 2014). The solubility of UO_3 in the imidazolium-based chloroaluminate was determined by Dai et al. at 65°C (Tian et al., 2010; Wellens, 2014). Other oxides which have been dissolved in ionic liquids include V_2O_5 in the ionic liquid 1-ethyl-3-methylimidazolium chloroaluminate by Bell et al. with the oxide being highly soluble in the basic melt but in acidic conditions it however reacted forming a volatile $VOCl_3$ compound (Tian et al., 2010). Further work that has been done on other metallic oxides has suggested the tendency of the solutions to be highly selective which can be used favourably for dissolving base metals whilst excluding the heavier transition metals (Tian et al., 2010). Ionic liquids have also been used for the extraction of base metals from their ores. For example the use of $BmimHSO_4$ for the recovery of copper from the chalcopyrite ore with a 95% extraction which was three to four times higher than in the traditional sulphuric acid- iron (iii) sulphate system (Whitehead, Zhang, Pereira, McCluskey, & Lawrance, 2007; Whitehead, Zhang, McCluskey, & Lawrance, 2009). The order of extraction efficiency of leaching chalcopyrite in ionic liquids was found to be $BmimHSO_4$> $OmimHSO_4$> $HmimHSO_4$. Whitehead, Lawrance and McCluskey (2004) carried out research on the recovery of metals from sulphidic ore using different ionic liquids with promising results. Park et al. (2014) also investigated the use of the solvents in the extraction of the metals from electric arc furnace dust. A lot of research has been carried out in the recovery of copper with the use of ionic liquids from various ores and wastes (Dong, Hua, Zhang, & Zhou, 2009; Kilicarslan, Nezihi Saridede, Stopic, & Friedrich, 2014; Carlesi, Cortes, Dibernardi, Morales, & Muñoz, 2016). With the electronic waste ionic liquids have also been investigated in the recovery of copper with over 99% recovery (Chen, Wang, Huang, & Chen, 2015; Huang, Chen, Chen, Chen, & Sun, 2014). Gold and silver recovery was investigated. These processes have shown that the recovery of metals using ionic liquids is very possible with a relatively even higher recovery than some organic solvents as was investigated by Whitehead et al. (2004) for gold and silver.

Electrodeposition of metals has also been investigated using ionic liquids and it has been found that almost all the metals that can be deposited from ionic liquids including the active metals such as Li, Na, Al, Mg and Ti which cannot be deposited from aqueous solutions (Abbott et al., 2005). The water-sensitive chloroaluminate first generation ionic liquids have been the ones that have been studied the most (Chen, Huang, Ogunseitan, Zhu, & Wang, 2015; Park et al., 2014; Tai, Su, & Sun, 2005). Another type of ionic liquids that is the air and water stable ionic liquids have also been investigated for the electrodeposition like the discrete anion based and eutectic solvents/ ionic liquids such as $ZnCl_2$, urea, ethylene glycol and choline chloride (Abbott et al., 2005; Abbott et al., 2016; Smith et al., 2014). However, to the best of our knowledge ionic liquids have yet to be investigated in the recovery of gold, silver, palladium and indium from e-waste. Hence this project aims to try and apply them in the recovery of silver, gold, palladium and indium with the aim of recycling the leachate in order to reduce the overall cost of the process. The possible environmental disposal methods of the other components of the e-waste will also be addressed in order to have a holistic view of the problem. The solid, liquid and gaseous by-products of the process will also be studied to ensure that the final product is a less hazardous component and can be safely landfilled.

The selection of the ionic was done after an ionic liquid matrix was constructed indicating some various properties of each ionic liquid and how they compare to each other the CxHy- methyl imidazolium chain was maintained because the higher carbon chain liquids have a higher viscosity which might affect the ability to leach metals. Factors like ionic liquid cost, the extraction percentage of metal, the oxidants required and reaction conditions were considered before selection. From the matrix three different types of ionic liquids where chosen that is 1-butyl-3-methy imidazolium hydrogen sulphate, 1-butyl-3-methyl imidazolium chloride and the 1-ethyl-3-methyl imidazolium chloride. Two of these three ionic liquids have previously being successfully used on the recovery of silver and gold from the ores.

3. EXPERIMENTAL WORK

The experimental work consisted of three phases which include the pre-treatment of the sample done using physical and mechanical methods, the chemical leaching stage and finally the optimisation of the process. The physical and mechanical pre-treatment of the waste included the size reduction which was done using various methods like cutting, shredding and pulverisation. After the size reduction of the waste there was mechanical pre-treatment by use of magnetic separation. Chemical pre-treatment was also done on some of the sample using different solvents to ensure the effectiveness of the leaching stage. The chemical leaching stage which was of the waste treatment included the selection of a suitable lixiviant and suitable leaching conditions. The third phase was to find optimal conditions for the leaching process by finding the most suitable operating conditions. The leaching performance was mentioned with reference to the measure of the extent of noble metal dissolution and the selectivity of the leach for precious metals.

Prior to the waste printed circuit boards treatment, they had to be stripped from old computers and this was done in various ways which included the manual removal of some of the major components like lithium batteries and some of the boards surface components like capacitors and fans. This was done as a health and safety precaution, for equipment safety and to try and ensure that the valuable metals would be more concentrated because they are found in only some parts. After disassembly the size reduction by use of different mechanical methods mentioned above was done on the selected components which is the PCBs and the RAM. This generated different size samples for the leaching stage.

Different samples were generated during the treatment process through chemical and mechanical pre-treatment methods. These samples were then used for the leaching tests: they included the control feed sample which underwent manual dismantling, was mechanically cut and then chemically treated to remove the epoxy resin layer which covered the surface of the boards, protecting some of the value metals. This sample group was also used to determine the extent and effect of metal loss and how it would affect the metal recovery because of shredding, pulverisation and magnetic separation that the other samples had to go through.

As already mentioned, samples of waste used were analysed and had to undergo shredding, pulverisation and magnetic separation treatments. This was done for the size reduction of the e-waste to increase the surface area for the leaching tests, to separate the ferrous from the nonferrous metals, and to concentrate the noble metals. The concentration of the noble metals was done by reducing the concentration of the other substances in the waste. This would also assist in determining the extent to which the presence of iron had on value metal concentration, and also determine the advantages of carrying out this separation versus not separating on metal loss. Another sample had to undergo chemical pre-treatment to determine the effects of the base metals on the value metal leaching and lixiviant consumption.

Various lixiviants were used in the leaching tests and these included three different types of ionic liquids bought from SIGMA Aldrich that is 1-butyl-3-methyl imidazolium hydrogen sulphate, 1-butyl-3-methyl imidazolium chloride and 1-ethyl-3-methyl imidazolium chloride, non-ionic liquids were also used that is H_2O, H_2SO_4, and aqua regia. Aqua regia which is a very strong lixiviant was used as a control to determine the quantification of the metal concentrations in the waste circuit boards.

The aim of the experimental work was to determine the process with the highest recovery whilst still being sustainable with the least degree of environmental impact. A high selectivity which would greatly increase the profitability of the e-waste leaching process by reducing the cost of the downstream process of extraction of the metals from the solution was also required. Having all the metals in solution greatly increases the cost and steps of downstream stages of processing the leaching solution to extract the metals. Figure 3.1 shows the flowchart of the metal treatment process.

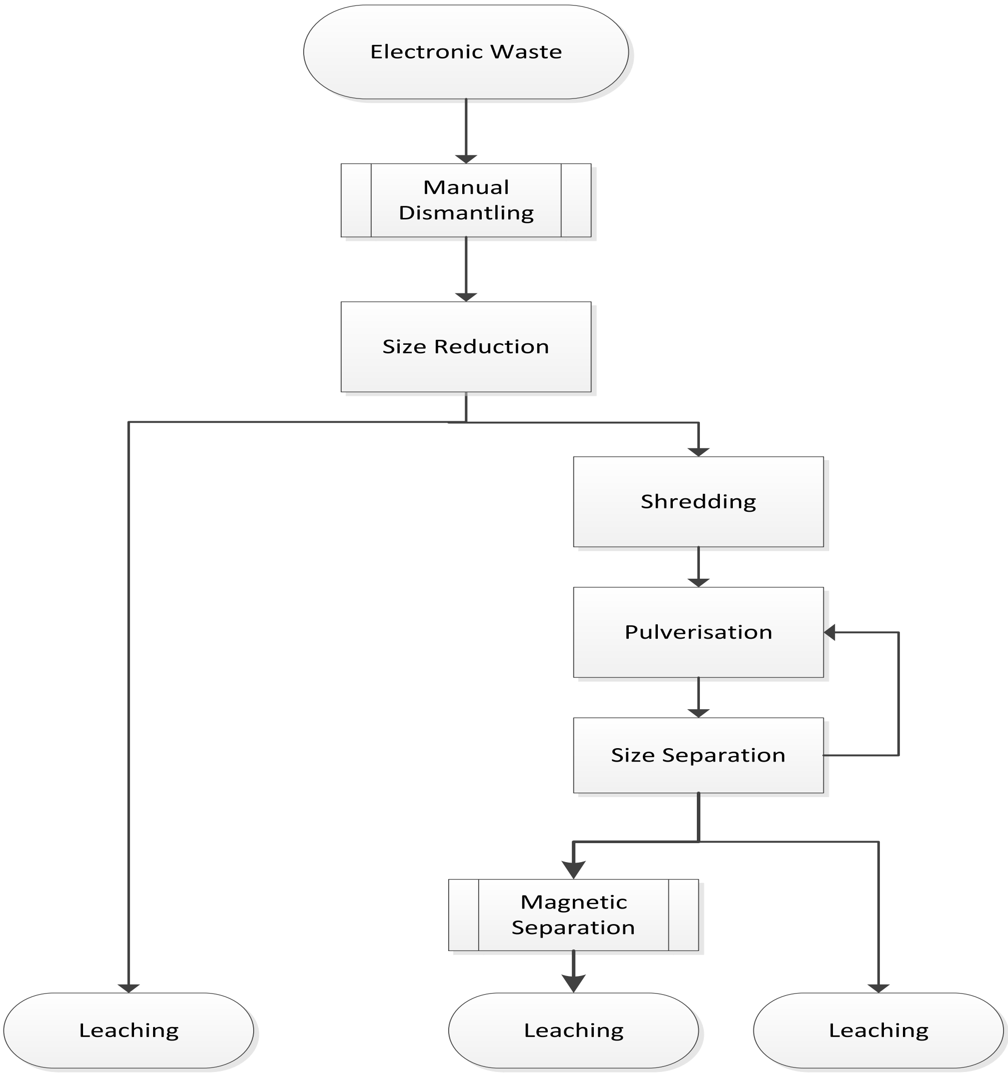


Figure 3.1 Flowchart for the treatment of e-waste

3.1 Sample Analysis

Different analytical methods were used on the samples. Qualitative analysis of the samples was done using either AAS or ICP-OES to determine the elemental metal composition of the waste. The ICP machinery used was the Spectro ARCOS ICP-OES (Cleve, Germany) whilst the AAS equipment was an Agilent Technologies Series 200 Atomic Absorption Spectrometer. For quantitative analysis XRF (PANalytical Axios X-Ray Fluorescence spectrometer) and XRD-SEM (XRD-Bruker D2 phaser) were used to determine the structures of the waste. These analytical methods helped to determine the contents of the metals and how the respective mechanical treatment methods had affected them.

3.2 Sample Mechanical Pre-treatment

The sample had to undergo various types of pre-treatment methods as mentioned above prior to going through the leaching process. In summary there was manual dismantling of the old PCs to remove some components followed by size reduction through mechanical means, then the chemical treatment. Different sizes of the sample were used in this work with the aim of trying to determine the most suitable size fraction for the selective leaching of the e-waste. Metal loss, surface area for reaction and pollution were of importance in the research. The sample was reduced in size and then sieved to come up with different samples sizes which could have an elemental qualitative analysis done on it before undergoing further treatment. Table 3.1 shows the different size fractions produced from the different equipment used in the work. To limit the number of experiments only three size fractions were used in the work and these were based on the equipment used, and the concentration of the metals found on them.

Table 3.1 Size Fraction of the Waste Samples

Equipment	Size
Cutter	30X50mm
Crushing Mill	+212µm-10mm
Pulveriser	+45µm-212µm

3.3 Sample Chemical Pre-treatment

Further pre-treatment which was done on the waste involved removing the epoxy resin covering on the surface of the PCBs which had the size of 30mmX50mm. The epoxy resin was removed because it would prevent leaching of the value metal during the tests, this process was more of a dissolution reaction. The solution used is sodium hydroxide. Chemical treatment was also done on the crushed sample and it involved pre-leaching in nitric acid to try and remove the base metals which are found in e-waste and could be a hindrance to value metal leaching or the ability of the equipment to analyse the other metals because of interferences. The inorganic solutions used in this phase of the experiments were basic NaOH and the acidic HNO_3. The physical and mechanical pre-treatment of the waste does not affect the chemical properties of the slab 30X50mm sample or promote any form of liberation (Hoffmann, 1992), however the case was different for the pulverised sample +45-212µm sample.

From the preliminary analysis and the topographical image of the waste, numerous possible interferences and consumers of the lixiviants used in the leaching experiment were identified and these included the base metals, ceramics and the plastic fibres. The different sizes of the e-waste samples used in the leaching experiments where then taken for digestion and ICP analysis. The waste was analysed for only a very limited number of metals because of the very wide spectrum of materials found in the waste. All the material found in the e-waste could not be covered by this research.

The second phase of the experiments included trying to determine the most suitable lixiviant for the selective recovery of noble metals. Three different ionic liquids were chosen for the trials and these included EmimCl, BmimCl and $BmimHSO_4$. Dilute concentrations of the ionic liquids were used throughout the experiment to cut down on the cost of the experiment. Certain factors had to be taken under consideration during the experimental work and these included the chemistry and thermodynamics of the metals of interest. Gold and palladium the most stable of the metals are generally the most difficult to leach hence it had to be considered when determining the conditions necessary for the leaching stage. The chemistry and thermodynamics of gold, silver and palladium show that it is only reactive under very specific conditions of pH, oxidation potential and other factors. In addition, because gold is very stable as already stated it is very reluctant to give up its electrons and be ionised, it only reacts in the presence of an oxidising agent. Once the gold ion has ionised it requires a complexing agent to bind with so that it can stabilise in the solution. Hence both an oxidising agent and a complexing agent were used in the experimental work. The oxidant used was Fe^{3+} and the complexing agent was thiourea because of the reasons given.

