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APPLICATION OF IONIC LIQUIDS IN THE LEACHING AND EXTRACTION OF PRECIOUS METALS FROM ELECTRONIC WASTE

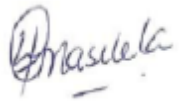
Mthobisi Delisa Masilela

A research report submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in partial fulfilment of the requirements for the degree of Master of Science in Environmental Sciences.

Johannesburg, 2018

DECLARATION

I declare that this research report is my own unaided 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.



……

(Signature of Candidate)

22nd day of June, 2018

(day) *(month)* *(year)*

DEDICATION

To my parents, family, mentors, colleagues and friends, who have always supported and encouraged me to pursue excellence in all my endeavours – I will always appreciate and thank you!

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I wish to express my heartfelt gratitude and appreciation to all individuals and institutions that made invaluable contributions and supported me in every way as I pursued this research. Special thanks unreservedly go to the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, under which I conducted this study, and in particular to Professor Sehliselo Ndlovu, who guided me on this research work. Similarly, I would like thank the members of the Hydrometallurgy Research Group for their support and encouragement through this research. I would also like to acknowledge the School of Animal, Plant, and Environmental Sciences at the University of the Witwatersrand for their assistance during this study. Lastly, I would like to acknowledge all my colleagues, friends and family who have supported me throughout this long journey but most of all, to God the Almighty, for allowing me the opportunity to undertake this project.

ABSTRACT

Electronic waste (e-waste) contains valuable materials such as metals, which may be recovered using different processes such as conventional pyrometallurgy or hydrometallurgy. Existing metal recovery methods have a number of limitations which include adverse environmental footprints, therefore necessitating the investigation into other methods or reagents. In this research, ionic liquids were investigated for both leaching of gold (Au) and silver (Ag) from e-waste material and their extraction from leach solutions. The ionic liquid [Bmim][HSO_4] together with thiourea as a lixiviant and $Fe_2(SO_4)_3$ as an oxidant was investigated for the leaching of Ag and Au from pulverized printed circuit board sample containing 162 g/t Au and 618 g/t Ag. On the other hand, [Bmim][Tf_2N], [Bmim][PF_6], and Cyphos 101 were investigated as extractants for Ag and Au from chloride and glycine-histidine leach liquors of the printed circuit board samples.

Ag and Au dissolution in the ionic liquid [Bmim][HSO_4] leaching system was observed. However, the leaching efficiencies recorded were low with Au efficiency at 24% in a leaching solution of 30% [Bmim][HSO_4] and the efficiency of Ag only at 3% in the same solution. The ionic liquids [Bmim][Tf_2N], [Bmim][PF_6], and Cyphos 101 were efficient for gold extraction from aqua regia leach liquor with more than 90% of Au extracted. Ag extraction was lower compared to Au, with no extraction recorded for [Bmim][Tf_2N] but over 90% extraction was recorded for both Cyphos 101 and [Bmim][PF_6]. The ionic liquids did not extract any of the two metals from the alkaline glycine-histidine leach liquors.

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LIST OF ABBREVIATION

Ag	Silver
Au	Gold
[Bmim][HSO_4]	1-Butyl-3-methylimidazolium hydrogen sulphate
[Bmim][PF_6]	1-Butyl-3-methylimidazolium hexafluorophosphate
[Bmim][Tf_2N]	1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
BP	Blood pressure
Cd	Cadmium
Cu	Copper
Cr	Chromium
Cyphos 101 IL	Trihexyl(tetradecyl)phosphonium chloride
EU	European Union
E-WASTE	Electronic Waste
Fe_2O_3	Iron III Oxide
$Fe_2(SO_4)_3$	Iron III Sulphate
g/t	grams per tonne
H_2O_3	Hydrogen Peroxide
HCl	Hydrochloric acid
HCN	Hydrogen Cyanide
Hg	Mercury
HNO_3	Nitric acid
ICT	Information, Communication and Technology
IL	Ionic Liquid
NaOH	Sodium hydroxide
Pb	Lead
PBB	Polybrominated biphenyls
PBDE	Polybrominated diphenyl ethers
ppm	parts per million
PCB:	Printed Circuit Board
RoHS	Restriction of hazardous substances
UN:	United Nations
UNU:	United Nations University
US EPA	United States Environmental protection Agency
WEEE	Waste electric and electronic equipment
µg/g	microgram per gram

Chapter 1

INTRODUCTION

1.1 Background

The rapid growth and advancements in the electric and electronics industry in recent years has led to the phenomenal benefits received by mankind (Veit & Bernardes, 2015). This industry has brought revolutionary changes to the way human societies have survived. Electric and electronic equipment has found its use in different spheres of human life which include key areas such as medicine, communication, commerce and trade, defence, and education among others (Mikre, 2011; UNCTAD, 2008; Ogu & Oyerinde, 2014). Consequently, electronics have penetrated different market bases in both developed and developing countries due to their exponentially increasing demand, along with reduced costs of devices (Lundgren, 2012). Computers, mobile phones, television sets and navigation devices are some of the common consumer electronics used, which have made communication and information sharing more efficient and less costly. Global trade has been immensely enhanced by global communication networks which have their backbone on the electronics industry (Dutta & Bilbao-Osorio, 2012). Furthermore, the industry is one of the significant players in many national economies as it provides employment to millions of people across the world.

While focus has been on the benefits brought by the electronics industry as discussed above, the environmental and health impacts of the electronic industry have been left neglected or unidentified (Kamberović *et al.*, 2009). Electronic devices are associated with a wide range of adverse environmental and health effects such as radiation and its consequences on health and the environment (Zamanian & Hardiman, 2005). Fatal

diseases such as cancer and brain tumours are becoming more prevalent and these are closely linked to radiation effects, some of which are attributed to electromagnetic radiation from some electronic devices and their transmitting antennas (Valentini *et al.*, 2007). Other major impacts of the industry include the high demand on scarce input material such as metal elements (Chatterjee & Kumar, 2009; Perkins *et al.*, 2014). This results in pressure on mineral resources, depletion of finite deposits and environmental impacts associated with mining and processing of minerals (Veit & Bernardes, 2015).

Electronic waste (e-waste) is described as any electronic device, gadget, equipment or component thereof, which has spent its functional lifespan (Namias, 2013). The generation and accumulation of hazardous e-waste, which results in environmental contamination and degradation (Chehade *et al.*, 2012) is one of the main adverse impacts associated with the electronic industry. While landfill disposal of e-waste leads to soil and water contamination by the toxic constituents of e-waste, incineration of e-waste on the other hand causes air contamination, with the use of high incineration temperatures activating more toxic chemicals than those in unburnt waste. Consequently, e-waste is also often categorized as hazardous because of the toxic chemical constituents of electronic equipment (Cui & Zhang, 2008; Zhou & Qiu, 2010). These include polymers, brominated flame retardants, biphenyls, ethers, and metals (Dimitrijevi et al., 2013; Kamberović et al., 2009; Veit & Bernardes, 2015). When disposed, these chemicals may be leached in water and transported in the environment causing contamination, which may lead to different eco-toxicological effects.

Printed circuit boards (PCBs) are components of electronic devices which serve as platforms on which electronic circuits are assembled. These components are made up of different materials with metals accounting for up to 40% weight of the PCB material on average (Chehade et al., 2012; Zhou & Qiu, 2010). Copper is the most abundant metal in PCBs with gold and silver present in smaller amounts along with other metals. Although the gold content is as low as 0.0016% and silver at 0.0189% of the total weight

of PCBs, gold alone accounts for more than 65% in value of metals found in PCBs (Dimitrijevi *et al.*, 2013). In the year 2014, approximately 9.3 Mt of ICT e-waste were discarded worldwide (Baldé *et al.*, 2014). Assuming the percentage composition of this waste was 0.0016% gold (Dimitrijevi *et al.*, 2013), it may be concluded that 0.0001488 Mt or 148.8 tonnes of gold was discarded as waste in landfills all over the world, translating to billions of dollars lost from the economy. This also implies that there will be more demand on gold for future production of electronic equipment to replace discarded gadgets and meet future market needs.

Recovery of metals from e-waste is one significant means of sustainably utilising mineral resources while averting metal contamination in the environment as well as the adverse effects associated with mining. This activity has a number of economic and environmental benefits which include reduced costs of production, less environmental impacts associated with mining, decreased energy and water requirements, among others (Montero, Guevara & Torre, 2012). Mining causes land degradation, atmospheric and aquatic contamination by different chemicals released during mining processes, as well as acid mine drainage and associated impacts. The reclamation of metals from waste reduces contamination of the environment by metals. The US EPA states that recovery of metals from e-waste is energy saving and less polluting compared to mining (Cui & Zhang, 2008). Dimitrijevi et al. (2013) further states that some electronic waste are richer in metal content compared to natural ores, thus, become more attractive as secondary sources of the metals.

In view of the adverse environmental impact of the electronics industry with regard to toxic metal contamination as well as pressure on mineral resources (Chehade *et al.*, 2012; Veit & Bernardes, 2015), different technologies have been developed to recover and recycle metals from e-waste (Jadhav & Hocheng, 2012; Huang, Guo & Xu, 2009; Cui & Zhang, 2008). These have been based on traditional metallurgical processes such as hydrometallurgy and pyrometallurgy (Tuncuk et al., 2012). While these methods have

been used successfully in the processing and recovery of metals from primary ores, they do have some limitations when applied in the processing of e-waste. This is mainly because of the varying chemical composition of e-waste.

Pyrometallurgy is a metallurgical process which utilises high temperatures to extract and purify metals. The process has been successfully used for reclaiming metals from e-waste (Shuey & Taylor, 2005). However, this process is associated with high costs of energy in furnace smelting, as well as negative environmental effects caused by emissions during incineration (Huang, Guo & Xu, 2009). Dioxins, furans and other toxic gases are emitted during the smelting of metals from PCBs, which contain other components such as plastics and other organic compounds. Hydrometallurgy, on the other hand, involves the use of chemical solutions to extract metals from different metal bearing sources. The use of hazardous chemicals such as cyanide, mineral acids and volatile organic compounds are the general shortcomings associated with hydrometallurgical processes (Kamberović, Korac & Ranitović, 2011; Lundgren, 2012). Such limitations together with other considerations which include healthy and safety, the environment, economics and efficiency spur the need for investigation into new methods, process routes as well as reagents which could overcome such shortcomings.

Ionic liquids (ILs) are a class of novel chemicals which have found their way into different applications in chemistry and industry (Plechkova & Seddon, 2008). These liquids are a class of salts which are liquid under room temperature (Mai, Ahn & Koo, 2014) and present a promising breakthrough in extraction sciences. Some of the investigations into the potential applications of ionic liquids in science and industry are found in extractive metallurgy (Park *et al.*, 2014). Research shows that this class of solvents can be used successfully in place of volatile organic compounds used as extractants in hydrometallurgy (Visser *et al.*, 2001). As a result, ILs have been investigated as extractants in solvent extraction of metals from aqueous solutions with appreciable

successes (Plechkova & Seddon, 2008). ILs have the following characteristics; adaptability, selectivity, negligible vapour pressure, non-flammability, wide electro-chemical window, environmental compatibility as well as chemical and thermal stability (Fischer et al. 2011; Hernández-fernández et al. 2010). These characteristics enhance the ability of ILs in their application as extractants for different substances such as hydrophobic, hydrophilic and polymeric compounds, making them more favourable as extractants compared to organic solvents. ILs have also been investigated to a lesser extent for their application in hydrometallurgy as leaching agents in different systems. ILs such as [Bmim][HSO_4] and [Bmim][Cl], have been studied as leaching agents in thiourea systems for the leaching of precious metals (Whitehead, Lawrence & McCluskey, 2004). The IL [Bmim][HSO_4] showed enhanced leaching efficiency for silver compared to the thiourea-sulphuric acid system. Other metals which were leached included base metals such as iron and copper.

This research investigates the application of ionic liquids in the leaching and extraction of precious metals (Ag and Au) from printed circuit boards of electronic waste. While there is only about 80-1000 g/t of gold in PCB waste and 110-3000 g/t of silver, these metals were selected on the basis of their intrinsic value, which accounts for over 65% of the total value of metals in PCBs (Park & Fray, 2009; Montero, Guevara & Torre, 2012). PCBs were selected as the source of metals to be recovered as they are characteristically composed of about 40% of different kinds of metallic material (Chehade et al., 2012; Zhou & Qiu, 2010).

1.2 Problem Statement and Rationale

Electronic waste is becoming a major global concern for many countries (Namias 2013). The fast changing lifestyles, models and trends in consumer electronics reduce the lifespan of devices and increases the demand for newer models (Lundgren, 2012). The high demand and short lifetime of electronic devices exerts pressure on scarce resources such as rare and precious elements used as raw material in the manufacture of PCBs of electronic devices. It also leads to environmental contamination as a large volume of this e-waste is continually being produced and discarded. Reclamation of metals from e-waste remains a fundamental measure for the prevention of environmental contamination and for advancement in the sustainable use of metal resources.

While metal recovery technologies such as hydrometallurgy and pyrometallurgy exist and are well established in metal extraction and recovery, they have considerable limitations and environmental impacts associated with their application in the traditional sense (Lundgren, 2012; Huang, Guo & Xu, 2009). Pyrometallurgy is associated with high costs of energy as well as environmental impacts due to gaseous emissions. The use of toxic reagents, concentrated mineral acids as well as volatile organic compounds has presented its own shortcomings for hydrometallurgy. Consequently, new process routes, techniques and reagents remain at the centre of research for continual improvement of leaching, extraction and recovery methods. There is also a further drive to focus on techniques and materials which favour higher process efficiency, minimal costs and environmental friendliness. Ionic liquids fall under a class of ‘green solvents’ with favourable solvent properties (Plechkova & Seddon, 2008) which make them worth investigating for the recovery of precious metals from e-waste.

1.3 Research Objectives

The main objective of the study is to investigate the feasibility of the application of ionic liquids in leaching and extraction of precious metals from printed circuit boards.

The specific objectives are to:

- Leach precious metals from printed circuit boards (PCBs) in aqua regia, organic acid and ionic liquid systems.
- Perform solvent extraction of Ag and Au from aqua regia and organic acids aqueous solutions using [Bmim][Tf_2N], [Bmim][PF_6], and Cyphos 101 ionic liquids.
- Determine the leaching efficiency of the ionic liquid [Bmim][HSO_4] in an acidic thiourea leaching system.
- Determine the extraction efficiency of [Bmim][Tf_2N], [Bmim][PF_6], and Cyphos 101 on Ag and Au from chloride and alkaline glycine-histidine leach solutions.
- Draw conclusion on the use of ionic liquids in the leaching and extraction of precious metals from electronic waste.

Research Questions

The research questions which the study seeks to address are:

- Can ionic liquid [Bmim][HSO_4] be used in place of concentrated H_2SO_4 in the acidic thiourea gold leaching system for e-waste?
- Can the hydrophobic ionic liquids [Bmim][Tf_2N], [Bmim][PF_6], and Cyphos 101 be used as extractants for Ag and Au in chloride and alkaline glycine-histidine leach liquors of e-waste?

1.4 Scope, Methods and Limitations

The study focused on the use of ionic liquids in liquid-liquid extraction of precious metals from chloride and alkaline glycine-histidine leach solution of PCBs. The study employed two different leaching routes for extraction studies as discussed under the methods section. The study also investigated the use of ionic liquid [Bmim][HSO_4] in a leaching system to determine if ionic liquids can be used for direct leaching of precious metals from e-waste.

The scope of the research thus covered preparation of leach solutions from a PCB powder sample, to the extraction of Ag and Au using ionic liquids. This also involved performing analytical tests for leach liquors to determine leaching and extraction efficiencies. Deposition of metals from the ionic liquids was outside the scope of the project. As aqua-regia dissolves all metals present in sample, the ionic liquids proposed for use were identified based on their selectivity for precious metal extraction from leach liquors.

The limitations of the study included the high costs of analysis which resulted in fewer replicates being analysed, and thus led to only the metals under study being analysed. It would have been beneficial to perform a full analysis on leach solutions to verify selectivity of precious metals as well as other side reactions which may have occurred.

1.5 Layout of research report

This section summarizes the organization of the chapters and sections in this research report.

Chapter 1 - *Introduction*: This section presents the background of the research, the problem statement and rationale for undertaking this study. It further presents the aims, objectives and research questions which the study sought to answer.

Chapter 2 - *Literature Review*: This chapter discusses an organized account of literature which is related to the study. This includes literature on precious metals, their extraction processes, electronics and electronic waste, e-waste recycling, and ionic liquids along with their application in hydrometallurgy.

Chapter 3 - *Experimental:* This chapter describes the materials and methods used in the study as well as the rationale behind their selection.

Chapter 4 - *Results and Discussion:* This chapter presents the results from experiments conducted in the study. It further discusses the observed results with the aim of providing answers to the research questions.

Chapter 5 - *Conclusion and Recommendations*: This chapter summarises the main findings of the study, points out limitations and ultimately makes recommendations which emanate from the study.

Chapter 2

LITERATURE REVIEW

2.1 Introduction

The generation and accumulation of e-waste remains a major problem facing the electronics industry. This section presents a review of literature on the generation and accumulation of e-waste, the environmental and health effects associated with e-waste as well as e-waste recycling. Special focus is on the recycling of precious metals; gold and silver from e-waste as these are the metals under investigation in this research. The review further explores current processes and routes used for recovery of precious metals from e-waste. Recent developments in research and application of ionic liquids in chemistry and industry are also discussed, as well as their application in the extraction and recovery of metals from different sources.

2.2 Precious Metals: Gold and Silver

Gold and silver have been known for more than six thousand years and are without doubt, the first metals known and used by man (Butterman & Hilliard, 2004). With the chemical symbol Au, gold is a soft dense and bright reddish-yellow ductile metal found in gold-bearing ores in the earth's crust (Royal Society of Chemistry, 2016a). Silver, with the chemical symbol Ag, is a ductile metal with a bright grey colour found in silver-bearing ores in the earth's crust (Royal Society of Chemistry, 2016b). Both metals are rare and are found naturally occurring in different ores within the earth's crust. They fall under a category of metals known as precious metals along with platinum, palladium, iridium, ruthenium and rhodium because of their rarity and high economic value (Elements Database, 2015). Most precious metals are chemically unreactive and resistant to oxidation and corrosion, which is why they are sometimes referred to as

noble metals. These properties make noble metals attractive to several industrial applications that require materials resistant to oxidation and corrosion.

2.2.1 Occurrence

Gold naturally occurs in native form in the earth's crust often alloyed with either silver or mercury. The gold-silver alloy is commonly known as an electrum (Figure 2.1), while the gold-mercury alloy is known as an amalgam (Guisbiers *et al.*, 2016). Gold may also rarely occur naturally with other elements such as tellurium (calaverite: $AuTe_2$), silver and tellurium (sylvanite/krennerite: $AuAgTe_2$), lead-antimony-sulphur and tellurium (Nagayagite: $(Pb_5Au(Te,Sb)_4S_{5-8})$, and with silver and sulphur (Petzite: Ag_3AuS_2) (Renner *et al.*, 2000). Besides these, the metal may also be found in native form as nuggets or flakes in alluvial deposits. Gold may also be alloyed with arsenic, bismuth and other PGMs (Hough, Butt & Jörg, 2009) in naturally occurring ores. Electrum is the most common type of gold and contains more than 20% of silver.



Figure 2.1: An electrum nugget

Source: Lavinsky (2011)

Silver also occurs naturally in native form in the earth's crust. As a mineral, silver may be found as nuggets or in combination with other elements such as sulphur, antimony, arsenic and chlorine. Silver may also exist as mineral compounds of sulphide and chloride nature. It may also be found as an alloy with other metals such as gold (electrum ore) or lead (Butterman & Hilliard, 2004). To get these metals from their

different sources and use them in their pure form, different mining and mineral processing activities are fundamental. Some of these processes are discussed in the sections below.

2.2.2 Mining and processing

Placer mining, panning, sluicing, dredging and cradle are some of the ancient and conventional methods of gold mining (Silva, 1986). However, most of the world's gold comes from hard rock gold mining. This type of gold mining involves the extraction of gold-bearing rocks (ores) from within the earth's crust. Underground deep shaft and sometimes open-cast mining are used to extract these rocks from the crust to the surface, where they are then processed to extract gold from the different ores (Wai, Leong & Mujumdar, 2009). While gravity separation is used in small-scale gold processing, large scale processing of hard rock gold involves more complex chemical processes such as cyanidation, amalgamation, halide leaching and thiourea leaching, among others (Wai, Leong & Mujumdar, 2009). These processes are discussed in detail in subsequent sections.

The common methods for extracting silver from its ores are smelting and chemical leaching. In silver smelters, the ore is heated in a furnace with a reducing agent which drives a decomposition reaction. With chemical leaching, chemical reagents are used to leach silver into a solution from which pure silver is recovered (Butterman & Hilliard, 2004). The mining and processing of PMs from their natural ores is known to be energy consuming and results in land degradation, the production of massive volumes of waste and the chemical contamination of the environment (Mensah *et al.*, 2015; Randhem & Nilsson, 2008). In consideration of these drawbacks associated with mining and extraction of metals from virgin ores, the importance of metal recycling from secondary sources such as e-waste is critical. For example, e-waste recycling saves about 85% energy when recovering copper compared to copper extraction from natural ores. Further

examples include iron and steel which save about 75%, lead saves about 65% and zinc 60%(Cui & Zhang, 2008).

2.2.3 Uses of Ag and Au

While gold has traditionally been used for jewellery production and as a means of exchange for goods and services (trade and economic uses), modern applications of gold include aerospace technology, electronics, soldering, dentistry, medicine as well as food and beverage industry among other applications (Thomson Reuters, 2016). Besides its predominant use in jewellery and coin production, silver has several other different industrial applications. These include alloying, dentistry, electronics, nano-science, photography and medicine among others (Thomson Reuters, 2017). Figures 2.2 and 2.3 (page 14) summarize the different global uses for gold and silver for the period between 2006-2015 for gold, and 2007-2016 for silver.

Figure 2.2 shows jewellery as the leading sector in terms of gold demand in the world. Its annual average demand for gold between 2006 and 2015 was 2 200 tonnes per year, accounting for approximately 60% of the total demand for gold worldwide. Investment in the form of gold bars and coinage accounts for the second largest annual average demand for gold. This stood at about 1000 tonnes per year, which is about 30% of the total global gold demand. The electronics industry, which is of interest in this research, accounts for about 8% of the total demand for gold with an annual average demand of about 311 tonnes per year. Considering this high volume of gold going into electronics per year, interest in the recovery of this precious metal from e-waste is justified.

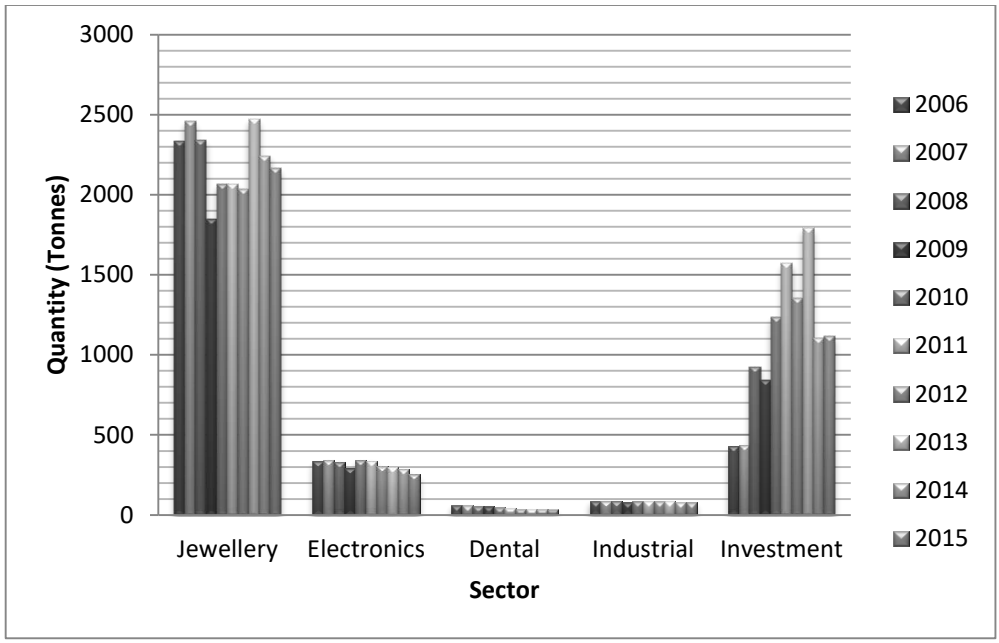


Figure 2.2: Global gold demand by sector: 2006-2015

Source: Thomson Reuters, (2016)

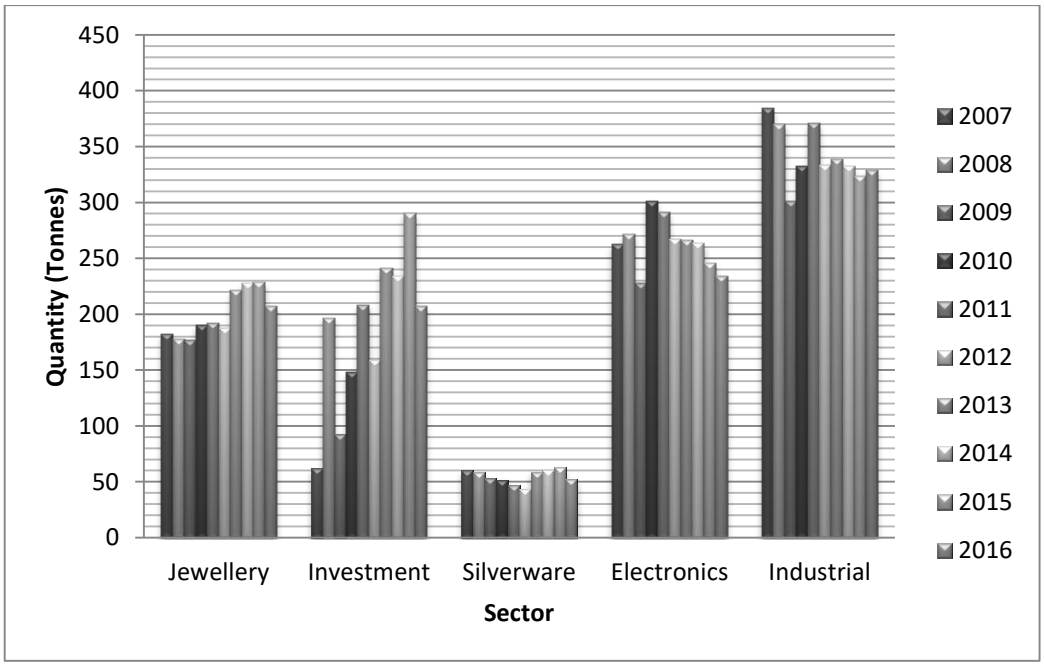


Figure 2.3: Global silver demand by sector: 2007-2016

Source: Thomson Reuters, (2017)

In electronics, gold is used as a conductor especially on contacts and as a copper coat because of its favourable properties, which include electrical conductivity and high resistance to heat and corrosion (Goodman, 2002).