An analysis was also done to see the ability of the ionic liquids in acting as a complexing agent with gold in solution. The amount used of each was calculated from the stoichiometry of the PCB compositions and then used in excess. The variables which could have affected the experimental work included temperature, time, pH, lixiviant concentration, solid to liquid ratio, oxidant, complexing agent concentration and waste composition. Considering all these factors in the experimental work would have been impossible because of financial constraints hence some of the variables were determined from literature and kept constant or fixed whilst the other factors could be varied during the work.

3.4 Factors Considered During Experimental Work

As already stated above different literature was used to determine the variables favourable for the leaching of noble metals. The properties of gold, for leaching to occur, there is a need for complexation between the metal and another substance in order that a stable solution to be formed. Thiourea was chosen as the complexing agent of choice because of its environmental benign properties. The rate of dissolution of gold is rapid and increases with increasing concentrations of thiourea and of oxidant, being controlled partially by chemical and by transport phenomena (Groenewald, 1977). The leaching reaction kinetics for gold and silver which are some of the main metals of interest are variable depending on the mineralogy of the sample (Jinshan Li & Miller, 2007) though most studies have found the leaching rate to be fast initially then to become slow with an increase in time. An oxidising agent Fe^{3+} was also used in the reactions which would enable the reduction of the gold and favour the reaction with thiourea. The leaching of the sample is to be done in different solutions in the presence of thiourea and Fe3+ as oxidant. The half reactions are given in equation 1 and equation 2:

The rate of dissolution decreases with the age of the liquor (Groenewald, 1977).

$Fe^{3+} \longleftrightarrow Fe^{2+} + e^-$……………………………………………(1) $E^{\Theta} = +0.77V$

$2CS(NH_2)^{2+} \longleftrightarrow (CS(NH_2)_2)_2^{+} + 2e^-$………………………..(2) $E^{\Theta} = -0.42V$

In acidic conditions the iron (III) provided the electrons required for the oxidation of the gold and silver. The leaching of Au and Ag in thiourea is a rapid reaction which is shown in equation 1 and equation 2.

$Au^+ + CS(NH_2)^{2+} + Fe^{3+} \longleftrightarrow Au(CS(NH_2)_2)_2^{+} + Fe^{2+}$………(3)

$Ag^+ + CS(NH_2)^{2+} + Fe^{3+} \longleftrightarrow Ag(CS(NH_2)_2)_2^{+} + Fe^{2+}$………(4)

Side reactions also occur which result in the decomposition of thiourea to various compounds which include formamidine disulphide and sulphur. The compounds formed in the side reaction will either leach the waste or result in passivation occurring.

$NH_2(NH)CSSC(NH)NH_2 + 2H+ + 2e- \rightleftarrows 2CS(NH_2)_2$……….(5)

$(SC(NH)(NH_2))_2 \longrightarrow CS(NH_2)^{2+}$ Sulfinic Compound…..……(6)

Sulfinic Compound $\longrightarrow CN.NH_2 + So$…………………………(7)

As already stated, the secondary products of the redox-reaction produced from the reaction of the thiourea appears to cause passivation on the surface of the gold. The rate of the passivation reaction appears to be rapid, and its effect has been observed as a grey-black film on the surfaces of gold exposed to the action of these solutions (Groenewald, 1977).

The reaction occurs in the presence of proton donors and ionic liquids were chosen for this purpose because of their abilities to act as protic acids and bases. The experiment was to determine the suitable conditions for use in the leaching process hence the lixiviants and time were under investigation. Different cations and anions were also of interest to view the effects each had on the rate or ability to leach the noble metal. Hence three different ionic liquids were chosen for various reasons which include the chemical properties, cost and ease of manufacture.

For palladium leaching similar complexation reaction needs to occur for the metal to ionise into solution. Research has found that one type of complex that palladium can form is with chloride ions forming different palladium chlorides (Viñals et al., 2006).

$Pd^{2+} + Cl^{-} \rightleftarrows PdCl^{+}$…………………………………………………..(8)

$PdCl^{+} + Cl^{-} \rightleftarrows PdCl_2$…………………………………………………....(9)

Hence palladium should be able to leach in these experiments. However, the reaction kinetics of this part of the experiment was not known from literature.

Apart from the lixiviants used other factors were also put into consideration which includes temperature, pH, Eh and time. Some of the variables were determined from literature and the stoichiometric values were also used.

Table 3.2 Fixed Parameters Used in the Experimental Work

Parameter	Fixed set point	Reason for parameter set point
Lixiviant concentration	10wt%	Based on expected metal content of the waste PCB samples, 1M would be sufficient for complete base metal extraction according to stoichiometry. Although sulphuric acid is diprotic, it is only a strong acid with regards to the donation of its first proton. Therefore, both nitric acid and sulphuric acid are tested at the same concentration.
Leaching time	6h-48hrs	Based on the literature survey a range of time durations was deemed sufficient for leaching time to draw meaningful conclusions with regards to leaching performance
Feed and Particle Size	30X50mm	Separate feed materiel were chosen some were simple to prepare (i.e. manual disassembly followed by cutting). The small particle size was chosen to ensure adequate liberation of metals and non-metals and to provide a large surface area for promoting efficient leaching.
Agitation speed	250 rpm	This agitation speed was the minimum agitation speed required to suspend particles.
Solid to liquid ratio	1:10 w/v	This S/L ratio has frequently been used in previous studies and was seen to yield satisfactory results.
Oxidant	Fe^{3+}-0.03g	The oxidant was chosen based on literature, the aim was to avoid using excess oxidant
Complexing agent	Thiourea-0.5g	This was a complexing agent which was chosen from literature which could complex with the metals of interest.

3.5 Methodology

The experimental work involved different methodologies which are given in this part of the research report.

3.5.1 Equipment

This section will give a detailed description of the different types of equipment used in the experiment.

3.5.1.1 Disassembly

The first step in the experimental work included the manual disassembly of the PC which was done with the use of screwdrivers of different sizes and pliers. The process involved the removal of the outer covering and the different components of the computers. The PCBs and hard drives were extracted from the inside of the computers and had to be stripped with the removal of components like the batteries and the magnets which could have caused harm to equipment downstream or contained harmful chemical like lithium.

3.5.1.2 Size Reduction

Different size reduction methods were used on the samples and these are explained.

Cutting

This was done using heavy duty saws which could cut the PCB components into the appropriate sizes which were -10mm+5mm

Milling

After the cutting of the PCBs were put through for milling in the Laarman Cutter mill which was the only equipment which could further reduce the size of the components. The mill produced 15% fines and used a 10mm screen. The process took 10min and was repeated for two cycles with high speed blades. Other machinery had failed to mill the sample. The heavy-duty shredder managed to reduce the size of the boards to a size of +/-10mm.

Pulverisation

A pulveriser was used to further reduce the size of the waste from -45µm to +10mm that is from a chip size into the powder state. The e-waste had to be in the pulveriser for 3 cycles or more with each cycle running for over 30min to achieve the required size. This mechanical process was time consuming because of the minimum amount of the e-waste that the pulveriser could hold at any moment.

Sieving

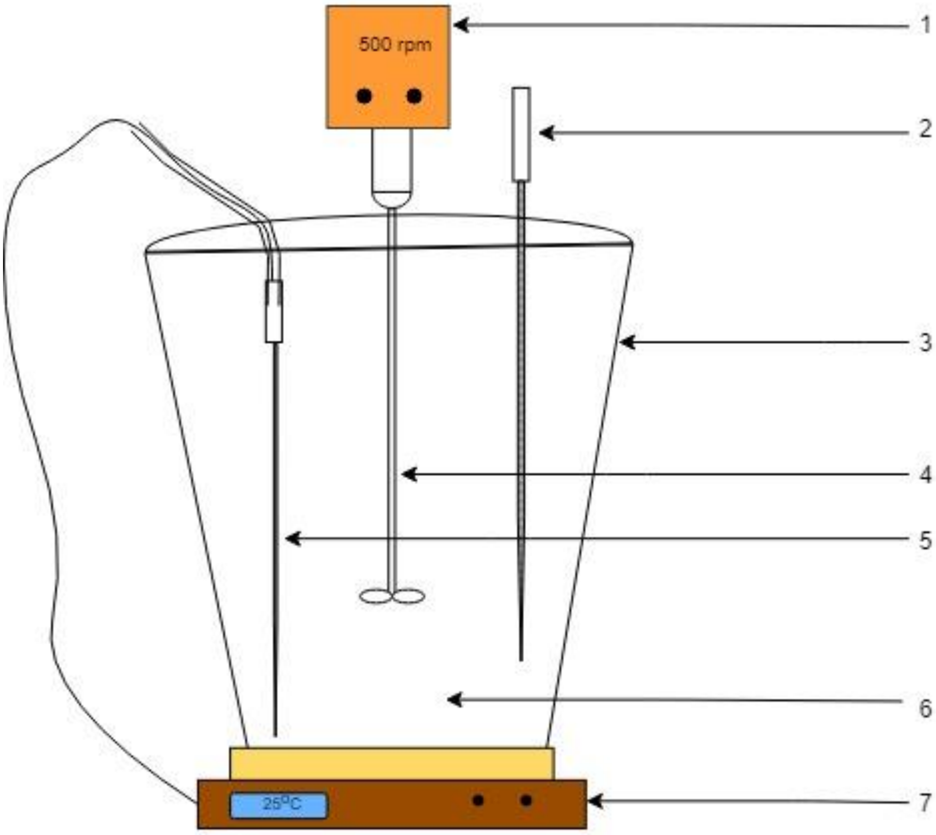
An automated sieve was used on the sample to get the different size fractions. The rotations of the equipment generated a high dust content and could have resulted in the loss of value metals however the loss would have been minimal. The sieves could be left shaking for 30min to allow as much separation as was possible and the process could be repeated in more than one cycle. The shaking of the sieve generated a lot of dust. The nature of the waste also resulted in the clogging of some of the sieve pores.

Magnetic Separation

A magnet was used on the sample to remove the iron part of the waste. This process was simple enough and used a strong permanent magnet and as well as paper. The use of a magnetic separator generated a high amount of dust and hence was avoided to prevent the loss of material. Wet magnetic separation was also used, and this process was efficient however had the additional step of drying which needed to be implemented as well. The wet magnetic separation process also used up large quantities of water which had no known further use downstream.

3.5.1.3 Leaching Experiment

The equipment used for the leaching experiment consisted of glass reaction vessel with a diameter of about 95mm and a working volume of approximately 500ml. the leaching experiment was carried out in a controlled temperature environment to prevent the loss or gain of heat. An overhead stirrer was used which had steel blade impellers with a diameter of approximately 70mm and an angle of 45^o. A glass coated thermometer was also used to monitor the temperature during the experimental work and a redox and pH electrode were also used to record the change in pH and oxidation potentials during the experiment. The set-up of the equipment is shown in Figure 3.2.



1	Overhead agitator stirrer	5	Glass thermometer
2	pH/Eh electrode	6	Leaching solution
3	Glass reaction vessel	7	Hotplate
4	Metal blades stirrer		

Figure 3.2 Diagram of experimental set-up leaching reagents

Sulphuric acid was found in the storage which had a concentration of 98wt%, whilst the nitric acid also from storage was at a concentration of 70wt%. The hydrochloric acid was obtained from SIGMA Aldrich with a concentration of 35wt%. SIGMA Aldrich also supplied the ionic liquids 1-butyl-3-methl imidazolium hydrogen sulphate which was a liquid at room temperature and had a percentage purity of 95%, 1 butyl-3-methyl-imidazolium chloride also from SIGMA Aldrich with a purity of 98% was a white powder at room temperature and needed to be dissolved in solution before use. The third ionic liquid used 1-ethyl-3-methyl imidazolium chloride with a purity of 98% was also a solid at room temperature but however needed to be put in a water bath at a temperature of $63^{O}C$ before it could be liquefied.

3.5.1.4 Analysis of Results

The qualitative analysis of the liquid sample conducted was with ICP-OES, ICP-MS and AAS depending on availability of equipment and the concentration of metal to be tested in the leachate. For the solid matter from the experimental work SEM was done for topology of the matter.

4. RESULTS AND DISCUSSION

The results obtained during the different stages of the experimental work are discussed and given in the section.

4.1 Phase 1: Screening

Phase one of the work involved the size reduction of the waste to an optimum size with the least amount of material lost, which could be practically leached with a high recovery of the value materials.

4.1.1 Dismantling and Pre-Treatment of Sample

The initial step in the e-waste treatment was the manual dismantling of waste computers into separate components, the components with the value metals which are mainly the PCBs and the ram were then taken for further treatment. Prior to the crushing and pulverisation of the waste there was further manual dismantling to remove some of the bigger components which were not required for the leaching process. The battery cell was removed because of the hazardous heavy metals it contains, other components were removed as well to reduce the non-valuables, non-metallic, magnetic and the hazardous phases of the waste. Some components that are harmful to the machinery used for the recycling process or to the environment through pollution also had to be removed. Figure 4.1 shows a complete circuit board with all it components prior to being removed during the pre-treatment dismantling phase of the waste. Figure 4.2 and Figure 4.3 show the transformation which the printed circuit board containing the value metal underwent as a result of the manual dismantling. Figure 4.2 shows the different pieces that were manually removed from the circuit board. The dismantling process included the removal of the lead battery, memory chips, capacitors and solder found in the original component and these are seen in Figure 4.2a to j. The removed components are made from various materials like aluminium, steel, and can each be used in a separate specific recycling process or repaired for reuse (Hoffmann, 1992). The cleared circuit board which is ready for crushing, then pulverisation is shown in Figure 4.3. The weight of the PCB reduced drastically after the removal of the components not suitable for the recycling process. The manual dismantling of the computer waste produced many different types of waste which each require careful disposal.

Figure 4.1 Complete circuit board from a computer

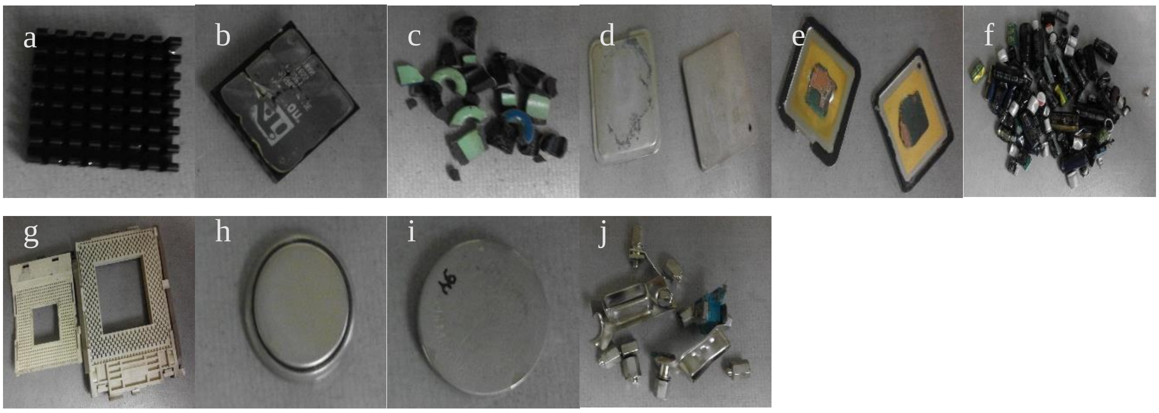


Figure 4.2 Removed components of the circuit board after manual dismantling: lead batteries, ferrous magnets, integrated circuits and capacitors

Figure 4.3 Dismantled circuits boards for further treatments

After the manual dismantling of the board it was taken for cutting and this produced the first sample which would be used for the leaching process shown in Figure 4.8a, the other sample was taken for crushing and pulverisation. The size reduction through crushing was done on the Laarman Cutter Mill machine shown in Figure 4.4a and Figure 4.4b in 2 cycles at durations of 10 minutes, the crushed printed circuit board is shown in Figure 4.5. The mill also contained a 10mm screen which is shown in Figure 4.4c to prevent the larger particles from passing through hence the output was particles of a size -10mm. The 2 cycles which were run managed to increase the efficiency of the process though producing 15% fines. Different types of machinery including the hammer mill and the ball mill were sampled for use in the crushing of the waste with no success. This is because of the properties of the PCBs which make it very difficult to mill using ordinary mineral ore machinery because of the material's elasticity which allows it to stretch and bend without size reduction. Once the sample has been reduced to -10mm it is easier to pulverise the material to the size required for leaching. Figure 4.5 shows the -10mm size sample produced from the milling machine. The pulverised waste is shown in Figure 4.6 and the surface topography of the waste is shown in the SEM image Figure 4.7. Figure 4.7 shows the different materials found in the pulverised waste, further analysis would be required to determine the elemental compositions and the distributions of the ceramics, fibres and metals found in the waste after pulverisation, which were not determined in this work, the image was magnified by a factor of approximately X108.

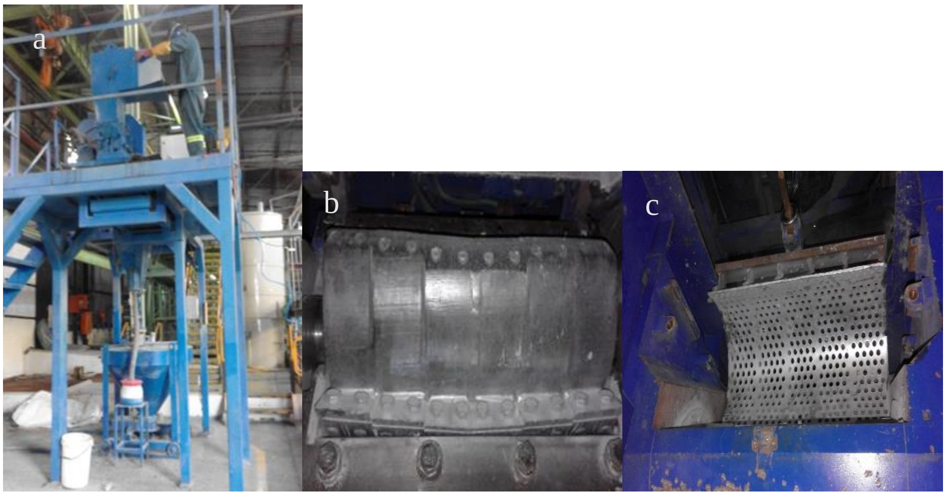


Figure 4.4a Sagging mill for crushing figure 4b the grinders in the mill and figure 4c the -10mm sieve

Figure 4.5 Crushed dismantled circuit boards -10mm

Figure 4.6 Pulverised e-Waste

Figure 4.7 SEM image of the pulverised e-waste DESCO sample enlarged by a factor of X108

4.1.1.1 Chemical Pre-Treatment of Sample

The chemical pre-treatment phase of the e-waste recycling was done on the two samples generated during the mechanical pre-treatment phase. The sample in Figure 4.6 had undergone cutting, crushing and pulverisation then sieving to generate a size range of +45-212 µm whilst the other sample underwent cutting to a size of 30X50mm. These sizes were used in the work, the pulverised sample which has been shown in Figure 4.6 and a second sample which was only cut using a cutter Figure 4.8a. Figure 4.8a shows the uncrushed board after manual dismantling to remove any other components. The sample which is 30X50mm was then chemically treated in a 10 molar concentration of sodium hydroxide for a period of 3 hours before being washed in distilled water to remove the epoxy resin surface covering the metals. Figure 4.8b shows the image of the e-waste sample after the chemical treatment. Leaving the sample in the NaOH solution for a period shorter than the 3 hours did not detach the epoxy resin covering from the slab. The use of the basic solution ensured that there was no loss of any value metals. More environmentally friendly ways of removing the epoxy resin exist which were not explored in this research but have been explored in other work by Zhu et al. (2012). The board did not undergo any further comminution. The treatment in the NaOH solution was to remove the epoxy resin which covered the surface of the board covering the metal, this was done without leaching any of the metals hence the use of this solution. The NaOH removed the epoxy resin covering and left the metal surface exposed and ready for the leaching process.

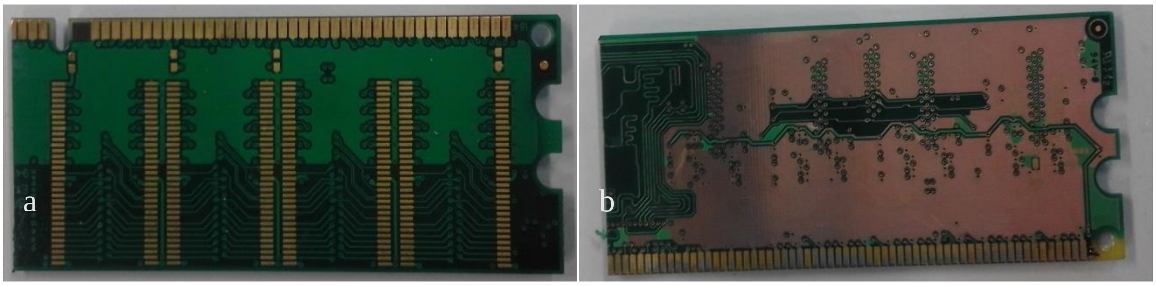


Figure 4.8 a PCB after cutting and 8b after removal of the epoxy resin in NaOH treatment

4.1.1.2 Sample Digestion and Analysis

The results of the metals of interest obtained from the digestion of the waste are shown in the Figure 4.9. As already stated, the graph does not exhaustively show all the different types of materials found in the waste because of the wide range of components in the waste. The concentrations shown in the graph are of the materials of interest which include the value metals gold, silver and palladium. The concentrations of some of the key base metals which include copper, iron and lead found in e-waste are also shown in the graph.

The research is focusing on the metallic phase of the waste and not the non-metallic or ceramic component as already stated. Different size fractions of the samples was tested, with most of the sample sizes being less than 2 mm because research has shown that this sample size has achieved complete metal liberation in the waste (Zhang & Forssberg, 1997) and is hence best for leaching. The three size fractions analysed were -45 µm, +45-180 µm, +180-212 µm and the PCB slab that had been cut to the size of 30X50mm. The results in Figure 4.9 show the metal distribution in the samples with copper and iron being in the highest concentration which agrees with previous results obtained in other research (Cui and Zhang, 2008; Calgaro *et al.*, 2009) whilst the rest of the metals are found in smaller quantities. The base and heavy metal concentration is much higher than the value metals, gold, silver and palladium as can be seen in the graph. The metal concentration differed depending on the size range under scrutiny however there was no identifiable trend coming from sample one size to another.

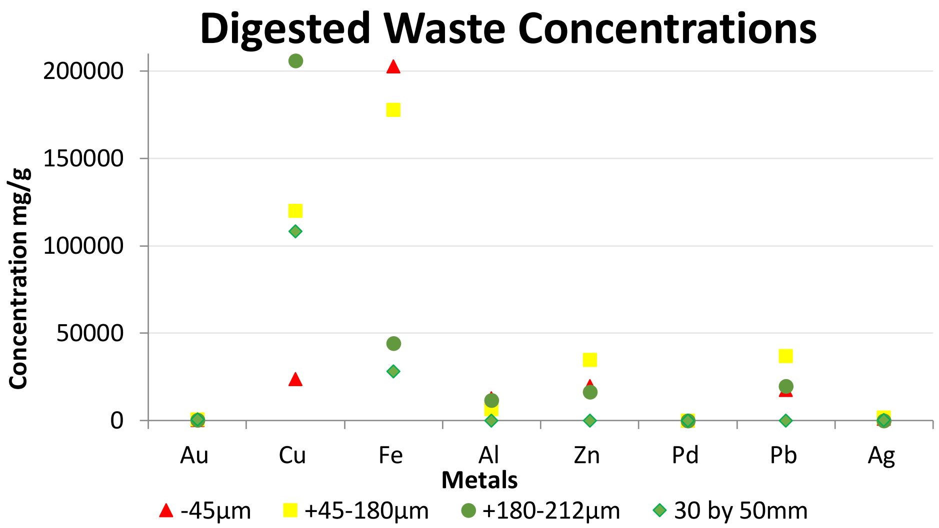
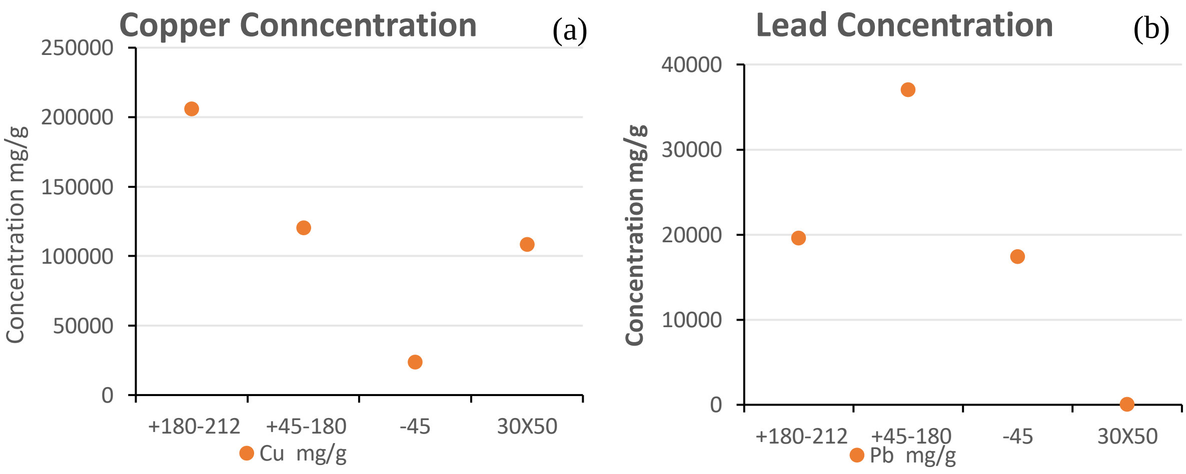


Figure 4.9 Concentrations of the metals in e-waste of different sizes digested and analysed using ICP-OES

Figure 4.10a to 4.10h shows the different sample sizes of the waste and how each size influenced the different metal concentrations. Each metal is shown on a single graph for clearer comparison. There was need to find a balance with the sample which would be used in the experiments. The sample used needs to have a low base metal concentration, with a high value metal (gold, silver, palladium and copper) concentration and a size that is easy to use for leaching in the lixiviants.