From Figure 2.3, industrial fabrication accounts for the largest demand for silver in the world. This sector has an annual average demand of about 340 tonnes which accounts for about 33% of the total global demand. The electronics industry is the second largest consumer of silver in the world following the other combined industrial applications. The sector has an annual average demand of about 260 tonnes of silver per year, accounting for about 25% of the world's silver demand. Similar to the assertion that the amount and value of gold in e-waste necessitates metal recovery as discussed in the preceding section, the amount of silver in e-waste further emphasizes the importance of precious metals recovery from e-waste. Silver is used in PCBs of electronic devices as an electrical conductor because of its high electrical conductivity and resistance to corrosion (Luda, 2011).

2.3 Electronics and electronic waste

The electronics industry is one of the largest industries in the world's economy. Employing more than 15 million people in the world, the industry is said to be making the highest revenue within the goods-producing sector (ILO, 2014). Electronics are a backbone to today's world economy with their applications ranging across different disciplines of human activities. The electronics industry further stimulates the performance of other industries which rely on electronics for their operation and ultimately enhances the global economy (Sturgeon & Kawakami, 2010). While this is the case, electronic devices have a very short lifespan due to either their 'poor' durability or rapid changes and developments in models and software (Namias, 2013). Consequently, the volumes of e-waste discarded in the world continue to increase, thus causing environmental and health impacts associated with toxic materials which make

up part of the waste. This section presents an overview of the electronics industry as well as the generation and accumulation of e-waste. It further discusses current trends, successes and challenges facing the recycling of electronic waste.

2.3.1 Electronic devises and their uses

Each year, the electronics industry produces a wide range of products which are used in daily human life to support areas such as communication, education, trade, recreation and social media, among others (Sturgeon & Kawakami, 2010). The most common type of electronics is consumer electronics. These devices are described as electronic or digital devices which are often used by individuals mainly in a home and office environment (Soo, 2014). The devices in this category include digital entertainment sets (televisions, DVD players, video games), communication devices (telephones, cell phones, tablets), and office machines such as personal computers, printers, copiers and scanners. Figure 2.4 shows some of these commonly used consumer electronics.



Figure 2.4: Commonly used consumer electronics

Source: (Konkle, 2013)

Electronic devices are made up of different components which consist of different materials. These components include plastic casings, transmitters, transistors and PCBs (Veit & Bernardes, 2015). Each of these components is made up of an array of chemicals which include both organic and inorganic chemicals. The components are summarized in Table 2.1.

Table 2.1: Components of electronic devices ***Source:*** *Grant et al. (2013) and Veit & Bernardes (2015)*

Organic components	Inorganic components
Polychlorinated Biphenyls	Metal Elements (Fe, Cu, Hg, Pb, Be, Cd, Cr)
Phthalates	
Plastics	
Brominated flame retardants	
Polyvinyl chloride	
Dioxins	
Polyaromatic hydrocarbons	

When electronic devices are discarded, the above mentioned materials make up part of the toxic constituents of e-waste which contribute to the classification of e-waste as toxic and hazardous. The section below describes e-waste and its characteristics as well as trends of production and management across the world.

2.3.2 Electronic waste

Most electronic equipment, in particular consumer electronics, has a short lifespan of about two to five years (Baldé *et al.*, 2014, Figure 2.5). This leads to the disposal of large volumes of gadgets which tend to malfunction or become obsolete after this period of time (Chehade *et al.*, 2012). Disposal is further exacerbated by the modern culture of not fixing malfunctioning equipment, often because there is normally a trivial margin between the costs of fixing malfunctioning devices and that of purchasing new

ones. The disposal of electronic equipment is not regulated or organized in many developing nations (Lundgren, 2012). This leads to the accumulation of e-waste in landfills and other disposal areas (sometimes illegal areas) leading to the hazardous environmental and health consequences associated with the improper disposal of toxic waste.

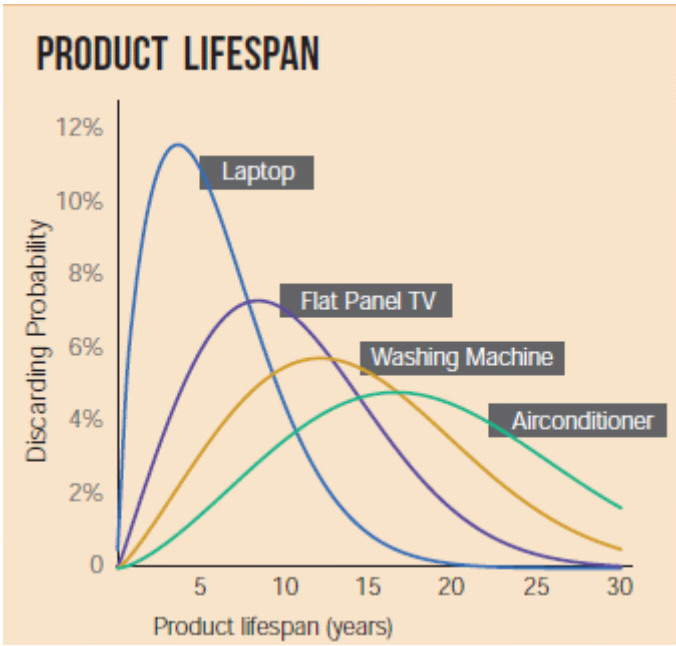


Figure 2.5: Lifespan of some consumer electronic devices

(Baldé *et al.*, 2014)

It is estimated that millions of tonnes of e-waste is generated each year with computers, mobile phones and television sets, accounting for about 25% of the total tonnage (Veit & Bernardes, 2015; Baldé *et al.*, 2014)

2.3.2.1 Global e-waste production trends

The total volume of e-waste generated in the world rose from 33.8 million tonnes in 2010 to 41.8 million tonnes in 2014 showing a percentage growth of 24% (Baldé *et al.*, 2014). Consumer electronics which include small IT devices, screens and other small equipment accounted for 19.3 million tonnes; a 40% equivalence of the total volume of e-waste

generated in the same year. With this trend, the volume of e-waste generated per year is projected to grow by 4-5% per year, and to reach 50 million tonnes in the year 2018. The statistics are summarized in Figure 2.6.

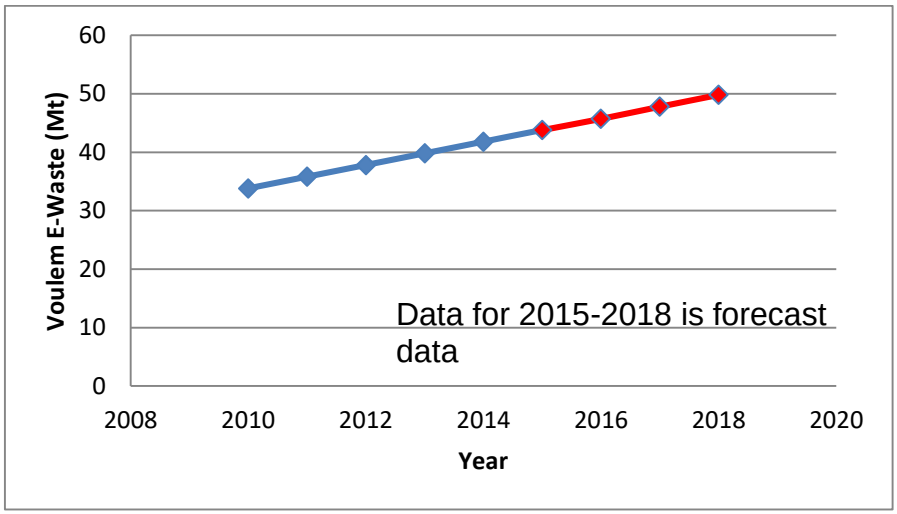


Figure 2.6: Global e-waste generation 2010-2014

Adapted from Baldé *et al.*, (2014)

While the data presented in Figure 2.6 shows the global outlook of e-waste generation, the variations in generation per region are vast, with developed nations leading the list in volumes of e-waste generated per capita. From the 48.1 Mt of e-waste generated in 2014, Asia led the list in total volume generation with 38% of the total waste. Asia was followed by America and Europe at about 28% each, with a minimal margin between the two. Africa produced only less than 0.5% of the world's total e-waste (Baldé *et al.*, 2014). The data as discussed is presented in Figure 2.7 (page 20).

The data presented in Figure 2.7 suggests that Asia is the largest producer of e-waste in the world. This is true given the large human population in the continent, which is about 60% of the world's total (Population Reference Bureau, 2016). In addition, there are a number of high-tech countries in Asia such as China, Japan, South Korea and Singapore (Ismail, 2013) which produce large volumes of electronics, thus, contributing to the high e-waste volumes in Asia. However, it is often asserted that the largest producers of e-waste in the world are the developed countries particularly in Europe and America (Baldé

et al., 2014). This assertion is validated when one considers per capita generation data instead of general total volumes. Per capita generation data shows the volumes of e-waste generated in a particular region per inhabitant. Under this consideration, Europe becomes the largest producer of e-waste with up to 15.6 kg/inhabitant. Oceania is the second with 15.2 kg/inhabitant, Americas the third with 12.2 kg/inhabitant, Asia the fourth with 3.7 kg/inhabitant and the least being Africa with only 1.7 kg/inhabitant (Baldé *et al.*, 2014) The proportion of e-waste generation per inhabitant is given in Figure 2.8.

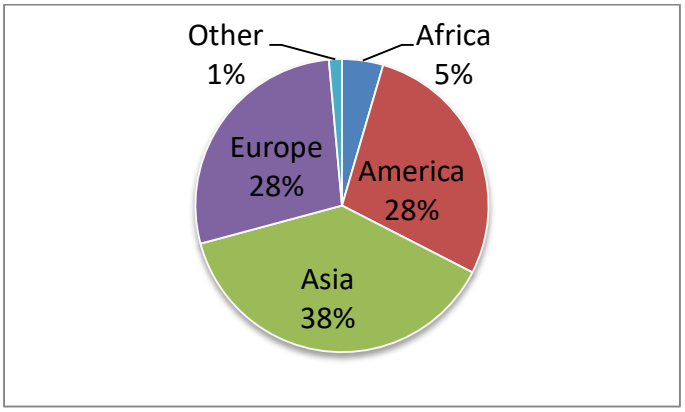


Figure 2.7: Proportion of total e-waste generated

Adapted from Baldé *et al.*, (2014)

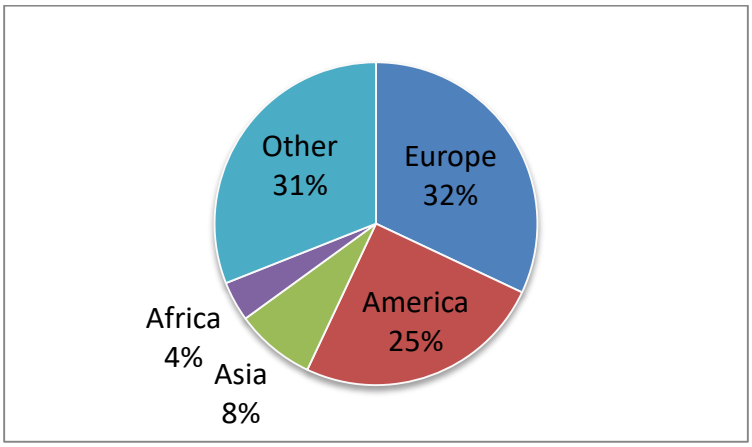


Figure 2.8: Global proportion of e-waste generated per inhabitant in 2014

Adapted from Baldé *et al.*, (2014)

From the data presented in Figure 2.8, it may be concluded that developed nations are the largest producers of electronic waste in the world as most countries in Europe and

America, in particular North America, are classified as developed countries. With this conclusion, it becomes fundamental to discuss e-waste disposal and trade, which has become a major problem especially for developing countries as they tend to inherit the adverse effects of e-waste from developed countries through illegal e-waste trade (Lundgren, 2012). E-waste trade results in the less developed countries facing severe environmental and health effects of e-waste as volumes of e-waste are often shipped to less developed countries, particularly in Asia and Africa, for re-use and disposal.

2.3.2.1.1

2.3.2.2 E-waste disposal and trade

Due to the hazardous nature of e-waste, a number of developed countries have implemented stringent legislations prohibiting the disposal of electronic waster because of environmental and health impacts associated with it (Veit & Bernardes, 2015). The disposal of e-waste is further discouraged because of the loss of valuable resources which could be reclaimed for future use thus reducing the exploitation and depletion of scarce resources (Luda, 2011). With the continuous increase in e-waste volumes, recycling remains one of the viable alternatives that can address the accumulation of e-waste and the associated adverse environmental and health effects associated with its disposal.

Apart from Europe, the USA, Australia, China and some of the developed nations, most countries have not yet been successful in setting up legislations which govern the disposal, reuse and recycling of e-waste (Baldé *et al.*, 2014). The Waste Electrical and Electronic Equipment (WEEE) directive and the Restriction of the Use of Certain Hazardous Substances (RoHS) directive are examples of stringent legislations that regulate e-waste management within the EU (Goosy, 2004). The WEEE directive, for instance, states that it remains the responsibility of the manufacturer of electronic devices and gadgets to collect, recycle, or dispose electrical and electronic waste. Consequently, in Europe, the collection, reuse and recycling of e-waste is very organized and standardized.

On the other hand, the RoHS bans the use of some hazardous substances such as Hg, Cd, Cr(VI), Pb, PBB, PBDE in the manufacture of a number of products that include electrical and electronic devices. These chemicals are known to be very toxic to human beings and ecosystems. They tend to accumulate in the environment due to among other reasons, the disposal of waste which contains some of these chemicals.



Figure 2.9: E-waste trade

Source: (Sustainable Electronics Initiative, 2010)

Strict e-waste legislation in developed countries and the high costs of e-waste management influences the export of e-waste from developed countries (Figure 2.9) where it is expensive to manage (Perkins *et al.*, 2014). Consequently, e-waste finds its way to less developed countries especially African countries (notably Nigeria), as well as Asian countries, (notably India) where environmental, health and safety legislation, if it exists, is not strict at all (Baldé *et al.*, 2014).