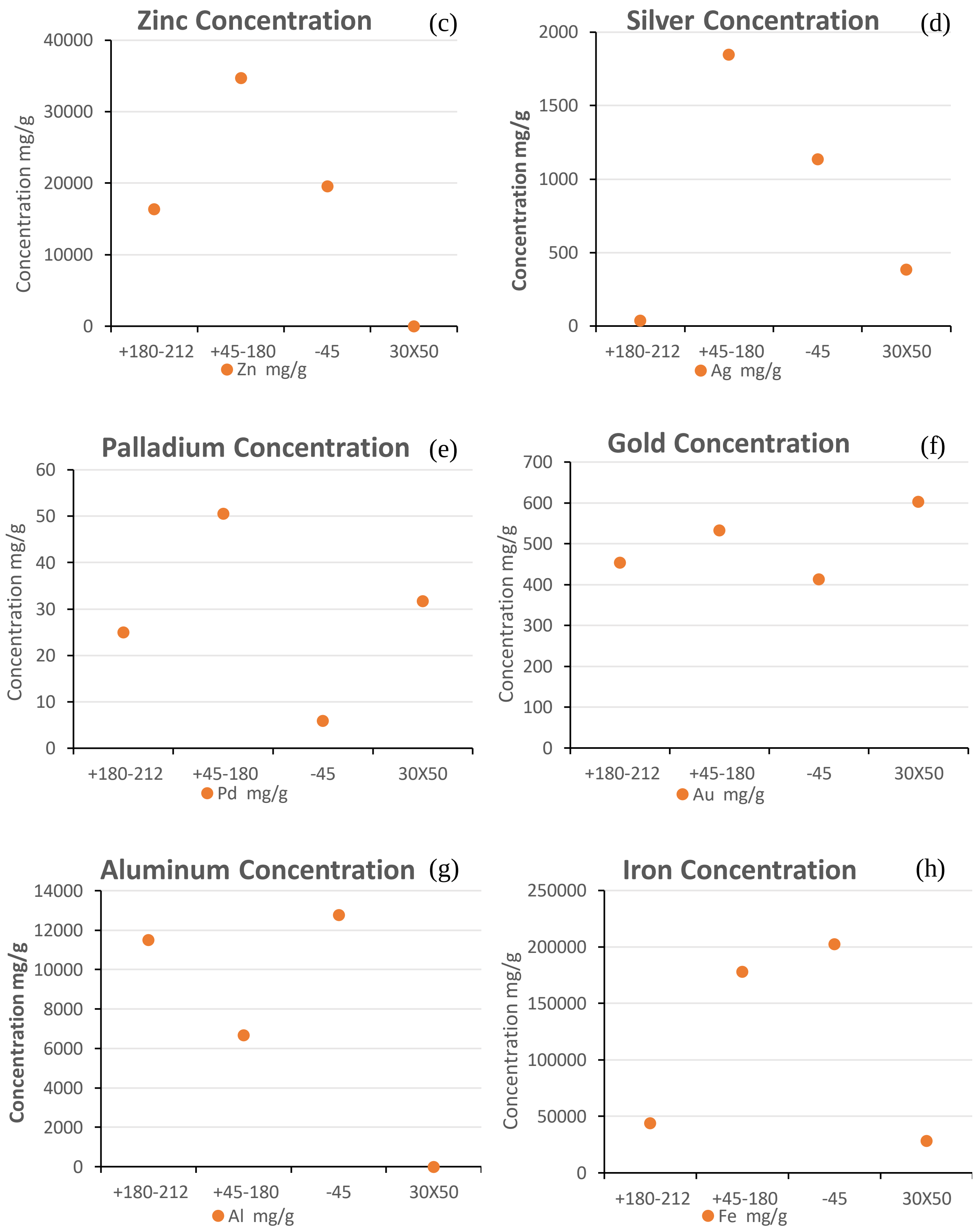


Figure 4.10 a-h Concentrations of the metals in e-waste of different sizes digested and analysed using ICP-OES. The sizes used are +180-212 µm, +45-180 µm, -45 µm and the slab which is 30mm by 50 mm (30X50mm)

As can be seen from the graphs there is no consistent trend for the metal concentration which could conclusively determine the sample to use. The size of the sample had different effects on the metals in the waste depending on metal properties like hardness and malleability of the metal. The smallest size fraction -45µm has a relatively low concentration of most of the base metals analysed except for steel which recorded the highest concentration of 73% higher than all the other metals and highest in all the different sample sizes analysed. Hence the use of this sample size would require a pre-treatment stage to reduce iron concentration if it is not the target metal. The rest of the metal concentrations decreased with the size of the sample which is similar to results obtained by the research conducted by Huang and colleagues (2014) who showed that the concentration of the metals decreased with the decrease in particle size of the waste. The sample also has a comparatively low palladium concentration of 0.002% compared to the 0.1% in other samples, the palladium concentration generally has the lowest concentration in the samples which would also affect the metal recovery from the waste. The metal distribution in this size fraction was affected by the particle size greatly. The middle size fraction of +45-180µm shows a relatively high concentration of most of the metals except with palladium which has the lowest value. Silver and gold percentage concentration were almost constant in all the samples and also relatively low compared to the metals ranging from 0.1% and 0.4% respectively. The biggest size fraction +180-212 µm had the highest concentration of copper metal at 69% with all the other metals being average except silver which had the lowest concentration of 0.01%. The concentrations of the other metals in this size fraction are relatively lower but the gold concentration is average. The slab which had not undergone any mechanical treatment (crushing, milling and pulverisation) but underwent cutting had a comparative high concentration of the gold with an average concentration of silver, palladium and copper at 0.5%, 0.02%, 0.3% and 79% respectively. The absence of any mechanical pre-treatment resulted in no value metal loss which usually occurs during the pre-treatment stage, this could have been what resulted in the high value metal concentrations. This was favourable especially for gold which increased from 0.1% to 0.5% and copper which increased to the highest concentration of 69% to 79%, other metals like iron then decreased to a low of 20%, silver also decrease from 0.5% to 0.3% of all the metals. The iron concentration was averagely low. This sample had favourable base metal concentration which were low. The homogeneousness of the sample was greatly in question and could have affected the concentrations of the other metals. From the results obtained in this analysis the size fraction which is +45-180µm was chosen for use in this experimental work because it seemed to give required concentrations of the metals of interest especially gold, silver and palladium, other factors from research were also considered like the optimum leaching size used in previous work (Whitehead et al., 2004).

4.1.2 Magnetic Separation

Dry suspended magnetic separation was done on the ground samples because of the high iron concentration and this lowered the concentration of the iron and all the other metals. Magnetic separation was done on the sample which had been chosen for use in the leaching work which was the +45-180μm size sample for reasons given above. Figure 4.11 compares the concentrations of the metals in the sample which has undergone magnetic separation and the sample which has not. The sample which has undergone dry magnetic separation shows a significant decrease in the concentration of iron from approximately 47% to approximately 4%, for other metals the decrease was present but not very significant. The magnetic separation process did not achieve 100% removal of the magnetic phase which is similar to results from previous studies (Veit et al., 2005). Numerous reasons could have contributed to the poor recovery which include the poor magnetic field strength of the equipment used in the experiment and or the number of cycles used. Agglomeration also occurred between the metallic fraction and the non-metallic fraction in the waste contributing to the reduced efficiency of the process. This resulted in the attraction of the ferrous metals to the non-ferrous and could have caused the value metal loss. The use of dry magnetic separation resulted in the generation of dust particles which polluted the air and caused material loss, the increased number of cycles also increased the loss of material experienced in the treatment stage. Wet magnetic separation could not be used because of the hydrophobic nature of the waste which would have required the use of wetting agents to adjust this state (Calgaro et al., 2009). The SEM diagram of the residue of the magnetic separation is shown in Figure 4.12 and the average elemental analysis of the components are shown in Table 4.2. The results show a very high concentration of iron and its alloys as well as other elements like bromine which is used in the epoxy resin and titanium used in the ceramics. The results confirm that the magnetic separation did not only remove the iron. The iron was also attached to fibres hence when they were being separated, they were removed together. The analysis did not pick up any value metals meaning it was below detection level for this equipment and hence there was a very limited loss which occurred. The magnetic separation did manage to remove most of the iron alloy, hence the high presence of other elements like carbon. The preliminary treatment of the waste provided the samples needed for the leaching experiments. Magnetic separation has the greatest influence on the iron concentration as shown by the graph with a decrease of approximately 97%, copper concentration also decreased by approximately 45% which was slightly concerning. The change in concentration of the other value metals was not really significant except with the silver which increased and doubled in concentration signifying that the silver might have been previously masked by the high iron concentration.

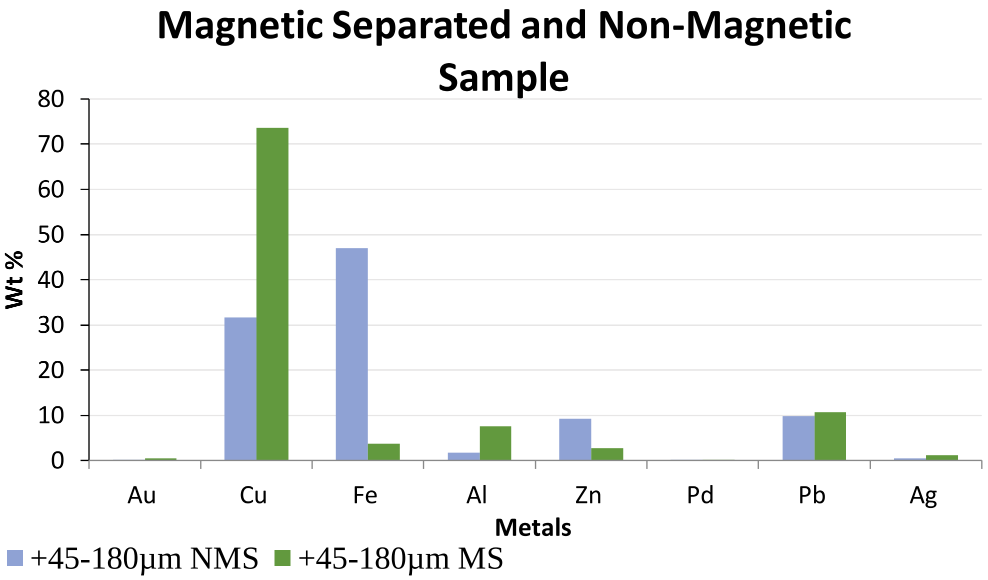


Figure 4.11 Weight percentage of the metals after magnetic separation (MS) and before magnetic separation (NMS)

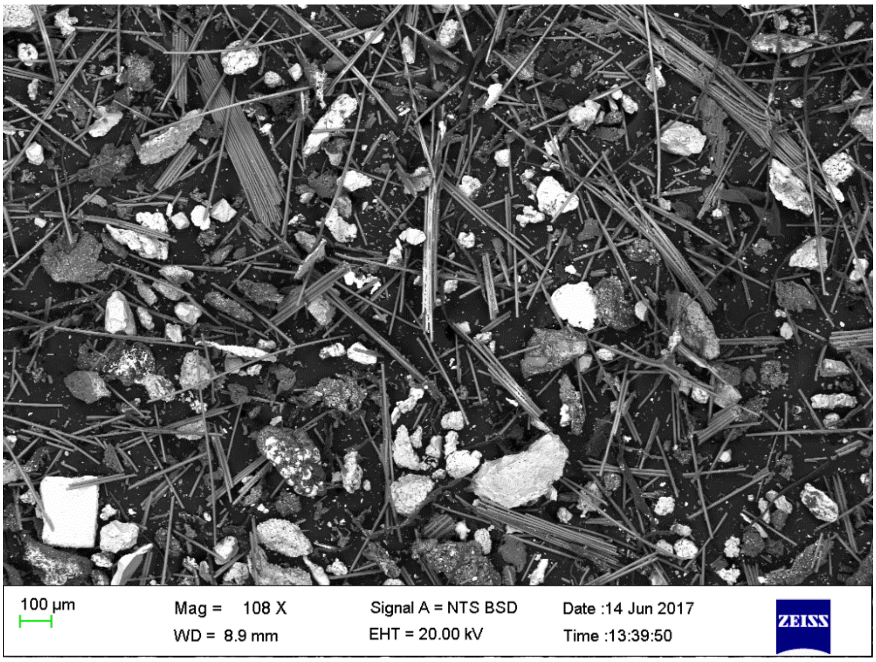


Figure 4.12 SEM image of the magnetic separation residue magnified by a factor of X108

Table 4.1 Weight Percentages of the Elements found in Magnetic Separation Residue

	C	O	Mg	Al	Si	Cl	Ca	Ti	Mn	Fe	Ni	Cu	Zn	Br	Sn
Wt%	50.9	31.1	0.11	1.14	3.49	0.17	2.06	0.23	0.68	6.51	0.36	0.52	0.72	1.85	0.2

4.1.3 Conclusion from Phase One

From the analysis of the results it was concluded that the size fraction which would be used for the leaching of the value metals was the +45-180µm which gave favourable results for gold, silver and palladium with a favourable an average concentration of the other base metals. The copper concentration in this size fraction was lower than for the other sample sizes however a compromise was required therefore from the crushed waste the size which was chosen for use was the +45-180µm. The 30X50mm slab was also chosen for use in the experiments because of its relatively high gold and palladium concentrations with a favourably low iron concentration, there was also the reduced cost of processing which would reduce the overall cost of the waste treatment. The value metal loss experienced as a result of the magnetic separation resulted in this sample not being used in favour of the other samples mentioned above. The other sizes also had downsides which prevented them from being used in this work.

4.2 Phase 2: Leaching Experiments

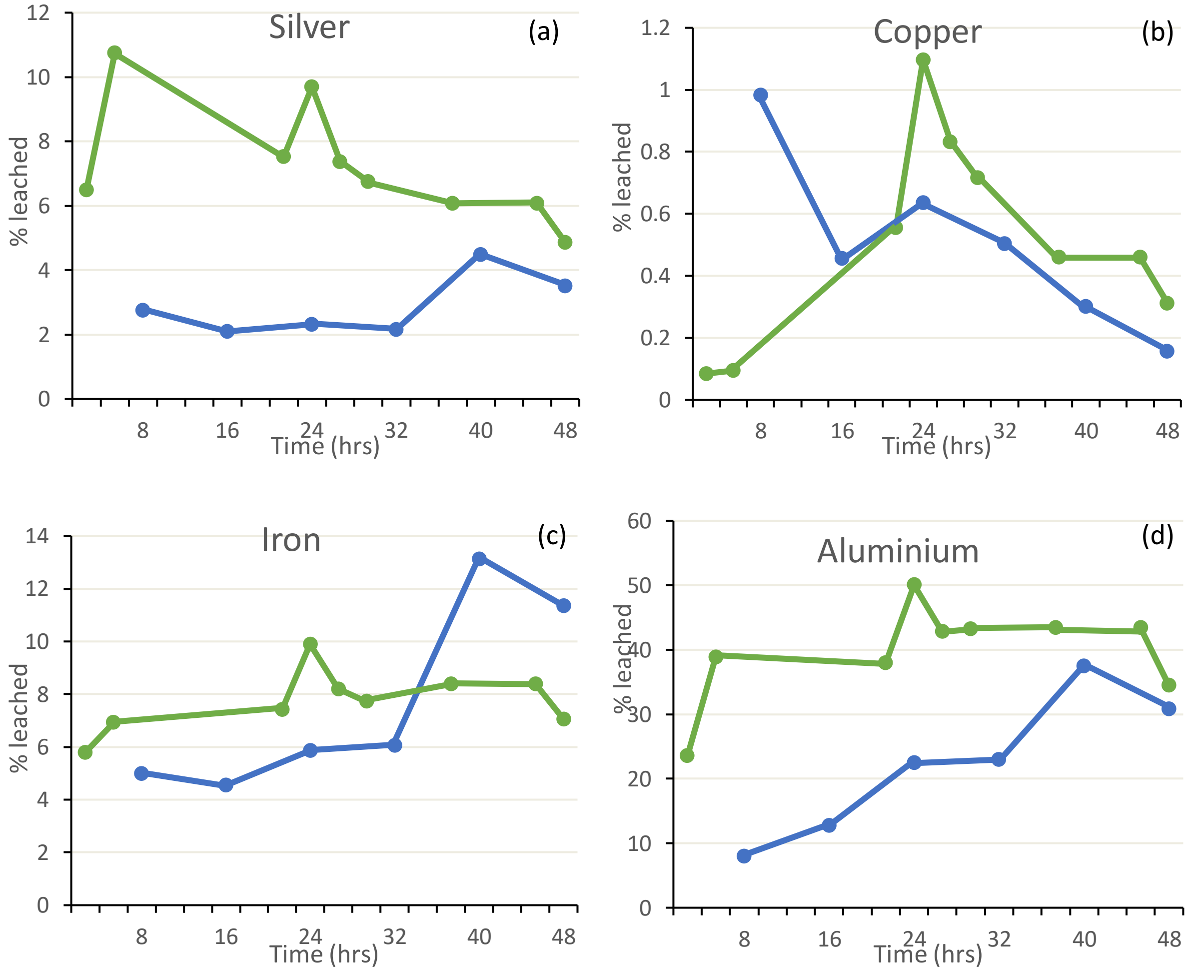
The second stage of the experiment was to determine the suitable conditions for use in the leaching process hence the lixiviants, temperature and time were under investigation. The leaching of the sample was to be done in different solutions in the presence of thiourea and Fe^{3+} as oxidant. According to research done previously the rate of dissolution of gold is rapid and increases with increasing concentrations of thiourea and of the oxidant, being controlled partially by chemical and by transport phenomena according to literature (Groenewald, 1977) however a balance is required to ensure the cost of the process does not skyrocket. The leaching reaction kinetics for gold and silver which are some of the main metals of interest are variable depending on the mineralogy of the sample (Jinshan Li & Miller, 2007) though most studies have found the leaching rate to be fast initially then to become slow with an increase in time. The rate of dissolution decreases with the age of the liquor (Groenewald, 1977) hence the solutions were prepared just before use.