With the information highlighted above, it is important to note that as a result of e-waste export by developed countries; most harmful environmental and health effects associated with e-waste are more severe in developing nations. This is mainly because developing

nations have become victims of e-waste trade and disposal partly due to poor economies, and the poor health and environmental legislations which regulate disposal and management of e-waste. Taking into account the discussion above on e-waste disposal and trade in developed and developing countries, management and recycling trends of e-waste in developed and developing countries will be discussed in subsequent sections. The discussion will highlight the vast differences in operation and management styles. However, the composition of e-waste which influences the toxicity as well as the rationale for recycling and management is discussed first in the next section.

2.3.2.3 Composition of e-waste

E-waste comprises of different types of electronic equipment. Each of these devices has different components which are also made up of various chemical elements and compounds, most of which are toxic, and hence e-waste is classified as toxic waste. These chemicals include toxic metals such as lead as well as toxic organic compounds such as biphenyls and ethers (Khaliq *et al.*, 2014). When these are disposed, they may contaminate the environment leading to different eco-toxicological effects on humans and the environment.

PCBs (Figure 2.10 on page 24) are found on all electronic devices and they control the digital operation of electronic devices. These components contain a number of different valuable metals which may sometime be in high concentrations (Cui & Anderson, 2016). The valuables metals which are commonly found on PCBs include base metals such as Cu, Al, Fe, and Zn, as well as precious metals such as gold, silver, platinum and palladium. The average composition of metals in PCBs based on different authors is given in Table 2.2.

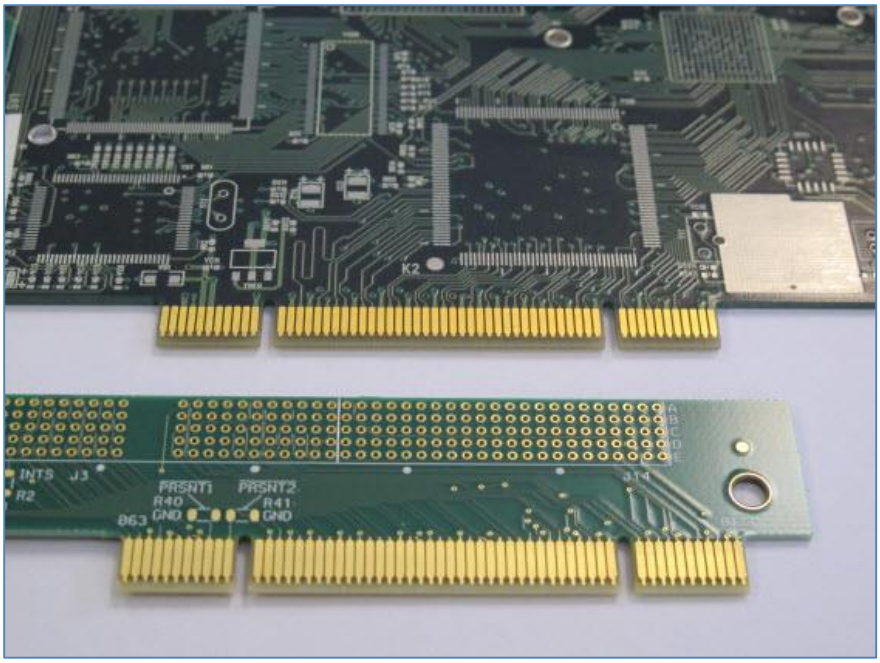


Figure 2.10: Picture of gold-rich PCBs

Source: (Norbert, 2012)

Table 2.2: Average metal composition of PCBs (Cui & Anderson, 2016)

Metal	Average Composition
Cu (wt%)	**25**
Al (wt%)	**6**
Fe (wt%)	**5**
Sn (wt%)	**4**
Ni (wt%)	**1**
Zn (wt%)	**1**
Pb (wt%)	**3**
Mn (wt%)	**<1**
Sb (wt%)	**<1**
Au (ppm)	**184**
Ag (ppm)	**696**

2.3.2.4 Environmental and health effects of e-waste

The disposal of electronic waste has significant impacts on the environment (Gaidajis, Angelakoglou & Aktsoglou, 2010). Components such as metals (Pb, Hg, Cr, Cd), and flame retardants which are made of polybrominated biphenyls and polybrominated biphenyl-ethers are highly toxic constituents of e-waste (Chatterjee & Kumar, 2009). When e-waste is disposed in the environment, toxic metals are leached and they enter ecosystems through soil and water. These materials are non-biodegradable and they tend to bio-accumulate and bio-concentrate in organisms up the trophic levels. Figure 2.11 shows a dump site for e-waste in Ghana (Africa) and the consequent environmental implications of improper disposal of e-waste.

Toxicants found in e-waste not only affect living organisms but they also have detrimental effects on human health. These toxicants may either have acute or chronic effects depending on a number of factors such as duration of exposure, dosage, route of uptake, speciation, and resistance among others (Wright & Welbourne, 2002). Lead toxicity for example, may result in biochemical defects which include failure to produce haemoglobin, kidney diseases and damage to the nervous system.



Figure 2.11: An E-waste dump in Ghana

Source: (Selcuk, 2014)

Chromium affects the kidneys, the liver and the central nervous system. Cadmium is associated with bone, kidney and lung diseases (Martin & Griswold, 2009). Organic compounds found in e-waste, particularly brominated flame retardants, are categorized as carcinogenic and they further affect other physiological processes such as the action of the immune system against bacteria and viruses (Birnbaum & Staskal, 2004). A profile of all the toxic materials found in e-waste is summarized in Table 2.3.

Table 2.3: Toxic materials found in e-waste.

(Martin & Griswold, 2009; Gaidajis, Angelakoglou & Aktsoglou, 2010; Birnbaum & Staskal, 2004)

Pollutant	Components where found	Human health effects
Arsenic	Semiconductors, diodes, microwaves, LEDs, solar cells	Cacinogen, neurotoxicant, pulmonary and cardiovascular diseases, diabetes.
Barium	Electron tubes, fillers (plastic and rubber), lubricant additives	Respiratory problems, High BP, brain, liver, kidney, and heart disease.
Brominated flame retardants	Casing, PCBs, cables	Gene mutants, affect the liver and thyroid levels. Associated with reproductive and neurotoxicity.
Cadmium	Batteries, pigments, solder, alloy, PCBs, CRTs	Cardiovascular, reproductive, kidneys, eyes, and brain problems.
Chrome	Dyes, pigments, switches, solar cells	Carcinogen, DNA damage, allergen.
Cobalt	Insulators	Respiratory, heart and thyroid problems
Copper	Conductors, coils, circuits, pigments	Low BP, Anaemia, heart disease, kidney failure.
Lead	Batteries, solar cells, transistors, PVC	Affects brain, renal and nervous systems. Cause high BP.

The effects listed in Table 2.3 further emphasize the need for proper management, disposal as well as the recycling of e-waste in an attempt to promote environmental protection as well as salvage valuable resources in e-waste.

2.3.2.5 Recycling of e-waste

E-waste recycling is considered an environmentally and economically sustainable venture because of the value of materials found in e-waste (Chatterjee & Kumar, 2009). However, the costs of recycling are considerably high (Perkins *et al.*, 2014) and as a result, waste ends up being preferably exported from developed to developing countries where the environmental, health and safety legislations are not enforced, if in place at all. As a result, there is a huge distinction between e-waste recycling trends in developed countries and trends observed in developing nations.

2.3.2.5.1 E-waste recycling in developed countries

Developed countries such as Australia, Canada, Qatar, the EU, and the USA have legislations which regulate e-waste management (Baldé *et al.*, 2014). As a result, there are sound e-waste management practices in these countries. As discussed in preceding sections, the EU has the WEEE directive (Goosy, 2004) which makes it compulsory for producers of electronics to collect e-waste for proper management and recycling. Canada, on the other hand, has an industry standard which guides the recycling and processing of e-waste (Baldé *et al.*, 2014). Consequently, e-waste recycling in the developed world is characterized by formal and organized establishments. There is a high level of infrastructural investments and mechanization in recycling plants. The environmental, health and safety performance of recycling plants is enhanced by the use of environmentally friendly processes as well as the enforcement of health and safety legislation. Figure 2.12 (page 28) shows an example of a formal e-waste recycling operation in Qatar, where recycling operation is formal and more organized.



Figure 2.12: E-waste recycling in Qatar

Source: (Construction Week, 2011)

2.3.2.5.2 E-waste recycling in developing nations

As stated in the previous section, a greater proportion of e-waste produced in developed nations is often exported to vulnerable and less developed nations mainly in Africa and Asia (Baldé *et al.*, 2014). The recycling of e-waste in the developing world such as Africa is primitive in nature. In most countries however, e-waste is dumped and burnt in unmonitored landfills or dumpsites (Breivik *et al.*, 2014). On the other hand, in countries where the volume of e-waste is low, it is common to find that e-waste is stored in large warehouses or storerooms without any definite intention for disposal (Baldé *et al.*, 2014). In countries or areas where recycling is practiced, it is often carried out in informal recycling areas where physical dismantling and sorting is used to recover useful components from e-waste. Incineration in open sites is often one other major recycling method for most African countries particularly in West Africa. Countries such as Ghana and Nigeria receive a lot of e-waste from developed countries and treat the waste as described in the next paragraph (Breivik *et al.*, 2014; Baldé *et al.*, 2014).



Figure 2.13: : E-Waste recycling in Agbogbloshie, Ghana

Source: (BBC, 2014)

The defunct junk is taken to incineration sites such as Agbogbloshie in Ghana (Figure 2.13). In such sites, volumes of e-waste along with other sorts of waste containing metals are set on fire. The rationale is to separate metals from the non-metals by melting the non-metallic materials and collecting the remaining metals after incineration. Among the poor recyclers in these impoverished regions, incineration is cost-effective as well as efficient in terms of time compared to other means of separation which would require expensive infrastructure, reagents and have slow reaction kinetics. However, the environmental and health impacts associated with the clouds of toxic gases from these areas are critical. Recycling in African countries is also characterized by the lack of PPE for recyclers and standardized procedures for recycling.

In the Asian continent, India is one of the countries which produce large amounts of e-waste (absolute quantities) and also receives e-waste imports from more developed countries. India has a number of e-waste recycling facilities (Rajya Sabha Secretariat, 2011). However, similar to African countries, most of the facilities are informal, and they evade labour laws and environmental legislations regulating the recycling of toxic waste. These informal facilities are characterized by labour intensive operations with socio-economically underprivileged women and children serving as the labour force. Workers

are often exposed to toxic chemicals without proper protective wear. As a result, such operations tend to have severe environmental and health effects on the working population.



Figure 2.14: E-waste recycling in Mundkar, India

Source: (Koshy, 2010)

Figure 2.14 shows young children working in an informal e-waste recycling site in India. From the Figure, it is observed that the operation, similar to the African setting, is informal with no signs of health and safety standards or legislation observed. This is contrary to what would be observed in recycling facilities found in developing countries as shown in Figure 2.12. The gap between the recycling trends in developed and developing countries is huge. Consequently, there is a need for developing nations to regulate recycling activities in an attempt to promote recycling while ensuring that the activities are safe and sustain the environment as well as the health and safety of those participating in recycling activities.

2.3.2.5.3 Barriers to e-waste recycling

While the recycling of e-waste is a critical measure towards the sustainable use of the earth's scarce resources and maintenance of a safe and healthy environment among

other significant benefits, it is fundamental to state that e-waste recycling faces a number of challenges that hinder the success of recycling programs. The challenges may be grouped into five broad categories namely; legislation, information, collection, recycling costs as well as the socio-economic status of the community (Ahmed & Panwar, 2014; Industrial Business Magazine, 2017). These factors are discussed below.

- *Legislation*: Many nations do not have enforceable legislation or regulations which regulate the use and disposal of e-waste (Baldé *et al.*, 2014). Consequently, disposal tends to be the cheapest and easiest option for most users because there is no compelling regulation to recycle. Furthermore, there is also absence of state incentives for programs which encourage the recycling of e-waste. Such an environment fails to promote recycling of waste. In countries where legislation is in place, the costs associated with conformance to certain regulations particularly environmental, health and safety regulations become exorbitant.

- *Information*: For most developing nations where great volumes of the e-waste ends, there is lack of knowledge on many aspects of e-waste. This includes inadequate knowledge on the toxicity of e-waste and other forms of hazardous waste as well as their effects on the environment and human health. Furthermore, most people lack knowledge about the valuable material that can be salvaged from e-waste. Those who know usually lack information about the methods of recycling which they can use.

- *Collection*: One of the major challenges facing e-waste recycling is collection. E-waste is not produced in one place but is spread over vast areas. Volumes talk to recycling economics and hence to get large volumes for recycling is fundamental for an economically sustainable venture. However, the problem is often that the sources of e-waste and available volumes are not often recorded. As a result, to know where and when waste becomes available remains a challenge. Collection also involves the cost and efficiency implications, which also hinder successful collection to one recycle point.

- *Recycling costs*: The high costs of transport, recycling infrastructure as well as energy and reagents (where used) are some of the major threats to e-waste recycling. The costs sometimes exceed the returns from sales and hence recycling projects become financially unsustainable and consequently, disposal becomes a preferred option.

- *Poverty*: For impoverished societies, scavenging is a common livelihood even if it is in highly hazardous areas. Governments and local authorities often fail to meet the basic requirements for their citizens. The collection of waste of any kind is often very poorly done, and hazardous waste often ends up in informal or even illegal dumpsites where it supports the livelihoods of some members of society. Consequently, collection of waste is flawed and hence recycling is often out of question.

The challenges discussed above are critical, and for the implementation of sound and successful recycling projects, efforts should be made by governments to address them. A number of successful and unsuccessful e-waste recycling projects exist. Lessons may be learnt from those projects and more comprehensive recycling plans may be crafted which would address the challenges discussed. Examples of such initiatives may include encouraging governments to pass regulations such as the EU's WEEE directive which prohibits the disposal of e-waste (Rajya Sabha Secretariat, 2011; Goosy, 2004). E-waste education (threats and opportunities) may be incorporated into mainstream environmental education programs, which are already rolled out in many developed and developing countries to educate citizens about e-waste as well as the possible recycling projects and their envisaged environmental and socio-economic benefits.