Side reactions also occur which result in the decomposition of thiourea to various compounds which include formamidine disulphide and sulphur some catalysed by the presence of Fe in the solution. The compounds formed by the side reaction will either leach the waste or result in passivation occurring. The secondary products of the redox-reaction produced from the reaction of the thiourea also appeared to cause passivation on the surface of the gold. The rate of the passivation appeared to be rapid, and its appearance to has been observed as a grey-black film on the surfaces of gold exposed to the action of these solutions (Groenewald, 1977).

4.2.1 e-Waste Crushed Sample

The lixiviants used in this process was the 10wt% ionic liquid $BmimHSO_4$ and sulphuric acid. The experimental work was carried out in the presence of 0.5g thiourea the complexing agent and 0.03g Fe^{3+} the oxidant at $25^{O}C$ which were all determined from literature. The oxidant could not be used in excess as it would then compete with the other metals in the solution and catalyse side reactions, hence it had to be kept low for activating the reaction. The +45-180µm size fraction was used in the leaching experiment. The time used in the reaction to try and get the best results from the reaction was 48hrs with a stirring speed of 150 rpm, the leaching results obtained are shown in the Figure 4.13a-4.13f. As already stated only a few core metals were analysed using ICP-OES. The leaching of silver and the base metals was achieved at a very low percentage, gold and palladium were however below the detection limit. The samples taken at intervals showed a decrease in the metal concentration in solution as can be seen in the graph, the longer time the experiment ran. Leaving the leached solution also resulted in precipitation occurring over time, the presence of the plastic fibres could also have resulted in the adsorption of the dissolved matter with time. Previous research has shown that the decomposition of thiourea occurs as shown in the equations in the previous chapter over time. Hence leaving the leaching experiment to occur for the long period of time approximately 48hrs in this case did not have much benefit. Levels of gold and palladium leached were below the detection limit of 0.1 ppm.

The use of the e-waste sample of size +45-180µm which has just undergone crushing and pulverisation gave a higher recovery in the ionic liquid BmimHSO4 for silver compared to the inorganic acid sulphuric acid. The highest point of recoveries for silver was at 7 hours in the ionic liquid with a percentage of approximately 10 compared to the highest percentage recovery experienced in the sulphuric acid at 40 hours which was at approximately 5%. For copper the highest percentage recovery was achieved at 24hours in the ionic liquid at a percentage of approximately equal to 1 whilst the highest recovery in the sulphuric acid was at 8hours with a percentage of 1. A decrease in the leaching capacity of all the metals was experienced for both liquids the longer they were left in solution. Lead leaching was the only one which gave a higher recovery in sulphuric acid compared to the recoveries obtained in the ionic liquid however both solutions eventually started showing a steady decrease in the metal concentration after the 8 hour mark. The other base metals recoveries were almost equal with aluminium giving the highest recoveries of all the metals after getting as high as 50%. The use of this sample waste did not result in any gold or palladium leaching. The lack of any gold and palladium leaching as well as the poor recoveries obtained for all the metals meant some changes needed to be made in the experimental work.



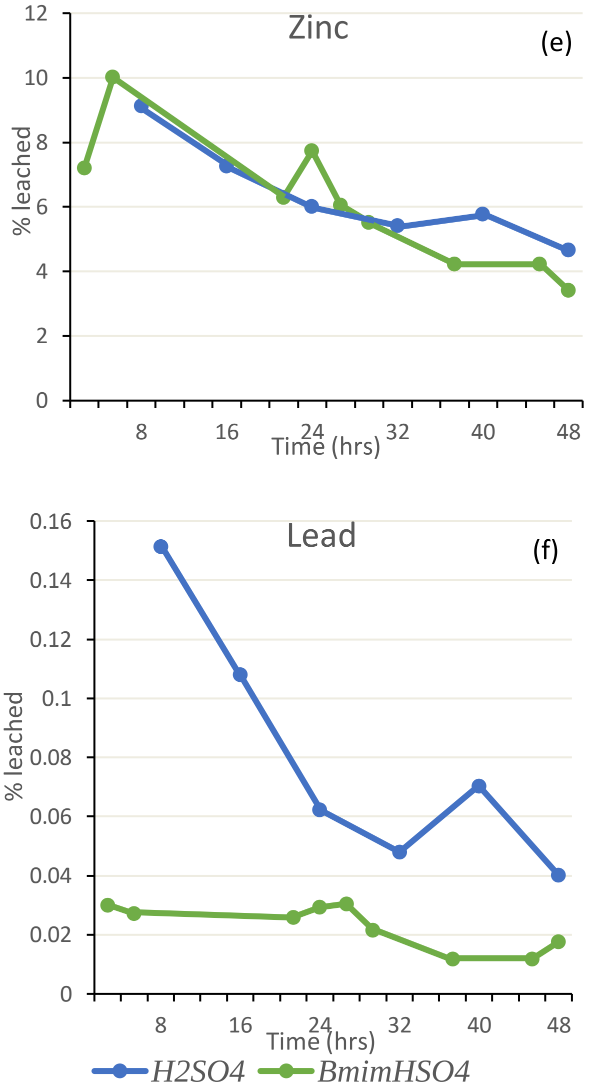


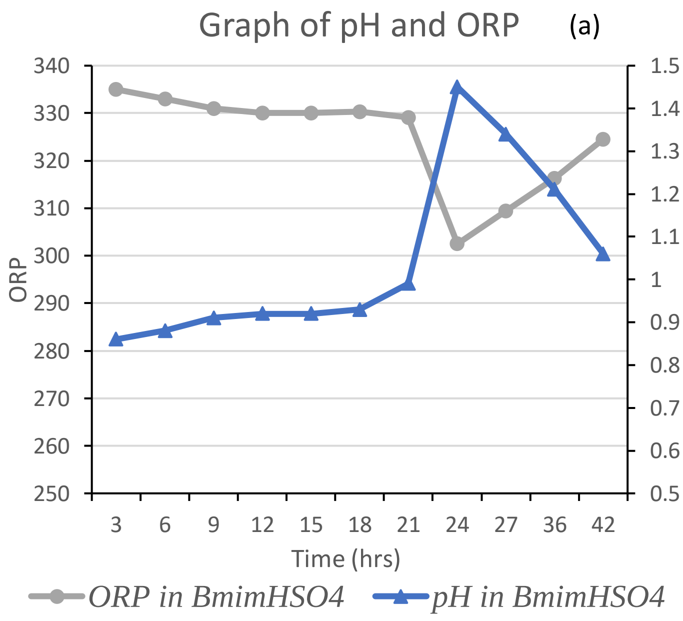
Figure 4.13a-f the leaching of the waste in 10wt% $BmimHSO_4$ and H_2SO_4 with 0.5g thiourea, 0.03g Fe^{3+} and $25^{O}C$ for 48 hours, a)silver, b) copper, c) iron, d) aluminium, e)zinc and f) lead recovered.

4.2.1.1 Effect of pH and ORP on Rate of Leaching

The redox potential and pH were affected by a number of things, which include the concentration of the lixiviant, the concentration of thiourea used and the concentration and type of oxidant used. Moderating these features was important to ensure that the process remains cost effective (Tanriverdi, Mordoğan, & Ipekoğlu, 2005). The general trend in the leaching of the e-waste showed an increase in pH and a decrease in ORP with time. Adjusting the pH by adding a solution of the ionic liquid and the inorganic acid at a rate of 10 mm/hr did assist in maintaining the pH and ORP relatively constant. Fluctuations were experienced however as a result of a lapse in the solution feed rate. The change in pH and ORP is shown Figure 4.14

taken as the experiment was being conducted and from the results it can be seen that the pH ranged from 0.86 to 1.45 whilst the ORP ranged from approximately 302 mV to the highest point at 335mV in the ionic liquid. For the sulphuric acid the pH ranged from 0.8 to 2.26 whilst the ORP ranged from 261 to 336mV. There was a correlation in the change in pH with the metal recovery experienced the high pH of 1.45 resulted in the decrease in the concentration of the valuable metal silver being leached which agrees with the data found in previous research that suggests that a lower pH is required for a higher recovery of the metals once the pH was adjusted down to 1.34 there was an increase in the concentration of the metal (Tanriverdi et al., 2005). However further adjustment only resulted in further decrease in the metal concentrations in solution.

The change in pH and ORP was also consistent in both the ionic liquid $BmimHSO_4$ and in the sulphuric acid. Decreasing when the one increased and increasing as the other is decreased. As a result of the drastic changes in values a buffer in the form of the solution was added at intervals to maintain the pH and ORP values of the solution.



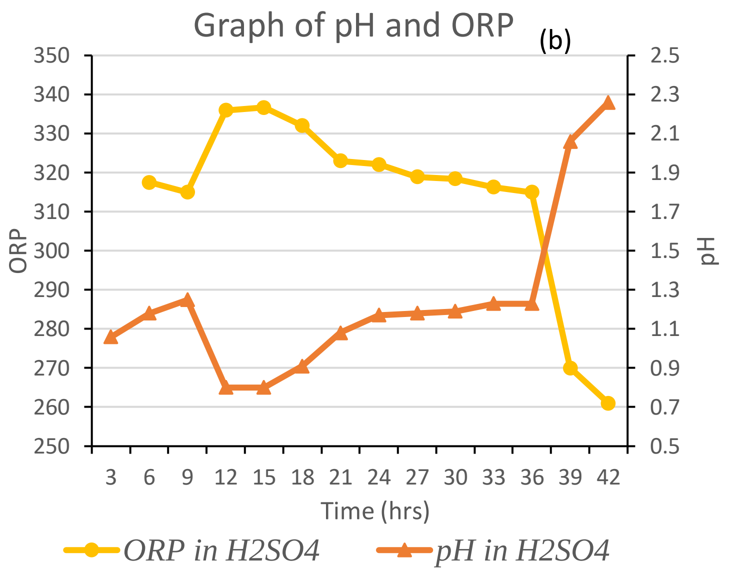


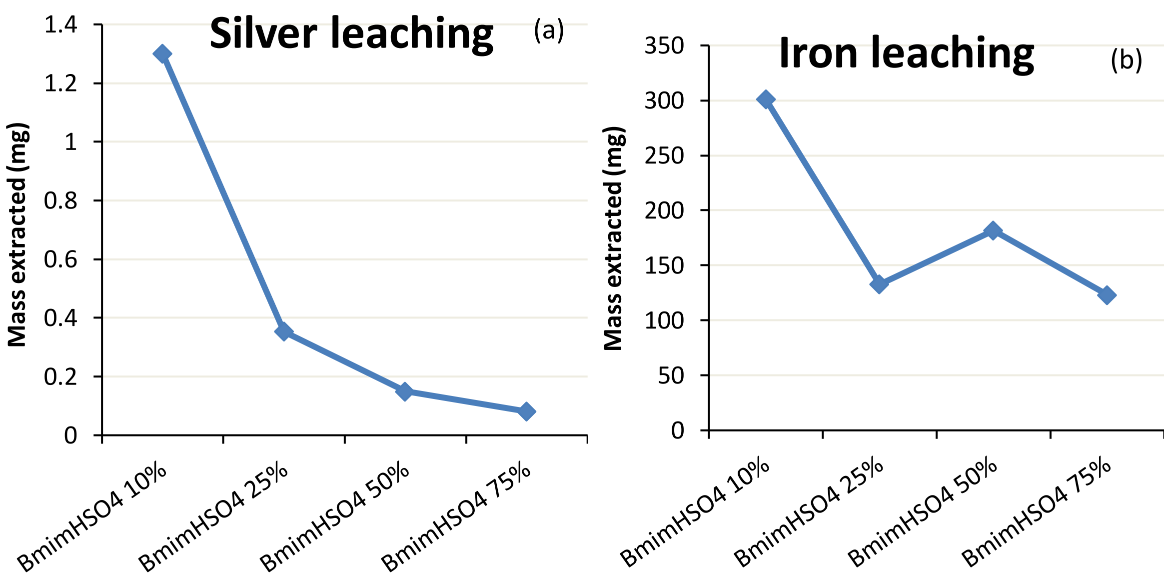
Figure 4.14a-b the graphs of pH and ORP for a) the reactions in 10wt% BmimHSO$_4$ and b) the reaction in H$_2$SO$_4$

The time used in this set of experiment was reduced to below 8 hrs from 48 hrs because of the results obtained in the initial experiment, the use of a longer time frame had failed to give results that are favourable. Different waste sizes were also used in the work to try and improve the recovery. The number of lixiviants and concentrations of lixiviants used was also varied and increased to try and get more accurate results. The waste also had to undergo some type of pre-treatment to increase the possibility of leaching gold and palladium from the process. The temperature used in the experimental was also varied with an increase in the temperature from 25^{O}C to 60^{O}C to provide the activation energy of the system.

4.2.2 Effect of Ionic Liquid Percentage on Leaching

After the first phase of experiments was completed with poor recovery a second set of experiments was conducted to improve the recovery of the waste. This set of experiments was carried out to determine the suitable concentration of ionic liquid for use as a lixiviant in the presence of thiourea and Fe^{3+} oxidant at 25^{O}C using the sample which had undergone crushing and pulverisarion with the size fraction of +45-180µm. The ionic liquid BmimHSO$_4$ was used as the solvent because at this stage fo the work because it had been able to leach silver in the preliminary work and because it had also been successfully used as a solvent in the research by Whitehead et al. (2006). Different concentrations of the ionic liquid was then used to leach the waste for a period of 7 hours and a sample was taken at the end of the process. The different ionic liquid concentrations used in the work were 10wt%, 25wt%, 50wt% and 75wt%

concentration of $BmimHSO_4$ and the results are shown in Figure 4.11a to 4.11c. It was observed that the higher the concentration of the e-waste the higher the viscosity of the ionic liquid solution. The results obtained from these experiments showed that the concentration of silver leached reduced, the higher the concentration of ionic liquid used with the 75wt% concentration giving the lowest recovery of silver. Iron gave its highest recovery in the 10wt% of the ionic liquid solution and it also reduced the higher the viscosity of the solution with the lowest results being at the 75wt% of $BmimHSO_4$. Copper recovery gave a different trend and the highest recovery was in the 75wt% liquid however the 10wt% concentration gave a good recovery as well with a reduction of about 50% from the higher concentration. From these results it was determined that a higher concentration of ionic liquid greater than 10wt% did not have any more of a positive effect on the metal recovery from the waste hence the leaching experiments would be carried out using the low ionic liquid concentration of 10wt%.



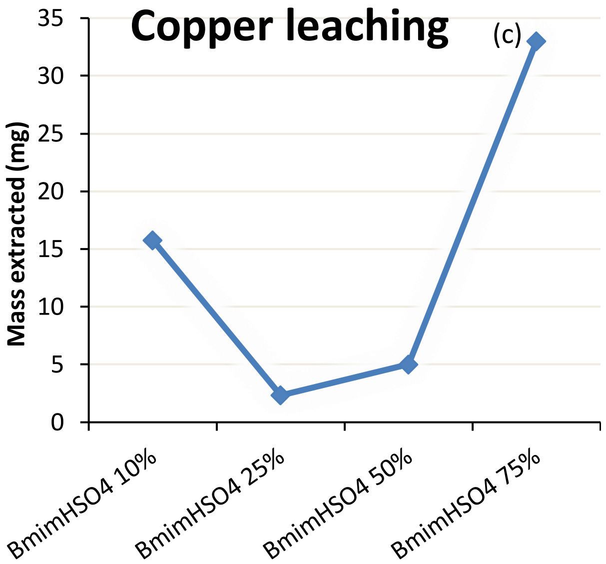


Figure 4.15a silver, 15b iron and 15c copper leaching at different concentrations of ionic liquid with 0.5g thiourea, 0.03g $Fe3^+$ and 25^OC for 7 hours

4.2.3 Effect of e-Waste Size

Since the experimental work was still giving a poor recovery of the value metals a different waste sample size was used in this part of the experiment. The sample size has the advantage of the reduced degree of pre-processing done which would reduce the recycling steps and hence the cost of the process. Additional solvents were also used to improve the recovery of the metals with the different sample size. The aim of this part of the experiment was to determine a suitable lixiviant which could be used to leach the value metals from the printed circuit board slab which was the 30mmX50mm. The thiourea concentration and oxidant Fe^{3+} were kept constant.

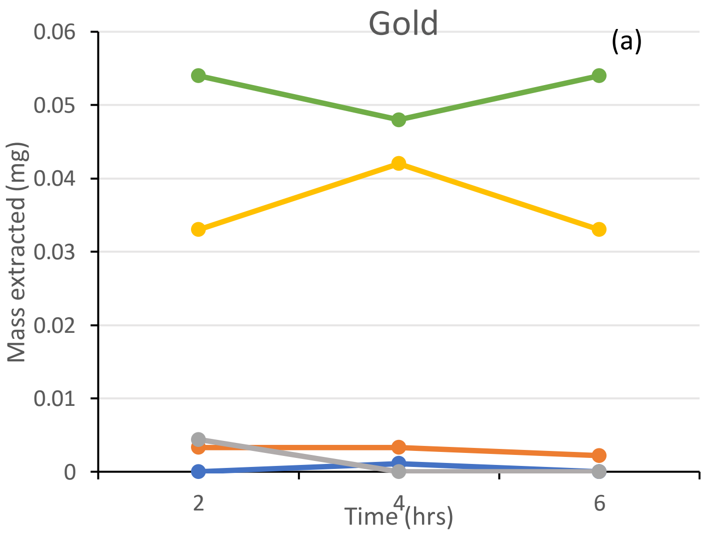
The lixiviants used in this experiment were H_2SO_4, H_2O, $BmimHSO_4$, EmimCl and BmimCl. The lixiviants used have different chemical properties and physical properties. Using three different ionic liquids allowed for the comparisons to be made between the anion and cationic carbon head. It also allowed for determining if the poor recovery was a result of the ionic liquid of choice or not and what effect the carbon length had on the process. The traditional sulphuric acid was also used which gave a standard measure. The figures show the leaching ability of the value metals and the base metals in the five lixiviants. The recoveries of the value metals gold, silver and palladium using a solid to liquid ratio of 1/10 at 60^OC in a 10wt% lixiviant solution are shown, with 0.5g thiourea and 0.03g Fe^{3+} for 6 hours. The graphs show the leaching of gold in the ionic liquids with the butyl cation head giving the highest extraction when compared to the ionic liquid with the ethyl cation head or the inorganic acid H_2SO_4 in the presence of thiourea as complexing agent and Fe^{3+} as oxidant. These results agree with those obtained by Whitehead et. al (2007) during the leaching of a sulphidic gold ore in $BmimHSO_4$.

4.2.3.1 Value Metal Leaching

Comparison of the different anions used show that the ionic liquid heads affected the recovery of the metals, the acidic HSO_4^- anion head had a higher recovery when compared to the Cl^- anions this agrees with the results obtained by Whitehead et al. (2007) with the gold ore. The anion head acts as the proton donor catalysing the reaction hence the acidic HSO_4^- is better suited for this process than the chloride anion. The leaching of silver had opposite results to that of gold with a higher recovery in BmimCl ionic liquid as shown in the Figure 4.16b which compares the silver leaching recovery between the different solvents, these results agree with those also found by Whitehead et al. (2007). The effect of the organic ionic liquid cation heads was also investigated in the research, giving different results with the longer carbon chain butyl imidazolium/Bmim chain giving better results than the shorter carbon chain ethyl imidazolium/Emim chain. These results could have been a result of the change in viscosity from one cation head to the next, an increase in the viscosity resulted in the decrease in the leaching ability.

The time used was greatly reduced as a result of the decrease in metal concentration with the increase time length obtained in the earlier experiments. The longer leaching time for the waste led to a great reduction in the leaching rate of silver after four hours which could have been because of the reasons already stated which include the decomposition of thiourea, the reduction of the oxidant to Fe^{2+} and the increased competition of the metals in the solution with the other base metals. Figure 4.16c shows that palladium did not leach in two of the ionic liquids used. There was however generally very poor results in all the lixiviants. Water, sulphuric acid and EmimCl gave low percentage recovery because of the conditions which are not favourable for palladium leaching. Trying to leach more than one value metal under the same conditions is the cheaper option but however is kinetically not feasible or very difficult. Palladium leached in the ionic liquid with the chloride anion and might have formed the complex $PdCl^{4-}$ however other complexes could have formed further tests would have to be conducted to determine if the palladium complexed with the thiourea.

There wasn’t much of an improvement in the leaching capabilities when the sample was changed from the crushed sample to the slab. However, the gold recovery increased from the non-detectable level in previous work to a recovery of just over 1% at 6 hours. However in general the use of a circuit board slab was not favourable for the leaching of the value metals even with the removal of the epoxy resin layer which was protecting the surface of the slabs with the highest silver recovery being at 0.4% in the ionic liquid BmimCl compared to the 1% obtained from the crushed sample in earlier experiments in $BmimHSO_4$. Palladium recovery also gave a very slight increase from being non-detectable in $BmimHSO_4$ and H_2SO_4 to giving a 1% recovery in EmimCl and an even higher recovery of 3% in H_2O at 6 hours. All the five lixiviants gave poor recovery for all the value metals. Some of the reasons which could have contributed to these recoveries include the lixiviants not being able to penetrate into the layers of the circuit board which is modelled by the shrinking core model and the reaction being controlled by diffusion through a solid product layer (Huang et al., 2014) which then requires the samples to be of a certain size. The poor recovery of the metals from the slab might have also been a result of the passivation which occurred on the surface of the waste which prevented the gold leaching into the solution this resulted from the large particle size which resulted in the lixiviants spending more time on the surface of the waste trying to penetrate into the surface as opposed to the them reacting. The passivation could have resulted from the side reactions of thiourea and the Fe^{3+} ion which occur. The size of the sample did seem to be detrimental for the ability to leach.



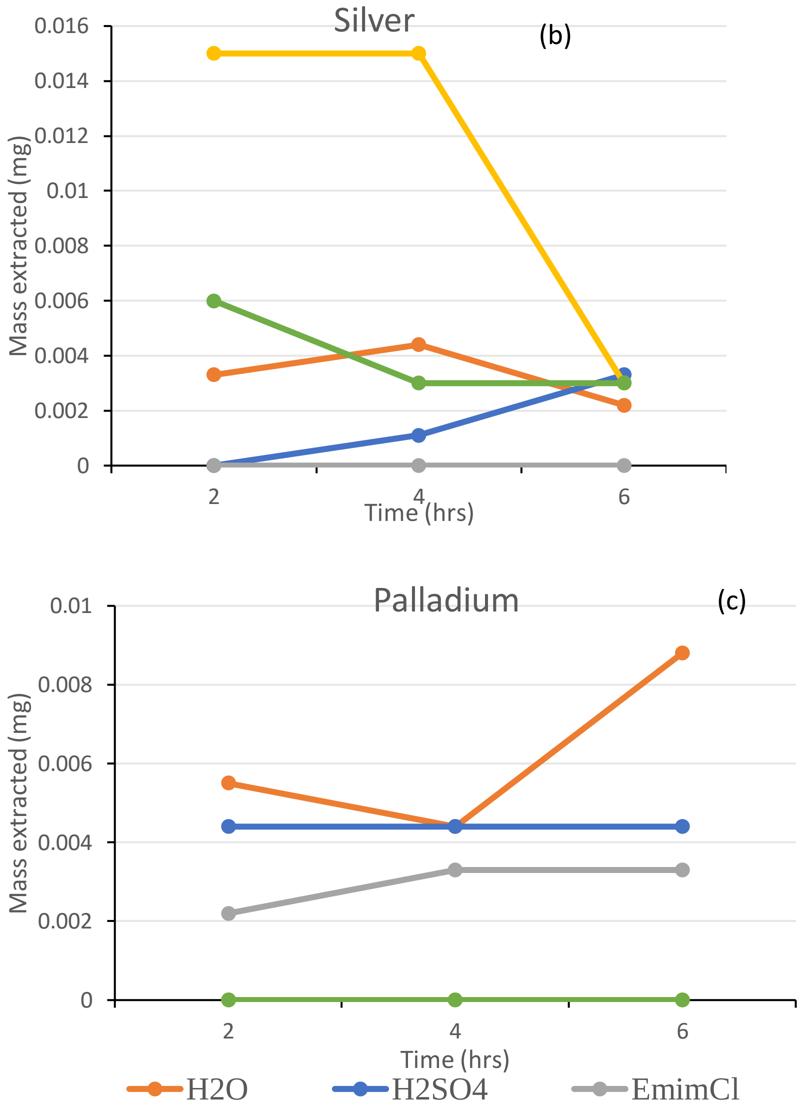


Figure 4.16a-c leaching of gold, silver and palladium respectively from a PCB slab in water, sulphuric acid, EmimCl, BmimCl and BmimHSO$_4$ for 6 hours at 60^{O}C

4.2.3.2 Base Metal Leaching

Figure 4.17 shows that the leaching of copper with the ionic liquid BmimCl had the highest extraction. The ionic liquid BmimHSO$_4$ gave a very low recovery which might be because of the selectivity of the ionic liquid which favours the recovery of the other metals. The use of the slab did not hinder the leaching of copper in the ionic liquid BmimCl. The other lixiviants H_2SO_4, EmimCl and H_2O all gave a steady increase in the leaching rate of the copper. The leaching of iron in the ionic liquids with the Bmim$^+$ cation head gave a better recovery than in all the other lixiviants including the inorganic acid