2.4 Recovery of precious metals from e-waste

Although the mass percentage of Ag and Au in e-waste is minimal, the intrinsic value of precious metals in e-waste is about 80% of the total value of metals found in PCBs (Montero, Guevara & Torre, 2012; Park & Fray, 2009). Au alone constitutes about 65% of the total value of all metals in PCBs. This finding underlines the selection of precious metals as the group of metals under consideration in this study. Different methods have been utilized for the recovery of precious metals (PMs) from electronic waste. Pyrometallurgical and hydrometallurgical processes are the main recovery routes which have been used to recover precious metals from e-waste (Namias, 2013). However, there are other methods which have been developed and used for metal extraction with notable success such as bio metallurgy (Huang, Guo & Xu, 2009). This section discusses the different metallurgical processes which have been investigated for the recovery of precious metals from e-waste. The successes and challenges encountered also highlighted.

2.4.1 Pyrometallurgy

Pyrometallurgy is the oldest extractive metallurgical process through which thermal energy is used to effect physical and chemical changes on materials which make it possible to recover valuable metals from their solid sources (Habashi, 2013; Park *et al.*, 2014). As a metallurgical process, pyrometallurgy may be subdivided into the following processes; calcination, roasting, smelting as well as sintering. These processes are discussed below.

Calcination: This is a pyrometallurgical process where thermal energy is used to effect a physical or chemical modification of its constitution (Lenntech, 2008). The change may be caused by the decomposition of a molecule or compound into its constituents. The decomposition of carbonates into metal oxides and carbon dioxide are good examples of calcination processes. Limestone subjected to high temperatures decomposes to form lime and carbon dioxide (Stanmore & Gilot, 2005). A similar process is observed when

carbonates of iron are exposed to high thermal energy in furnaces or other pyrometallurgical reactors (Bellihi, 1998).

Roasting: This is a pyrometallurgical process where as solid-gas reaction occurs in the furnace (Wai, Leong & Mujumdar, 2009). Sulphide ores are classical examples of ores which are treated through roasting to remove the sulphide from the ore. When the metal sulphide is heated in the presence of air the sulphide ore reacts with oxygen in the air to produce a metal oxide and sulphur dioxide gas (Michigan Tech, 2017).

Smelting: This is the process where high temperatures are used to turn the metal being sought into a molten phase. Temperatures above the melting point of the metal are required to smelt the metal which becomes fluid while impurities settle as slag below the molten metal (Wai, Leong & Mujumdar, 2009). Carbon is often used in the form of coke as a reducing agent in smelting of metal oxides. The carbon reacts with the oxygen of the oxide to yield carbon dioxide and a reduced metal. Some of the processed metals requiring the smelting of the mineral from the ore include iron, copper, and zinc, among others (Martin & Griswold, 2009; Kilicarslan & Saridede, 2013).

Refining: This process involves the removal of impurities from the desired metal, often after thermal processing (Chatterjee & Kumar, 2009; Rajya Sabha Secretariat, 2011). Refining may be achieved through the use of electrical or thermal energy. Those pyrometallurgical processes which use electricity for refining are referred to as electrolytic refining while in the case of thermal energy, they are referred to as fire refining processes (Randhem & Nilsson, 2008). From these steps, refined 'pure' metals may be extracted from their ores or other secondary sources. Copper is refined in this way after smelting in furnace (Randhem & Nilsson, 2008).

One of the critical considerations to take into account is the high costs of energy required in all of the pyrometallurgical processes described above (Habashi, 2013). Furthermore, the emission of toxic gases (Behnamfard, Salarirad & Veglio, 2013) as well as carbon dioxide (Randhem & Nilsson, 2008) is another major disadvantage of pyrometallurgy,

which has made it unpopular with many environmental organizations due to its contribution to the greenhouse effect and climate change. The use of pyrometallurgy in e-waste processing is further complicated by the chemical composition of e-waste which includes other complex compounds such as organics which may produce highly toxic furans and dioxin upon combustion (Perkins *et al.*, 2014; Veit & Bernardes, 2015). These assertions paint an unfavourable picture of pyrometallurgy and e-waste recycling when considering environmental performance and sustainability. With that said, it is however fundamental to discuss some of the key e-waste recycling projects that have used pyrometallurgical processes to reclaim valuable metals from the waste.

2.4.1.1 Pyrometallurgical processes used in the treatment of e-waste

Pyrometallurgy has been successfully used in the recovery of metals from e-waste (Khaliq *et al.*, 2014; Cui & Zhang, 2008; Luda, 2011). To that end, pyrometallurgy still remains one of the most practiced method of metal recovery from e-waste with Fe, Al, Cu, Pb, and PMs being the most recovered metals (Khaliq *et al.*, 2014). Smelting, incineration, combustion and pyrolysis are the common pyrometallurgical processes used in e-waste recycling. On large scale, e-waste is often recycled through smelting along with other metal scrap in furnaces such as copper-lead smelters. This is because other metals dissolve in smelt copper or lead. In this way, most metals are extracted from the solid waste into the molten copper or lead.

Recent research has shown that the addition of NaOH in the smelting process aids the separation of the metals from slag as NaOH acts as a slag-forming material (Khaliq *et al.*, 2014). The molten metals are then refined into pure metals using different methods. The Perker process which involves the use of zinc as an extractant of gold or silver from molten lead is one of the methods which are used if the PMs are dissolved in lead. The PMs are extracted by molten zinc from lead and zinc becomes the PM rich phase. As lead and zinc are immiscible, zinc is separated from lead and later evaporated from the

PMs. In the case of copper smelting, electro-refining is used to separate PMs from the molten copper.

Combustion and incineration are often used to ‘burn off’ the organic components of e-scrap so that the metal and glass components of the scrap are left and collected by the recyclers for sale, where the metal scrap may further be processed into pure metals (Chehade *et al.*, 2012). In these processes, along with pyrolysis, the organic components act as the fuel since they are combustible. Pyrolysis may also be used in formal recycling plants where environmental conditions may be controlled. An example is vacuum pyrolysis which has been used on e-waste to shorten vapour residence times in reactors as well as to lower temperatures for decomposition.

While pyrometallurgy is widely used as a metal extraction method (Kamberović, Korac & Ranitović, 2011), it is however, not environmentally friendly for the recovery of metals from e-waste because of the toxic components of e-waste which when incinerated, release toxic gaseous compounds (Kamberović, Korac & Ranitović, 2011). Furthermore, the recovery of metals is not efficient as some metals such as iron and aluminium are lost as slag. Ceramics may also increase the loss of some base and precious metals due to accumulation of slag. Incineration of e-waste containing plastics and flame retardants results in the release of toxic and carcinogenic compounds (Kamberović et al. 2009). Well-designed smelters are also associated with high costs for setting up. The furnace high temperature requirements for smelting consume enormous amounts of energy while generation of energy also has its own environmental impacts.

2.4.2 Hydrometallurgy

Hydrometallurgy is a field of extractive metallurgy which deals with the extraction and recovery of metals from their ores or from other source materials using aqueous chemistry as well as some elements of organic chemistry. As a broad field, hydrometallurgy may be

separated into different processes which are; leaching, concentration and purification as well as metal recovery (Kamberović, Korac & Ranitović, 2011).

Leaching: This is the initial step in hydrometallurgy. In this step, an aqueous leaching solution is brought into contact with an ore or any other material which is the source of the metals being sought (Luda, 2011). Certain properties such as the pH, redox potential, temperature, and viscosity are critical for leaching solutions. For refractory metals, additional materials such as oxidizing and complexing agents are necessary for the leaching of the metals into solution (Wai, Leong & Mujumdar, 2009). Figure 2.15 shows a generic flow sheet for a hydrometallurgical process.

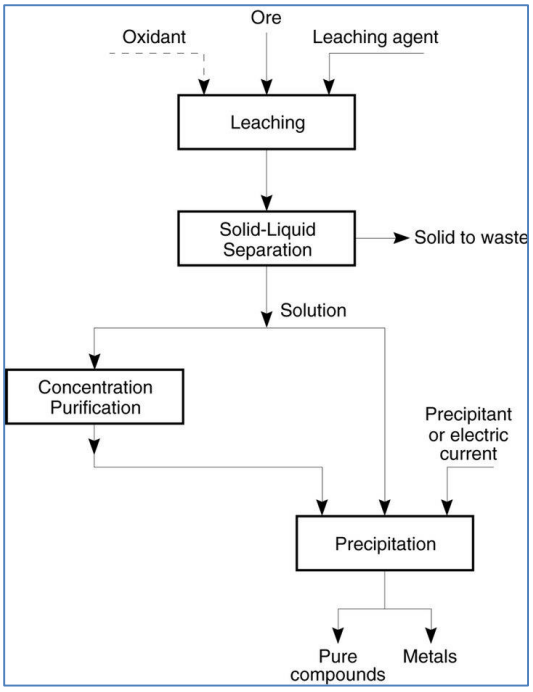


Figure 2.15: Generic Hydrometallurgy Flow Sheet (Habashi, 2013)

Due to the nature of the ore which bears the metals being sought, as well as the properties of the leaching solution, different leaching methods may be used. Some of these methods include; in-situ leaching, heap leaching, agitation leaching as well as autoclave leaching (Wai, Leong & Mujumdar, 2009). Fundamental to metal leaching are Pourbaix phase

diagrams. These diagrams represent regions of stable species of a particular element or compound in an electrochemical system. Pourbaix diagrams (Figure 2.16 and Figure 2.17) in the subsequent sections (page 43-44) show the regions where different species of Ag and Au are stable in their different electrochemical systems. The pH and the Eh are the controlling factors determining the stable species at any given region.

Extraction: After metals have been leached into dilute solutions, they have to be extracted from the solution. Solvent extraction or ion exchange may be used to separate the desired metals from the leach solution (Makertihartha *et al.*, 2017; Wai, Leong & Mujumdar, 2009; Waitz, 1982).

- Solvent extraction: Sometimes referred to as liquid-liquid extraction, solvent extraction uses an organic solution which acts as an extractant. The organic is mixed with a pregnant solution and left to separate resulting in a bi-phasic system with a loaded organic phase and a raffinate with metal depleted leach solution. The loaded organic phase is then separated from the raffinate and is treated downstream to recover the pure metal using one or a combination of metal recovery processes described on page 39.

  A major limitation of solvent extraction as used in PMs is the toxicity, volatility and flammability of organic extractants as alluded to in preceding sections. The use of ionic liquids in place of organic extractants as investigated in this research seeks to address some of these limitations. Furthermore, ionic liquids are re-usable and more environmentally friendly compared to the organic compounds.

- Ion Exchange: Ion exchange is a separation process whereby a pregnant solution is brought to contact with a solid material (ion exchange resin) which is capable of exchanging ions between the solution and itself.

Metal recovery: The final step in the hydrometallurgical process is metal recovery. In this step, the metals in solution are recovered as pure solid metals, which are the final metallurgical product. However, refining may be necessary if high grade metals are required by the market. The following are examples of metal recovery processes following on the first two steps; leaching and extraction.

- Precipitation: This is the process of precipitating either the desired metal or metal compound from the leach solution. This may be achieved by manipulating the physicochemical properties of the solution such as the pH, temperature, or through evaporation or the addition of a chemical which will effect precipitation of the metal desired. The precipitate would normally be a pure form of the desired material (Nicol, Fleming and Paul, 1992; Srithammavut, 2008).

- Electrolysis: In this process, electrical energy is used to separate charged species found in a solution or in a molten compound. From solution, and due to their positive charges, metal ions would normally be deposited on the cathode. On the other hand, metal dissolution would occur on the anode (Chmielewski, Urbtiski & Migdal, 1997; Nicol, Fleming & Paul, 1987; Wai, Leong & Mujumdar, 2009).

- Gaseous reduction: This is a chemical process in which a pure element is produced by reduction, especially through the use of hydrogen as a reducing gas (Wai, Leong & Mujumdar, 2009).

Hydrometallurgy has a number of advantages as an extractive metallurgical process (Habashi, 2013). This is particularly true when the source of metals (ore) has a complex composition which ultimately requires flexible treatments for the extraction and recovery of the metals. Table 2.4 summarizes some of the positive characteristics and limitations of hydrometallurgy.

Table 2.4: Advantages and disadvantages of hydrometallurgy (Habashi, 2013)

Advantages	Limitations
Flexible for the treatment of complex ores	Require sophisticated controls of numerous parameters
Flexible for the production of different by-products as may be desired	May be more expensive for high grade ores compared to other processes
Revenue may be created from by-products thus making process more economically attractive	
Can be suitable for low-grade ores	
High separation efficiency	
Less energy consumption	
Low pollution rates	
High chemical specific and flexible	

Following the description of the metallurgical processes above, it is fundamental to compare their characteristics and evaluate their suitability for a defined application as the application determines the appropriate process to be used. Table 2.5 gives a summary of the comparison of the two processes.