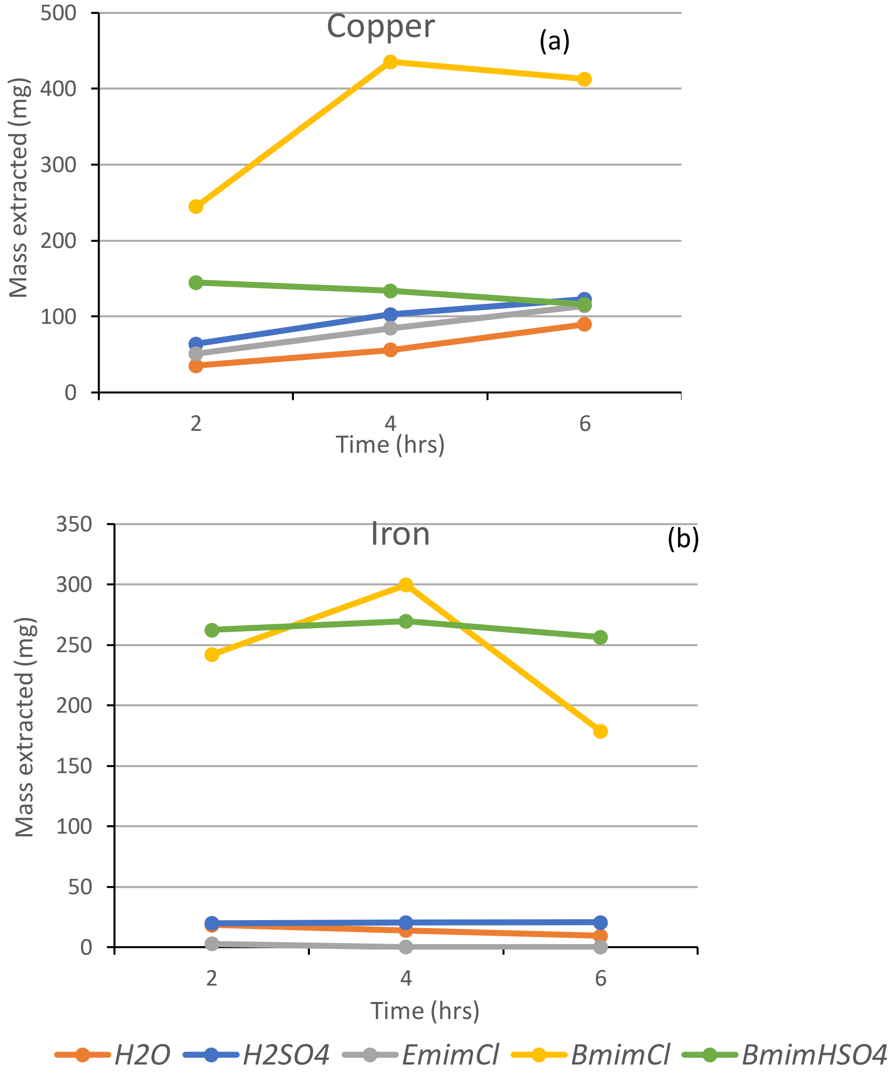


Figure 4.17 a-b leaching of copper and iron respectively from a PCB slab in water, sulphuric acid, EmimCl, BmimCl and BmimHSO$_4$ *for 6 hours*

The ionic liquid BmimCl gave the highest recovery of 46% of the copper metal at 2 hours which suggests that this ionic liquid under these conditions is selective for this metal. Whilst iron gave very high recoveries in both BmimCl and BmimHSO$_4$ of over 98%. This also suggests that the use of these ionic liquids under these conditions does produce a good leaching ability for these two base metals and just not for the other metals especially the metals of interest that is gold, silver and palladium. These results also suggest that the presence of the base metals does add to the interferences of the leaching of the value metals and hence a chemical pre-treatment might be necessary to reduce base metal concentration.

4.2.4 Leaching of the Pre-treated Waste

The following section of results shows the leaching of the chemically pre-treated sample. A chemical pre-treatment was also carried out on the pulverised sample. The sample was chemically pre-treated by leaching for 3 hours in 25wt% of nitic acid at room temperature. The leaching of the waste in nitric acid was very exothermic and produced a brown pungent gas. Figure 4.18 shows the percentage loss of value metal which occurred as a result of the nitric acid pre-treatment. There was a great reduction in the concentration of some of the base metals like lead, zinc, iron and copper which each had reductions greater than 89%, lead was as high as 98%. Gold, silver and palladium had losses of 9%, 18% and 19% respectively, the base metal reduction was much greater than the value metal reductions which was good news. The main reason for the loss of the base was because of the ease at which the base metals will leach into solution in an inorganic acid compared to the noble metals because of the high reactivity of the base metals. The environmental dangers which resulted from the process were however of some concern like the brown pungent gas which was formed in the experiments would have some environmental impacts and would need waste management process.

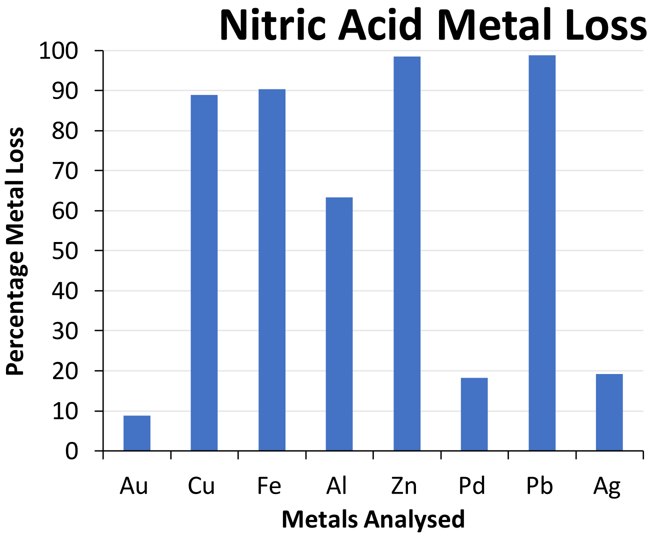
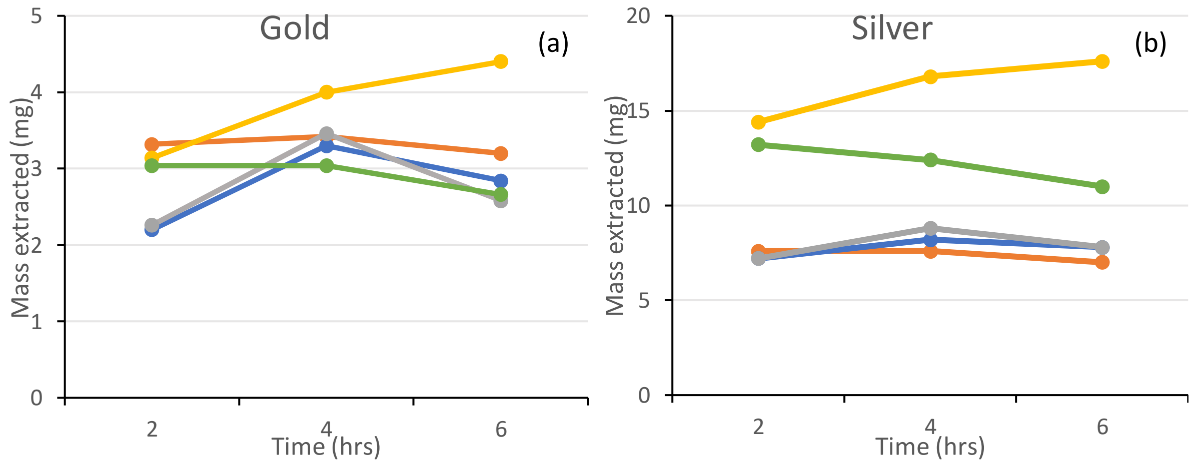


Figure 4.18 Percentage concentration of metals lost or reduced during pre-treatment in nitric acid for 3 hours

The sample that resulted was then leached in the five lixiviants which had been used on the other samples.

4.2.4.1 Value Metal Leaching

After pre-treatment in the nitric acid the waste was washed with distilled water to remove any residual acids, dried before being leached in the five lixiviants already mentioned. Figure 4.19 shows the results obtained from leaching this sample which has a size fraction of +45-180 µm. The graph shows that the pre-leaching of the base metals increased the ability of the lixiviants to leach the value metals. Water gave the highest recovery for both silver and gold. These results suggest that there was some residual acid in the waste from the pre-treatment in nitric acid. The increased recovery of the gold could also have resulted from the reduced consumption of the thiourea which occurred because of the removal of the base metal ions. The pre-washing also played a role in increasing the leaching ability as suggested by the research done by (Jinshan Li & Miller, 2006) by reducing the thiourea consumption. The leaching of palladium gave relatively poor results in all the lixiviants though the ionic liquid BmimCl gave results which were higher than in the other solutions. This could have been because of the ability of the ionic liquid to ionise in water producing the Cl^- ion which then complexes with the palladium to form different types of complexes which can include the $PdCl_3^-$ and $PdCl_4^-$ as shown in equations 6 and 7 above:



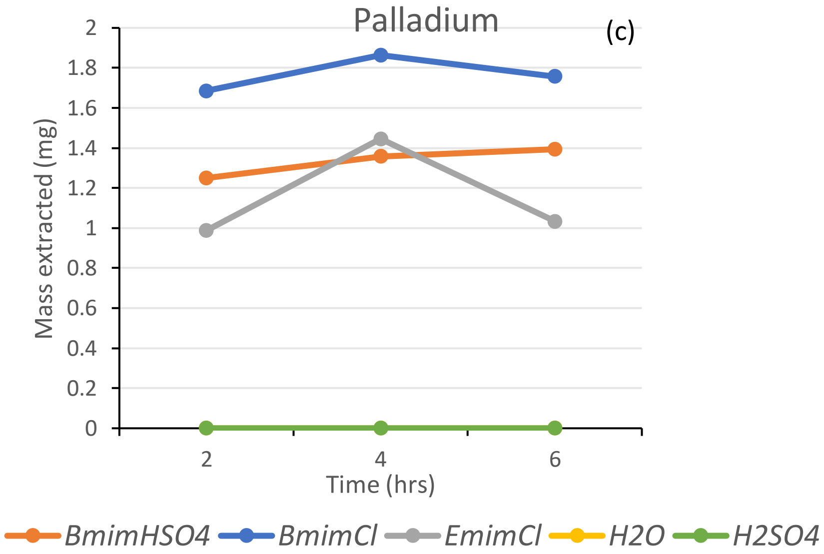
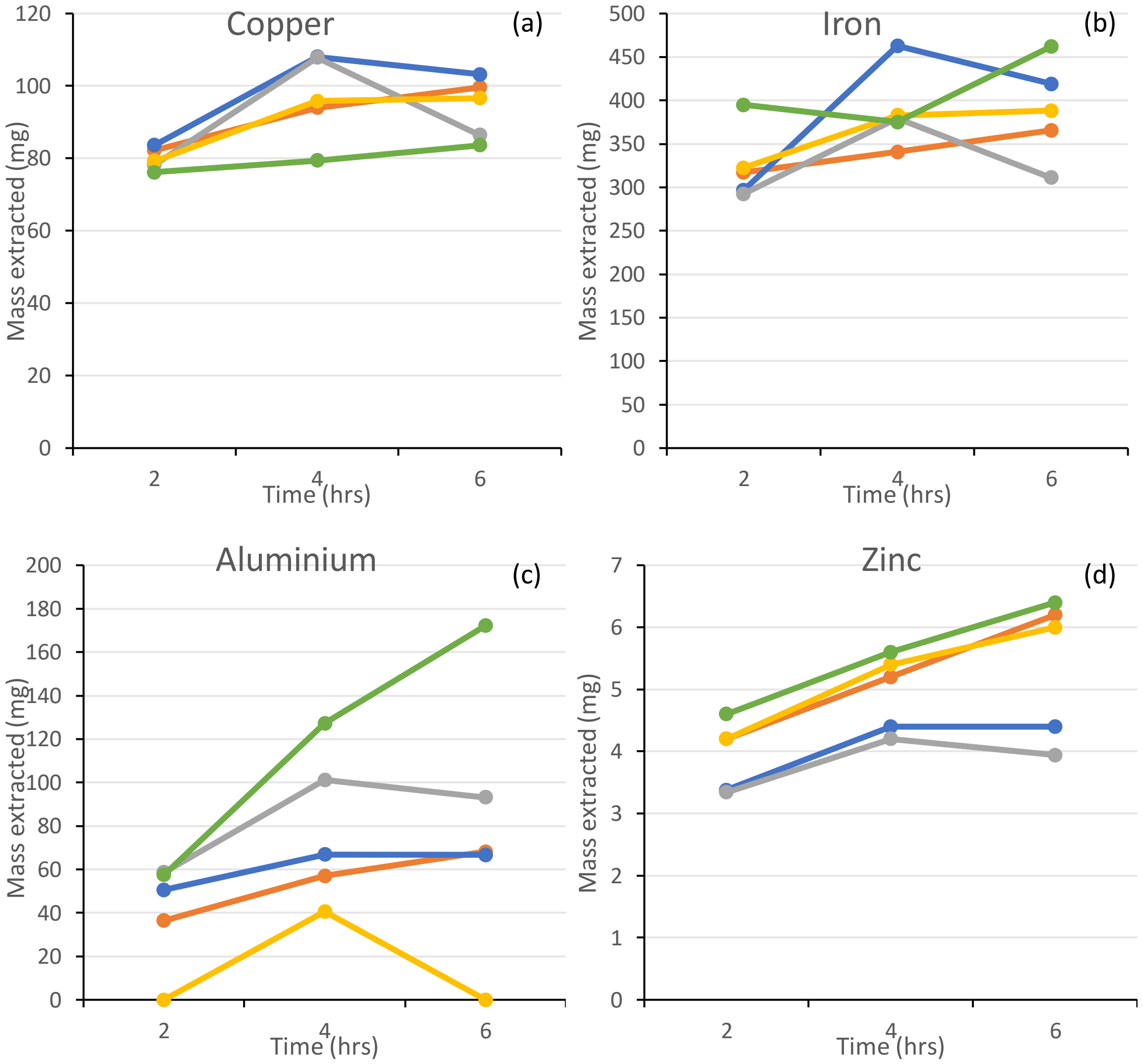


Figure 4.19 a-c leaching of gold, silver and palladium respectively from a PCB sample which had been treated in nitric acid in water, sulphuric acid, EmimCl, BmimCl and BmimHSO$_4$ *for 6 hours*

The pre-treatment of the waste improved the percentage recoveries greatly with gold leaching at over 65% in the ionic liquid BmimHSO$_4$ and even higher recoveries in the H_2O with the pre-treated sample there seems to be advantage of advantage of using either solvent with only a slight advantage found in the water and BmimHSO$_4$ at the end of the experiment. Silver recoveries also increased greatly though the highest recovery was in water similar to gold though the second solvent was then sulphuric acid. There was no advantage in using the ionic liquids for this part of the experiment either. Palladium leaching was below detection levels in the water and sulphuric acid but managed to give high recoveries in the three ionic liquids especially the BmimCl. The presence of the Cl^- seems to favour the leaching of the metal in from the waste. The recoveries of gold and silver from the waste needs to considered with respect to the metal loss experienced as a result of the metal pre-leaching. The base metal leaching are also given which again suggest there was no selectivity which occurred in this leaching work as the base metals also leached.