Table 2.5: Comparison between hydrometallurgical and pyrometallurgical processes

Measure	Pyrometallurgy	Hydrometallurgy
Use in high-grade ore	More economically attractive	Less economically attractive
Use in low-grade ore	Unsuitable as very high energy consumptive	Suitable with a selective leaching agent
Use in complex ores	Unsuitable as separation is challenging	Flexibility of process allows treatment of complex ores
Use in secondary resources	Mostly unsuitable	Mostly suitable
Separation of chemically similar metals	Not possible	Possible
Economics of process	Suitable for large scale operations with high grade ores Requires huge capital investments	Suitable for small – large scale operation, especially for low grade ores Requires less capital investments
Reaction rate	Rapid physicochemical reactions due to high temperatures	Slower reaction rates due to lower temperatures
Throughout	High throughout	Small throughout

Materials handling	Handling of molten metals, slags, mattes more challenging	Handling of chemical solutions and slurries easier
Environmental pollution		
Solid waste		
Toxic gases	More toxic gases released and release mitigation is highly costly	A few gases released and plant may be designed to evade gas releases
Process feed	Suitable for non-homogeneous feed	More suitable for homogeneous feed
Operation	Non-complex design	Complex design with sophisticated controls

From the comparison given in the Table 2.5, it is evident that hydrometallurgy is the preferred process in the recovery of metals from e-waste. This is supported by the fact that e-waste is generally a low-grade secondary source of PMs (Chehade *et al.*, 2012). Furthermore, e-waste has a complex chemical composition with a lot of other constituents such as organics, which are highly toxic under high temperatures (Gaidajis, Angelakoglou & Aktsoglou, 2010). The flexibility of hydrometallurgy and its ability to produce by-products which may create more revenue due to the selectivity of the process add to its benefits in this research work. In addition, hydrometallurgy allows for small scale operation with reasonable capital investments, which would be ideal for e-waste processing plants.

2.5 Hydrometallurgy and Precious Metals

Hydrometallurgy has been widely employed in the extraction and recovery of metals from e-waste (Veit & Bernardes, 2015; Luda, 2011; Kamberović, Korac & Ranitović, 2011). Different metals ranging from base metals to rare earths, as well as precious and platinum group metals have been reclaimed from e-waste using different hydrometallurgical methods. As described in previous sections, for hydrometallurgical processes, the treatment of an ore begins with leaching, followed by extraction and ultimately recovery (Habashi, 2013). Below is a description of the common leaching systems which have been used on e-waste to leach metals, extraction of metals from aqueous media, as well

as metal stripping. The description is however, focused on precious metals as they are the class of metals under study.

2.5.1 Leaching systems for Au and Ag

The extraction of gold from its ores through hydrometallurgical processes dates back to more than a century ago (Fleming, 1992). Due to its noble nature, gold is resistant to most simple leaching agents such as strong acids and bases. More complex leaching systems are required to dissolve gold into solution (Nicol, Fleming & Paul, 1987). A lixiviant which has the ability to form gold complexes as well as a suitable oxidant is necessary for the dissolution of gold. As a result, a number of leaching systems for gold have been developed. Common lixiviants which are used include; cyanide, thiosulphate, thiourea, and halides; Br^- and Cl^- (Nicol, Fleming & Paul, 1987).

Due to pressure on the industry as a result of the increasing environmental and health effects of some current metal recovery processes and reagents such as cyanide (Hilson & Monhemius, 2006), new methods and chemicals need to be investigated. Ionic liquids (Park *et al.*, 2014), organic acids (Oraby & Eksteen, 2015) as well as bio-reagents (Hilson & Monhemius, 2006) are some of the new techniques developed for metal recovery. In the next sections; cyanide, chloride, thiourea and thiosulphate gold leaching processes are discussed. Furthermore, the emerging leaching systems involving ionic liquids (Whitehead, Lawrence & McCluskey, 2004) as well as organic acids (Oraby & Eksteen, 2015) are presented.

The dissolution of metals in the different leaching systems is governed by the pH as well as the redox potential of the leaching system (Figures 2.16 and 2.17). The Pourbaix diagram for gold (Figure 2.16) shows that the leaching of gold requires highly oxidative conditions; the metal undergoes dissolution at high Eh values. The metal also requires either very acidic or very basic conditions for dissolution. This is influenced by the lixiviant used to form the gold complexes in solution. Thiourea for instance, works well in acidic

conditions while cyanide works best in basic conditions. The Pourbaix diagram for silver (Figure 2.17) shows that the pH of the leaching system has no significant effect on the dissolution of silver, but the redox potential of the solution determines the level of silver dissolution in a leaching system, hence silver ions are found in all pH ranges.

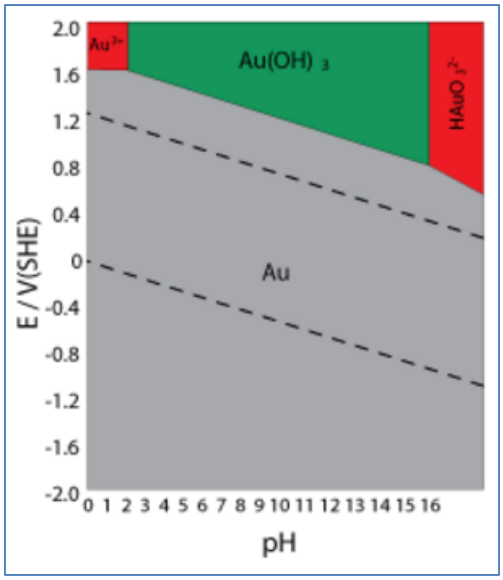


Figure 2.16: –Eh-pH diagram for Au in Au-OH system (University of Cambridge, 2017)

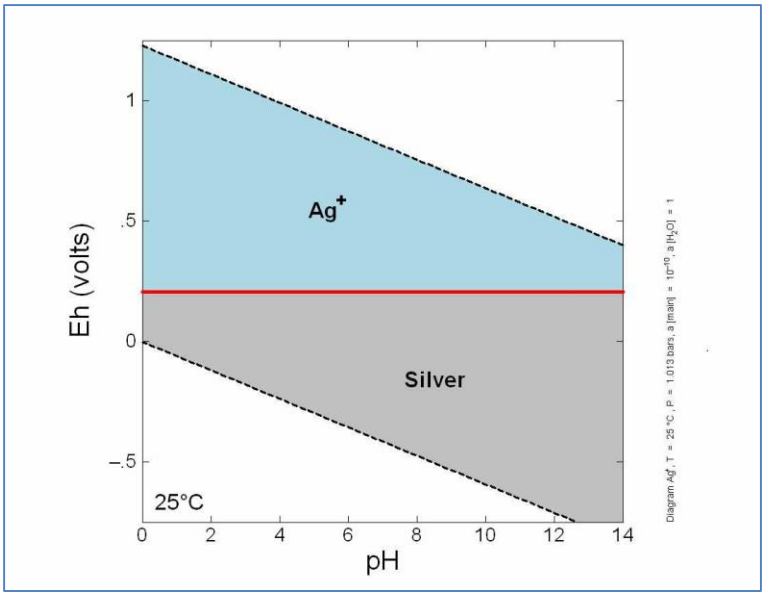


Figure 2.17: –Eh-pH diagram for Ag- water system (Coal Geology & Mining, 2010)

2.5.1.1 Cyanide Leaching

Due to the cost effectiveness and efficiency of cyanide leaching, the leaching of gold and silver ores using cyanide solution remains one of the extensively used industrial hydrometallurgical processes for the leaching of gold and silver (Norman & Raforth, 1994). This is despite the high toxicity of cyanide to humans and its impacts on the environment (U.S. Department of Health and Human Services, 2006). The gold cyanidation process involves the comminution of the ore into fine powder which is then mixed with a cyanide solution (typically potassium or sodium cyanide) and oxygen. The oxygen may be supplied by purging air or pure oxygen into the reaction. Cyanidation requires highly basic conditions with the pH ranging between 10 and 11. The cyanide ion in this system acts as the lixiviant while the oxygen purged through acts as the oxidizing agent, which is essential for the leaching of gold.

Equations 2.1 and 2.2 (Srithammavut, 2008) show the reactions of a cyanide solution of sodium when it is reacted with a gold-silver sample in the presence of oxygen. The products of the reaction are four molar gold and silver cyanide complexes and 4 molar NaOH solutions.

$$4\,Au + 8\,NaCN + O_2 + 2\,H_2O \rightarrow 4\,Na[Au(CN)_2] + 4\,NaOH \qquad \text{Equation 2.1}$$

$$4\,Ag + 8\,NaCN + O_2 + 2\,H_2O \rightarrow 4\,Na[Ag(CN)_2] + 4\,NaOH \qquad \text{Equation 2.2}$$

Besides the PMs, cyanidation also leaches base metals such as copper, iron and zinc if present in the ore being leached. After leaching in cyanide, PMs may then be recovered from leach solutions using different extraction methods such as ion exchange resins, precipitation, and extraction by carbon pulps as well as electro-winning.

However, due to its toxicity, the use of cyanide has been challenged by numerous environmental organizations which are against the use of cyanide in gold mining and

other applications (Hilson & Monhemius, 2006). This follows a number of environmental accidents which have led to the contamination of the environment with cyanide. Cyanide poisoning may occur as a result of exposure to different compounds or forms of cyanide which include cyanide salts, solutions, and gases such as HCN (Gökelma *et al.*, 2016). Cyanide solution may enter bodies of organisms including human beings through the dermal route. The acute health effects due to exposure to cyanide compounds include; headaches, dizziness, disturbed heart rates, respiratory problems, low blood pressure, seizures, and ultimately fatalities in just a few minutes of exposure. Neurological problems may be experienced by those who survive fatalities. Chronic exposure to cyanide may result in permanent paralysis, kidney diseases, nervous lesions and miscarriages for women (U.S. Department of Health and Human Services, 2006).

In view of the environmental and health effects of cyanide and the ban of cyanide use in some countries in the world, the need for an investigation into alternative leach systems which will be environmentally and economically sustainable may not be over emphasized. Cyanide is further said to be less efficient in the leaching of refractory ores of gold, which also warrants investigating lixiviants that would be effective for refractory ores (Senanayake, 2004). Copper bearing gold ores, for instance, consume cyanide while ores with carbon lead to the adsorption of the gold-cyanide complexes on the carbon, thus limiting dissolution of the metal into solution.

2.5.1.2 Thiosulphate

While cyanide leaching remains the most widely used gold leaching process (Srithammavut, 2008), its limitations such as toxicity and slow reaction kinetics propelled active research to suitable alternatives. Thiosulphate is less toxic and more environmentally compatible than cyanide. Thiosulphate is said to lower the interferences caused by impurities, especially metals such as copper. On the other hand, some researchers state that thiosulphate kinetics are faster than cyanide leaching kinetics (Ha *et al.*, 2010). Consequently, thiosulphate leaching has been used for gold and silver

leaching for more than a century. The chemistry of gold leaching in thiosulphate is given in equation 2.3.

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \rightarrow 4Au(S_2O_3)_2^{3-} + 4OH^-$$ Equation 2.3

Copper (II) sulphate has been used as an additive to the process, which speeds up the chemical reaction. The high consumption of thiosulphate as well as copper sulphate have led to thiosulphate being unfavourable for industrial application due to the high losses of reagents and associated costs (Ha *et al.*, 2010). Furthermore, gold extraction occurs as an oxidation reaction, which requires the addition of an oxidant for progression. Thiosulphate, on the other hand, is a reducing agent and it depletes the oxygen required by the reaction therefore requiring the addition of even more oxygen for progression. Due to these limitations, thiosulphate application in precious metal leaching is limited. Consequently, investigation into alternative lixiviants for gold leaching had to proceed. Thiourea is one other alternative lixiviant to cyanide and thiosulphate in gold leaching.

2.5.1.3 Halide leaching

Aqua regia has also been widely used for the dissolution of PMs from their ores. Aqua regia is a combination of HCl and HNO_3 in the ratios 3:1 (v/v) where the chloride ion from HCl acts as the lixiviant in the reaction and HNO_3 creates the oxidizing environment which is essential for the leaching of gold.

In an aqua regia system, gold forms the chloride complex. In the presence of an oxidizing agent such as HNO_3, the Cl_2^- complex is further oxidized into the Cl_4^- complex which is the desired gold-chloride complex in chloride leach systems. The overall reaction kinetics for the leaching of gold in aqua regia is given in the chemical reaction shown in equation 2.4.

$$Au + 4\,HCl + HNO_3 \rightarrow H^+ + AuCl_4^- + NO + 2\,H_2O$$ Equation 2.4

Silver in this system reacts with nitric acid to form silver nitrate which is soluble and remain in solution. The equation for the dissolution of silver in aqua regia is given in equation 2.5.

$$Ag + HNO_3 \rightarrow AgNO_3$$ Equation 2.5

After leaching in aqua regia, PMs may then be recovered from leach solutions using different extraction methods such as ion exchange resins, precipitation, and extraction by carbon pulps, and electro winning.

One of the main limitations of the use of aqua regia in leaching PMs is the presence of nitric acid in the system. Nitric acid tends to dissolve a whole lot of other metals which may be present in the sample or ore. These become a problem when PMs have to be precipitated from the leach liquor. Furthermore, after the leaching process is complete, the leach solution still requires a further step where the excess nitric acid is neutralized before ion exchange or precipitation of PMS. The use of concentrated mineral acids presents one of the major limitations for aqua regia in the leaching of PMs as these reagents are highly corrosive and hazardous. The reaction between nitric and hydrochloric acid also produces nitrous gases which are highly toxic, thus posing environmental and health effects. Consequently, aqua regia is not the most desirable leaching system for PMs.

While the chloride system has been the only halide complex discussed for gold dissolution, it should be noted that gold also complexes with the other halide ions (Nicol, Fleming & Paul, 1987). The common gold-halide complexes include; $AuBr_4^-$, $AuBr_2^-$, AuI_4^-, AuI_2^-, and $AuCl_2^-$ (Senanayake, 2004; Gökelma *et al.*, 2016).

2.5.1.4 Thiourea

Thiourea, similarly to thiosulphate has also been widely investigated as an alternative lixiviant to cyanide (Wai, Leong & Mujumdar, 2009; Fleming, 1992). Thiourea is also less toxic compared to cyanide and has faster initial reaction kinetics than cyanide if an appropriate oxidizing agent such as fine Fe_2O_3 is used. Furthermore, thiourea and Fe_2O_3 are stable under acidic conditions which are favorable for gold leaching. In the acidic thiourea leaching system, thiourea acts as the lixiviant, Fe_2O_3 is the oxidizing agent and sulphuric acid is used as the pH regulator, as acidic conditions are required for gold dissolution. The equations below (equation 2.6 and equation 2.7) show the chemical reactions for the dissolution of gold and silver in acid thiourea leach systems.

$$\mathbf{Au + 2SC(NH_2)_2 + Fe^{3+} \rightarrow Au(SC(NH_2)_2)_2 + Fe^{2+}} \qquad \textbf{Equation 2.6}$$

$$\mathbf{Ag + H_2SO_4 \rightarrow Ag_2SO_4} \qquad \textbf{Equation 2.7}$$

Thiourea will be used in this research as the lixiviant for gold and silver in an acidic thiourea leaching system with Fe_2O_3 as an oxidant. The difference in approach for this lixiviant would be that the solvent H_2SO_4 will be replaced by an ionic liquid alternative [Bmim][HSO_4] (Whitehead *et al.*, 2007), thus eliminating the use of mineral acid as a solvent in this system. This will enhance the environmental performance of the system as the ionic liquid to be investigated for use in this system is more environmentally benign compared to the mineral used conventionally in this system. Furthermore, the ionic liquid allows for direct stripping of PMs without solvent extraction, and it is also recyclable.

2.5.1.5 Amino acids (Glycine and Histidine)

Oraby & Eksteen (2015) investigated the leaching of gold and silver in alkaline glycine with hydrogen peroxide as an oxidizing agent. From their investigation, the researchers concluded that glycine can leach gold and silver at neutral and basic conditions at ambient or slightly higher temperatures. The researchers concluded that leaching gold in glycine after 48 hours was comparable to leaching in thiosulphate-EDTA systems. Oraby & Eksteen (2015) further investigated the leaching of gold in low concentration amino acids. The researchers concluded that a combination of amino-acids (glycine and histidine) is more effective in gold leaching compared to glycine alone. Amino acids are organic and less toxic compared to mineral acids and they are thus, a more environmentally friendly alternative to toxic solutions used in gold dissolution. This supports the choice of these acids as reagents under investigation for a sustainable processing of gold from e-waste

2.5.2 Extraction of Au and Ag from leach solutions

Different processes have been used for the extraction of gold from leach solutions. These processes include; carbon adsorption, Merrill-Crowe process, electro-winning as well as ion exchange and solvent extraction (Wai et al., 2009). These processes are discussed in detail below:

- *Carbon adsorption*: Sometimes referred to as carbon in pulp or charcoal in pulp, this process uses activated carbon to adsorb gold from leach solutions. The carbon used may be produced from wood, nut shells, cola, petroleum coke as well as other organic compounds. Durability as well as high adsorption capacities are the preferred characteristics of the ideal type of activated carbon for gold adsorption. Carbon in leach and carbon in column are modifications to carbon in pulp for the extraction of gold from leach solutions. In this process, the leach pulp is brought into contact with granular carbon (-8 to +20 mesh) in a series of agitation tanks

with adequate retention periods. The charcoal is then separated from the pulp using vibrating screens which retain the charcoal and allow the pulp through. The carbon is then stripped of the loaded gold in stripping columns (Davidson, 1974; McDougall *et al.*, 1980; Vences-Alvarez *et al.*, 2017; Jia *et al.*, 1998).

- *Merrill-Crowe process*: This is another process used for the separation of gold from leach solutions. In this process, the leach solution is filtered or decanted from the ore using counter current decantation. The solution is then clarified using different filters to yield clarified solutions. De-oxygenation follows by passing the solution through a vacuum de-aeration column. Ultimately, zinc dust is added to the solution, and since zinc has a higher affinity for cyanide than gold, gold is thus precipitated from the solution through a reduction reaction in which $Au(CN)_2^-$ gain an electron to form Au(0) (the desired metal) and 2 of CN^- ions which react with the Zinc dust. The gold precipitate is then separated from the solution and sent for refinement (Mmoloki, 2013; Martinez *et al.*, 2012; Vázquez *et al.*, 2014).

- *Electro-winning*: This process involves the electro-deposition of metals from their ores which are in liquid or aqueous forms. Electroplating is often used as a major technique in this process. An electric current is passed through the ore from an anode and the metal of interest is deposited on the cathode (Wai, Leong & Mujumdar, 2009; Nicol, Fleming & Paul, 1987)

- *Solvent extraction*: Sometimes referred to as liquid-liquid extraction, this process uses solvents, in particular, organic solvents which have a higher affinity for the dissolved metals than the aqueous phase. Since organic and aqueous solvents are hydrophobic, these two are mixed and then left to separate into a biphasic system. During mixing, the metals are re-distributed between the aqueous and the organic phase with the metals loading onto the organic phase. The loaded organic phase is separated from the aqueous phase and then sent for stripping (Makertihartha *et al.*, 2017; Wai, Leong & Mujumdar, 2009; Chmielewski, Urbtiski & Migdal, 1997; Nicol, Fleming & Paul, 1987).

- *Ion exchange*: The principle behind ion exchange is almost similar to solvent extraction, except that with ion exchange, instead of two liquids brought to contact, the loaded leach solution is brought to contact with an ion exchanger. This is often a solid material which has the capability of exchanging ions with another material that comes into contact with it. Consequently, an ion which is in the exchanger is replaced by an ion in the leach solution. The exchange of ions is stoichiometric. Ion exchangers may be developed from different materials such as minerals, ion exchange resins among others (Nicol, Fleming & Paul, 1987; Wai, Leong & Mujumdar, 2009; Waitz, 1982).

2.5.3 Stripping and recovery of Au and Ag from loaded extractants

Depending on the extraction method used to extract PMs from leach solutions, a number of stripping methods may be used to recover gold from extractants. For example, if activated carbon had been used to extract gold and silver from leach solutions, different eluents are then used to elute these metals from the activated carbon (Wai, Leong & Mujumdar, 2009). In this way, these metals are recovered from the extractants and may be refined into pure metals. In solvent extraction, acidic solutions are often used to strip metals from the loaded organic extractants into pure metal solutions which may then be sent for solid metal recovery.

2.6 Hydrometallurgy and e-waste

Hydrometallurgy has been widely and successfully investigated for the recovery of metals from e-waste (Chehade *et al.*, 2012; Luda, 2011; Kamberović, Korac & Ranitović, 2011; Cui & Anderson, 2016). Given the complex chemical composition of e-waste, hydrometallurgical processes are more preferable for the recovery of different valuable materials from e-waste to other processes such as pyrometallurgy (Cui & Zhang, 2008).

Dimitrijevi *et al.*, (2013) investigated the recovery of precious metals from e-waste using aqua regia as a leaching agent. The waste was characteristically made up of about 37% of metals which were mainly base metals. Gold was 10 ppm while silver was at 50 ppm. All metals were effectively leached in aqua regia at ambient temperatures. This was followed by selective reduction of gold and silver. Silver was recovered by dissolving the precipitate in aqueous ammonia followed by reduction with hydrazine hydrate while gold was recovered by reduction with sulphur dioxide. From their study, the researchers concluded that PCBs have valuable metals such as gold and silver, and 99% purity of these metals can be achieved using aqua regia as a leaching agent. This conclusion supports the choice of aqua regia as a leaching agent in this research, where leaching of PCBs with aqua regia is the baseline for leaching studies of Ag and Au from PCBs.

Similar to Dimitrijevi *et al.* (2013), Park and Fray (2009) also proposed a process for the recovery of PMs from e-waste using aqua regia as a leaching agent. In their process, the researchers used a fixed ratio 1:20 of the sample to the leaching agent. The leaching efficiency of the metals; silver and palladium were 98% and 93% respectively. Gold recovery was reported at 97%, which also shows that aqua regia is efficient in the leaching of PMs from e-waste. However, the environmental and health risks associated with the use of strong and concentrated acids such as mineral acids is one of the major limitations of leaching systems such as aqua regia.

Quinet, Proost and VanLierde (2005) investigated the use of acidic thiourea, chloride, and cyanide leaching systems for Au, Ag, Pd, and Cu from e-waste. In their study, the researchers started with an oxidative H_2SO_4 leach where Cu was leached along with parts of Ag. Following that, a chloride leach was used to dissolve Pd and Cu, and ultimately, the cyanide leach was used to leach Au. The researchers also recorded successful leaching of these metals from e-waste using these systems except for thiourea leaching in which the leaching efficiency was reported to have been very low.

Cui and Zhang (2008) conducted a review of the different processes of the recovery of precious metals from e-waste. The authors reviewed the use of both hydrometallurgical and pyrometallurgical processes in the recovery of metals from e-waste. They reported that hydrometallurgical processes are preferred to pyrometallurgical processes due to their favourable characteristics such as predictability, adaptability and ease of control, among others. The researchers reckon that, hydrometallurgical processes are more favourable for e-waste treatment, particularly because e-waste is made up of complex chemical compounds and as such, predictability, adaptability and ease of control are imperative during recovery processes. Table 2.6 gives a summary of some of the hydrometallurgical processes which have been used by different researchers in the processing and recovery of precious metals from e-waste.

While there has been a successful application of hydrometallurgical processes in e-waste processing, the use of highly toxic reagents such as cyanide, corrosive mineral acids and highly volatile and combustible organic extractants necessitates the development of alternative routes that use more environmental benign reagents.

Table 2.6: Use of Hydrometallurgy in metal recovery from e-waste

Reference	Reagents	Metals recovered
Behnamfard, Salarirad and Veglio, (2013)	H_2SO_4, Hydrogen peroxide, Thiourea	Au
Ha *et al.*, (2010)	Ammonium thiosulphate, Ammonia	Au
Petter, Veit and Bernardes, (2015)	Sodium thiosulphate, Ammonium hydroxide, Copper sulfate	Au,Ag
Chmielewski, Urbtiski and Migdal, (1997)	HNO_3 and aqua regia	Au
Zhou, Zheng and Tie, (2005)	HCl, H_2SO_4 and $NaClO_3$	Ag, AU, Pd
Sheng and Etsell, (2007)	HNO_3	Au

An innovative approach to the hydrometallurgical treatment of e-waste has been the use of a novel class of reagents, namely, ionic liquids in both the leaching and extraction stages of hydrometallurgy (Park *et al.*, 2014). Ionic liquids as well as their application in science and hydrometallurgical processes are discussed in the sections below.

2.7 Ionic Liquids

The use of ionic liquids in extraction sciences has gained considerable attention in recent years due to the attractive physicochemical properties of these reagents (Ghandi, 2014). Sometimes referred to as liquid salts (Fischer *et al.*, 2011), ionic liquids are salts which have melting points that are below 100^0C. As a result, these salts exist in liquid state at low temperatures. Room temperature ionic liquids (RTILs) are a distinct type of ionic liquids which have more lower melting points and thus, exist in liquid state under room temperatures and pressure (Mai, Ahn & Koo, 2014). These compounds are highly ionic which makes it ideal for the adsorption of ions on their surfaces (Plechkova & Seddon, 2008). Consequently, ILs are in the centre of research in metal extraction and recovery processes.

2.7.1 History and Classification of ILs

The discovery of ionic liquids is disputed between the first synthesis of ethanol-ammonium-nitrate which is a standard ionic liquid with a melting point of 52^0C, and ethyl-ammonium nitrate, a room temperature ionic liquid with a melting point of 12^0C. Ethanol-ammonium-nitrate $[C_2NH_8)][NO_3]$ was first reported by Gabriel and Weiner in 1888 (Ghandi, 2014) while ethylammonium nitrate $[EtNH_3][NO_3]$ was only reported by Paul Walden in 1914 (Plechkova & Seddon, 2008). Although ILs have been known for more than a hundred years, it is only in the last thirty to forty years that they gained more attention, and their use in science and industry grew considerably (Park *et al.*, 2014). With hundreds of types of ionic liquids, these chemicals are grouped into different classes

according to their forming ions, for ease of classification. These classes include; protic, aprotic, imidazolium, pyridinium, ammonium, and phosphonium ionic liquids.

2.7.2 Protic and aprotic ionic liquids

Ionic liquids can be grouped into two classes according to the nature of their forming cations. These may be protic ILs and aprotic ILs (Mai, Ahn & Koo, 2014). Aprotic ILs are composed of large organic cations (imidazolium and pyridinium cations) and large inorganic anions (Peric *et al.*, 2014). On the other hand, protic ILs are made of smaller ions which are normally derivatives of aliphatic amines and organic acids. Cations forming ionic liquids are often of unit charge formed by the addition of an H^+ or R^+ to a hetero lone pair of neutral substrates. The cations forming from the addition of an H^+ ion are protic and those from R^+ are aprotic. Aprotic ILs are characterized by a more stable and permanent positive charge on the cation while on the other hand, the positive charge of protic cations is dynamic. The distinctive characteristics of protic and aprotic ILs are summarized in Table 2.7.

Table 2.7: Characteristics of protic and aprotic ionic liquids (Plechkova & Seddon, 2008; Ghandi, 2014)

Protic ILs	Aprotic ILs
Formed by the combination of a Bronsted acid and a Bronsted base.	Formed by transfer of a non-proton to a basic site of the constituent reagents.
Formed by the addition of H+ ion	Formed by the addition of an R+ ion
Have a dynamic positive charge	Have a durable and permanent positive charge
Cation in equilibrium with neutral components	Cation not in equilibrium with neutral components

Have vapour pressure when ΔpKa <10	No vapour pressure (non-volatile)

Studies of ionic liquids have been more focused on aprotic ILs than protic ILs. However, focus into protic ILs is also increasing hastily (Plechkova & Seddon, 2008). The sudden shift towards protic ILs may be attributed to the favourable characteristics of ILs as a result of the 'free" H^+ proton (Pires, Balducci & Anouti, 2013; Menne, Vogl & Balducci, 2014) which may be manipulated for different applications in chemical bonding.