4.2.4.2 Base Metal Leaching

Base metals were also leached during the experiment and the results are shown in the graphs. Copper and iron gave almost similar trends for all the different lixiviants. Copper gave the highest recovery chloride based ionic liquids BmimCl and EmimCl compared to all the other lixiviants. This could have been affected by the presence of some residual acid from the pre-treatment of the waste. The pH of the process confirmed this hypothesis as shown in the graph:



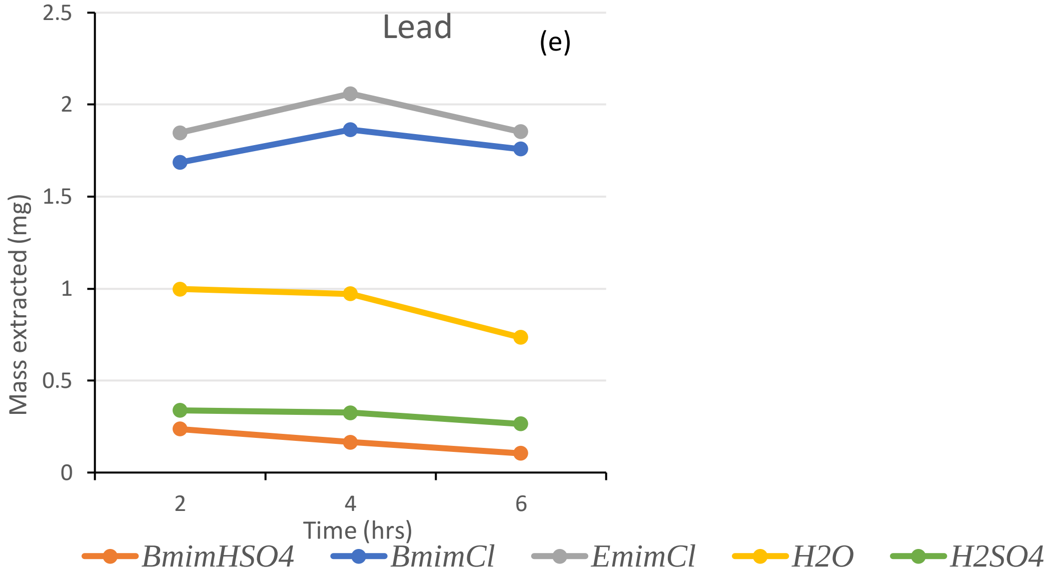


Figure 4.20 a-e leaching of copper, iron, aluminium, zinc and lead respectively from a PCB sample which had been treated in nitric acid in water, sulphuric acid, EmimCl, BmimCl and BmimHSO$_4$ for 6 hours

The metal leaching after the pre-treatment of the waste in nitric acid produced a higher recovery for all the metals in most of the lixiviants used as shown in the graphs. One of the main factors which could have aided in the increase in metal recovery is the presence of some residual acid after the washing of the waste. A look at the average pH of the reactions in the five lixiviants between the pre-treated sample and the untreated sample showed that there was a drastic decrease in the pH of all the solutions for the samples which had undergone pre-treatment in nitric acid shown on Figure 4.21.

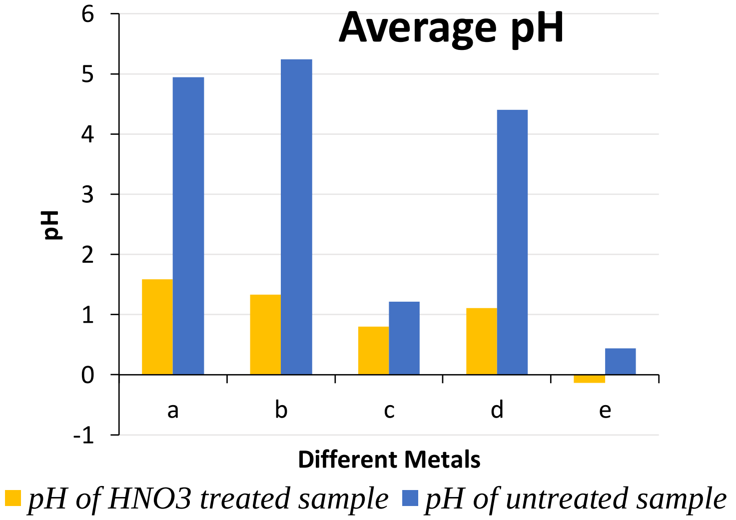


Figure 4.21 average change in pH for the metal leaching in a) EmimCl b) BmimCl c) BminHSO$_4$ d) H$_2$O e) H$_2$SO$_4$ in the presence of thiourea and Fe^{3+} after 6 hours of reaction

The figures 4.22a-d compare the different metal recoveries in the lixiviant 1-butyl-3 methyl hydrogen sulphate of the three different samples used in the experimental work which included the crushed waste treated in nitric acid, the untreated sample which had the size of +45-180 µm and the slab which was the 30X50mm size sample. From the results it can be seen that the treated sample gave high recoveries for all the value metals that is the gold, silver and palladium. Hence the pre-treatment of the waste gave the most favourable results. Copper gave a slightly different trend with the highest recovery being from the untreated crushed sample, this could have resulted from the high loss of copper which occurred as a result of the nitric acid treatment. The type of processing required for the metal recovery differed from metal to metal. The value metals gave good results with the crushed sample which had undergone pre-treatment whilst copper gave about a 20% decrease from the slab to the nitric acid treated sample. One of the factors which could have influenced the decrease in the ability to leach the metal was the way the leaching solution penetrated the surface of the waste. Hence though the slab gives favourable results in terms of the cost associated with the recovery of the metals it failed to give a good recovery.

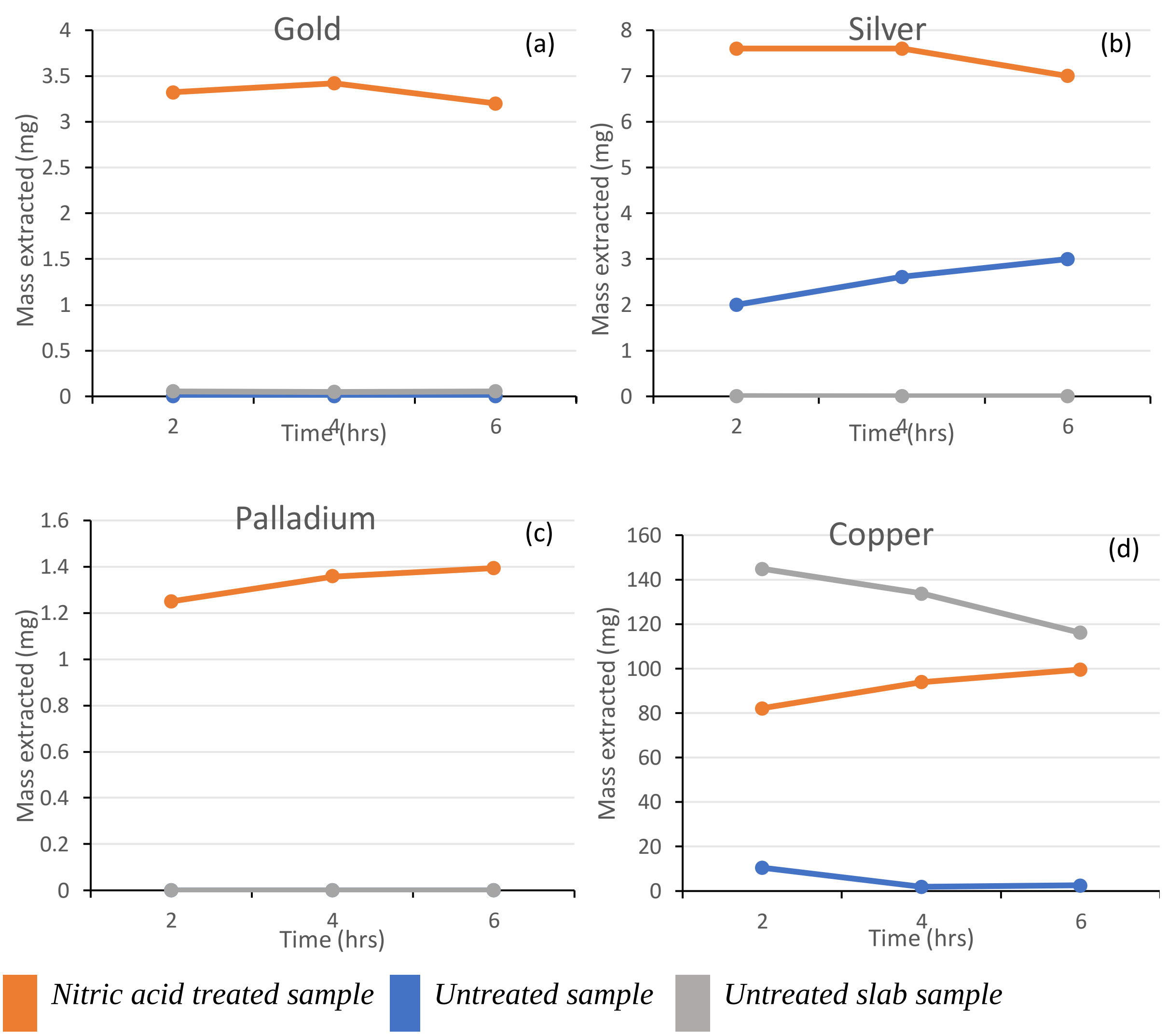


Figure 4.22 a-d the crushed waste size +45-180 µm treated in nitric acid, the untreated sample size +45-180 µm and the slab size 30X50mm size sample leached in $BmimHSO_4$, with 0.5g thiourea and 0.03g Fe^{3+} for 6 hours

5. CONCLUSIONS AND RECOMMENDATIONS

Conclusions are discussed according to the objectives given.

5.1 Effect of Mechanical Treatment

There is value in the manual dismantling of the e-waste into the separate components because it allows for the separation of the different components for targeted recycling, reuse or repair at different sites which reduces the workload from being in one place and improves efficiency of the overall process. The mechanical and physical treatment afforded to our target components which were the PCBs and the RAMs lead to different size fractions being produced, however the different size fractions did not produce a definite trends of metal distribution for all the metals. There was no evidence of significant metal loss in the samples which had undergone excessive size reduction through mechanical pre-treatment compared with the ones which had not although there was evidence of the effect of metal distribution depending on the size fraction with issues like metal malleability under question. Although the sample which was a slab had comparative high concentration of the gold with an average concentration of silver, palladium and copper at 0.5wt%, 0.02wt%, 0.3wt% and 79wt% respectively. The absence of any mechanical pre-treatment resulted in no value metal loss this could have been what resulted in the high value metal concentrations. This was favourable especially for gold which increased from 0.1wt% to 0.5wt% and copper which increased to the highest concentration of 69wt% to 79wt%, other metals like iron then decreased to a low of 20wt%, silver also decrease from 0.5wt% to 0.3wt% of all the metals. However, the metal distribution could have been affected by the homogeneousness of the untreated waste hence the results were not conclusive. However, mechanical pre-treatment can be conducted on an e-waste sample only with specific equipment without significant metal loss occurring. Processes like dry magnetic separation of the e-waste does result in metal loss because of numerous reasons which include the presence of fibres which result in the agglomeration of the different metals or the poor liberation of metals which occurs during the pre-treatment stage hence it needs to be practised with caution.

5.2 Leaching Experiments

The leaching of the crushed e-waste showed a lack of selectivity in all the solvents used. The high concentration of base metals with iron being as high as 73wt% of all the metal in some of the samples does hinder the leaching ability of the value metals in all the solvents including the ionic liquids, organic acids and even the distilled water. Factors like the oxidation potential and pH also have an effect on the value metal leaching either improving it or suppressing it. The higher concentration of the imidazolium based ionic liquid resulted in a reduction of the leaching ability of the metals mainly because of an increase in the viscosity. A temperature increase did improve the leaching ability of the system however further tests would be needed to determine the optimum temperature of the process. The use of a large particle size sample e-waste did not result in improved leaching capability in the solvents used, however it did result in the passivation occurring on the surface of the waste. This could be because of the presence of thiourea which reacts rapidly in a system modelled by the shrinking core model and whose reaction is controlled by diffusion through a solid product layer.

5.3 Leaching of the Pre-treated Waste

The pre-treatment of the waste in nitric acid resulted in a decrease of the base metals which then gave high value metal recoveries in the solvents used in the experimental work with results as high as 65wt% recoveries of gold compared to the previously gotten 1% recoveries in the untreated sample, in the ionic liquids. The chemical pre-treatment does produce a high concentration of both gas and liquid waste which would need to be disposed of accordingly. The earlier stipulated observation that the high base metal concentration was the main obstacle to the ability to leach the value metals was shown in this section. The selectivity of the ionic liquids in the leaching of the metals was however still not shown in these results as the other lixiviants like water and sulphuric acid did achieve greater recoveries 4.4ppm of gold in water compared to the 3.2ppm of gold in $BmimHSO_4$. The imidazolium based ionic liquids have the ability to leach noble metals from e-waste however they are not very selective to these metals over the base metals neither do the get higher recoveries when compared to lixiviants. They are hindered by the presence of a high base metal concentration just like what happens in the non-ionic liquids like H_2SO_4 and H_2O. Though the acid pre-treated sample did give higher recoveries it had a greater impact on the environment through the production of hazardous gases which were not present for the ionic liquid process.

5.4 Recommendations

Further work is required to test the other variables of the leaching process which include oxidant and complexing agent concentration, to see if these can help improve the leaching ability of the ionic liquids or improve the selectivity of the process. These factors could help improve the leaching ability of the process however the profitability would now be greatly under question. Other variables also need to be changed to optimise the process like a higher range of temperature differences, stirring speed and pressure. Concentrations of the oxidant and complexing agent would also need to be varied to determine how much is required for the highest recovery of the waste. The limited resources hindered the variations of these variables. The use of ionic liquids in the leaching of the e-waste still has a way to go before being viable mainly because of the high cost associated with the manufacture of the ionic liquids which make them not very marketable.

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