2.7.3 Imidazolium, pyridinium, ammonium and phosphonium ionic liquids

Ionic liquids may further be classified according to the chemical composition of their forming cation. There are several types of major cations which are used in the synthesis of ionic liquids. These include; imidazolium, pyridinium, ammonium as well as phosphonium cations (Ghandi, 2014).

- *Imidazolium based ionic liquids*: This class of ILs is synthesized by alkylation of an imidazole molecule to form an imidazolium cation which is then attached to a suitable anion of choice.
- *Pyridinium based ionic liquids*: Pyridinium ILs are synthesized from the alkylation of pyridine followed by subsequent addition of a desired anion.
- *Ammonium based ionic liquids*: This class is synthesized from the alkylation of ammonia followed by the addition of a suitable anion.
- *Phosphonium based ionic liquids*: Phosphonium ILs are synthesized from the alkylation of phosphine and subsequent addition of a suitable anion.

Other classes of ionic liquids based on this classification include sulfonium, pyrrolidinium, piperidinium, and morpholinium ionic liquids (Fang *et al.*, 2011). However, these are rarely found compared to the four main classes listed above. The type of cation in an ionic liquid affects a number of physicochemical properties of the IL such as viscosity, polarity,

thermal and chemical stability hence in synthesis; the combination of different cations and anions is carefully selected to manipulate the properties of the IL for different chemical and industrial applications (Jin *et al.*, 2013).

2.7.4 Hydrophilic and hydrophobic ionic liquids

Ionic liquids may further be classified according to their miscibility with water. As a result, there are hydrophylic and hydrophobic ILs (Plechkova & Seddon, 2008). The controlling factor of the miscibility of an IL with water is the nature of the anion. By carefully selecting an anion during synthesis, a resulting IL may be manipulated to be hydrophiilic or hydrophobic (Ranke *et al.*, 2009). Figure 2.18 shows some common anions used in the synthesis of ILs and classifies them according to miscibility with water, which would consequently determine whether the resulting IL would be hydrophillic or hyrdophobic.

Wate immiscible		Water miscible
$[PF_6]^-$	$[BF_4]^-$	$[CH_3CO]^-$
$[Tf_2N]^-$	$[OTf]^-$	$[HSO_4]^-$
$[BR_1R_2R_3R_4]^-$	$[N(CN)_2]^-$	$[CF_3CO_2]^-$
		$[NO_3]^-$
		Br^-, Cl^-, I^-
		$[Al_2Cl_7]^-$, $[Al_2Cl_4]^-$

Figure 2.18: Examples of common anions used in the synthesis of ILs and their water miscibility (Plechkova & Seddon, 2008)

The water miscibility or immiscibility of ILs is fundamental for different industrial applications. In the hydrometallurgical context for instance, hydrophillic ILs are important as leaching solvents as they completely mix with aqueos solutions. [Bmim][HSO_4], [Emim][HSO_4], and [Bmim][Cl] are examples of hydrophillic ILs which have been investigated as leaching solvents either as neat liquids or in aqueous solutions due to their perfect miscibility with water (Khaliq *et al.*, 2014). The immiscibility of some ILs

becomes important in their application for the extractation of metals from aqueous media. Consequently, they separate from aqueous solutions, thus making them ideal for extracting metals from leach solutions. Examples of such ILs include [Bmim][Tf_2N], [Bmim][PF_6] and cyphos 101(Park *et al.*, 2014; Alguacil, 2017).

2.7.5 Properties and use of ionic liquids in industry

Ionic liquids have a number of favourable physicochemical properties which allow them to be used in different industrial applications. These include; adaptability, selectivity, negligible vapour pressure, non-flammability, wide electro-chemical window, environmental compatibility as well as chemical and thermal stability (Fischer et al. 2011; Hernández-fernández et al. 2010). Some of these properties are described in Table 2.8.

Table 2.8: Physicochemical properties of ionic liquids (Park et al., 2014)

Property	Value
Melting point	Below 100 °C
Liquidus range	Often > 200 °C
Thermal stability	Usually high
Viscosity	Normally < 100 cP, workable
Dielectric constant	Implied < 30
Polarity	Moderate
Ionic conductivity	Usually < 10 mS/cm
Molar conductivity	<10 Scm2/mol
Electro-chemical window	Often > 4 V
Vapor pressure	Usually negligible

The properties described above are ideal for a number of industrial applications. This is further enhanced by the adaptive nature of ionic liquids. By carefully selecting an appropriate cation and anion in the synthesis of an ionic liquid, these properties may be

manipulated to adequately suit a desired application (Jin *et al.*, 2013; Plechkova & Seddon, 2008). For example, by carefully selecting cations and anions, a set of distinct ionic liquids which portray the positive properties of both protic and aprotic ionic liquids have been designed and developed. The application of ILs may be broadly categorized into solvents, electrolytes, as well as functional materials. The distinct applications are summarized in Figure 2.19.

Of interest to this research is the 'solvent' application of ILs in extraction and separation sciences. ILs have been studied for their application in the leaching of metals form their ores. Similarly, they have been investigated for downstream extraction of metals from leach liquors.

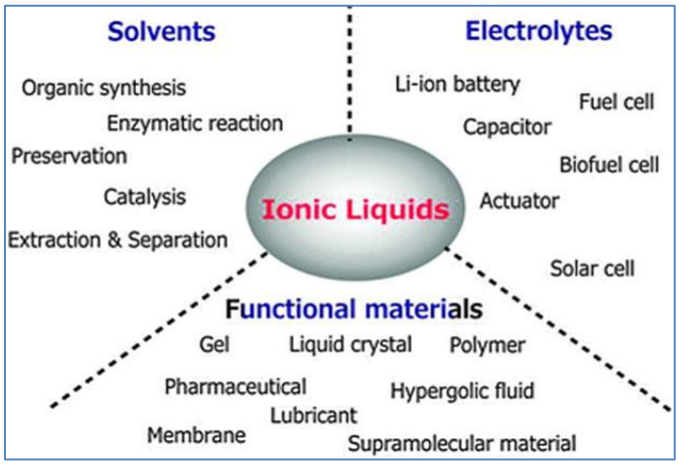


Figure 2.19: Some common uses of ionic liquids

(Source: http://www.eurare.eu/technologies/ionicLiquidExtraction.html)

2.7.5.1 Application of Ionic liquids in hydrometallurgy

Ionic liquids have been investigated for their application in different hydrometallurgical processes. Studies have been conducted for the use of ILs as leaching solvents for metals from their ores as well as their use as extractants for the extraction of metals from leach solutions by different researchers (Park *et al.*, 2014). Different researchers have reported

successes at different levels on the use of ILs in hydrometallurgy. Some of the key studies and findings relevant to this research are summarized in the subsequent sections.

2.7.5.2 Ionic liquids in leaching studies

Leaching of metals using ionic liquids as solvents has been conducted by a number of researchers (Park *et al.*, 2014). Metals which have been investigated include base metals as well as precious metals (Kilicarslan *et al.*, 2014; Whitehead, Lawrence & McCluskey, 2004; Whitehead *et al.*, 2007; Wellens *et al.*, 2014). This section presents a brief and concise summary of the successes reported by these researchers in their studies.

1-Butyl-3-methylimidazolium Hydrogen Sulphate [Bmim][HSO_4]

1-Butyl-3-methylimidazolium Hydrogen Sulphate is an imidazolium based IL with the empirical formula $C_9H_{18}N_2O_4S$ and structural formula as shown in Figure 2.20. The IL, [Bmim][HSO_4] is acidic and hydrophilic (Sigma Aldrich, 2016). While this IL has only been investigated to a less extent, the IL has a potential for use in a number of applications which include catalysis as well as hydrometallurgical applications. Its potential is further enhanced by the fact that the IL may easily be synthesized, is reusable, and less toxic (Niknam & Damya, 2009).

[Bmim][HOS_4] has been investigated as an alternative to H_2SO_4 in acidic thiourea leaching system for gold and other precious metals, with Fe_2O_3 or H_2O_2 and $KHSO_5$ as oxidizing agents (Whitehead *et al.*, 2007, 2009). The acidic and hydrophilic nature of the IL makes it ideal for use in this system as gold leaching requires acidic conditions. As stated above, the IL is less toxic and further portrays other advantages such as reusability (Whitehead *et al.*, 2007), thermal and chemical stability, environmental compatibility as properties of ILs (Ghandi, 2014) which are fundamental for sustainable hydrometallurgy. Other imidazolium ILs which have been investigated for leaching include [Hmim][HSO_4],

[Omim][HSO_4] and [Emim][HSO_4] (Poulimenou, Giannopoulou & Panias, 2015; Hu *et al.*, 2017)

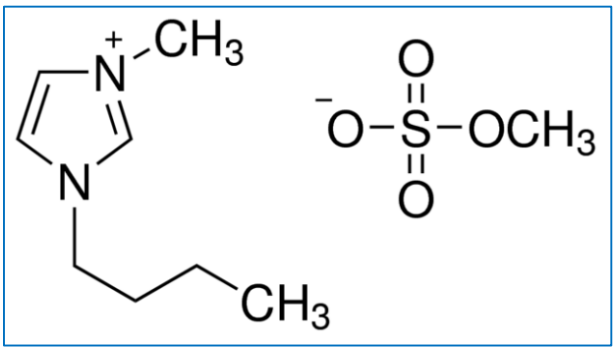


Figure 2.20: Structural formula for [Bmim][HSO_4]

Kilicarslan and Saridede (2013) investigated the leaching properties of [Bmim][HSO_4] on copper and zinc from brass waste. The study was conducted at ambient temperatures with H_2O_2 and $KHSO_5$ as oxidants. The researchers concluded that this particular IL is effective in the leaching of Zn as 99% of the metal was leached at ambient temperatures without an oxidant, while only about 24% of Cu was leached. However, with the addition of an oxidant, the leaching efficiency of Zn was above 99% while that of Cu shot from 24% to 82%. In both experiments, 50% v/v of the ionic liquid and water was used. [Bmim][HSO_4] is a hydrophilic IL and hence it has a perfect miscibility with water. This study proved that [Bmim][HSO_4] can actually be used in place of concentrated acid for the leaching of Cu and Zn from brass substrates.

An analogue of [Bmim][HSO_4] used by Kilicarslan and Saridede (2013), [Emim][HSO_4] was investigated by Davris, Balomenos and Panias (2014) for the dissolution of rare earth elements from bauxite residue, an aluminium ore which is mainly an armophous clayey rock. In their study, the researchers looked at the selective dissolution of rare earth oxides using ILs. The researchers discovered that [Emim][HSO_4] as a neat liquid, at 170^0C and 4 hours of reaction time leached about 80% of Fe, 68% of Sc, 60% of Ti and 20% of Al. However, at lower temperatures (130^0C), the dissolution of Fe was observed to be the lowest at about 5% while Al followed with 15%, Sc at 37% and Ti had the highest leaching

percentage at about 45%. This suggests that imidazolium ILs may effectively be used as a leaching agent for different metals from their ores.

More relevant to this research is the use of ILs in the leaching of precious metals, in particular Au and Ag. This topic was first invesigated by Whitehead and other researchers in 2004 (Whitehead, Lawrence & McCluskey, 2004). The researchers reported the first recovery of Au and Ag from an ore using ionic liquids. The study used [Bmim][HSO_4] to leach Au and Ag from an ore which was predominantly of chalcopyrite/pyrite/pyrrhotite/sphalerite mineralogy. In their experiments, thiourea was used as the complexing agent, Fe_2O_3 as an oxidant, and the IL acted as a solvent and pH regulator, thus eliminating the use of strong mineral acids such as H_2SO_4 during leaching. More than 85% of gold was recovered in 50 hours at ambient temperatures. This recovery is similar to that of the aqueous acidic system. Silver recovery was significantly enhanced to over 60%. From their study, the researchers concluded that the IL could be used successively after each cycle as it is recyclable.

Whitehead et al. (2007) further investigated the use of [Bmim][HSO_4] as a neat liquid or aqueous solution for the leaching of Ag, Au, Cu, and other base metals from sulphudic ores. Similar to their earlier study (Whitehead, Lawrence & McCluskey, 2004), thiourea was used as a complexing agent and Fe_2O_3 as an oxidizing agent. In this study, the IL was investigated along with its close analogues by varying the length of the alkyl chain on the imidazolium molecule as well as varying the anion from HSO_4^- to Cl^-, $CH_3SO_3^-$, $N(CN)_2^-$. The variation of the ions proved that the [Bmim][HSO_4] ion combination is the most ideal as a solvent medium in this leaching system. At ambient temperatures, gold recovery from the ore was greater than 85% while silver recovery was greater than 60%. The results showed an ehanced recovery for silver in particular, when compared to the 23% recovery rate observed in aqueous acid systems (1M - H_2SO_4) under similar reaction conditions. Eight other sulphur containing complexing agents were investigated with only two, other than thiourea, showing potential characteristics.

Subsequent to their study in 2007, Whitehead et al. (2009) conducted a comparative leaching study of Au, Ag, and other metals from sulphudic gold ore using ionic liquids and aqueous acid in the presence of a complexing agent (thiourea, Cl^-, Br^-, or I^-) and an oxidant which was either Fe_20_3 or HSO_5^-. The ILs which were used in the study were [Bmim][HSO_4] and [Bmim][Cl]. The recovery of gold and silver in thiourea and HSO_5- was greater than 85% in both [Bmim][HSO_4] and [Bmim][Cl] ionic liquids at ambient temperatures. The recoveries for other base metals were neglegible in the IL leaching system, which makes the IL described selective towards Au and Ag. In all the IL leaching studies, thiourea was used as the complexing agent as it is more selective for precious metals with high leaching efficiencies.

The positive findings from the studies as summarized above support the selection of the IL [Bmim][HSO_4] for the leaching studies of Au and Ag from electronic waste for this research. The physicochemical properties of the IL as described in preceeding sections further supports this selection.

2.7.5.3 Ionic liquids in extraction studies

A number of ionic liquids are hydrophobic and hence form biphasic systems when mixed with aqueous solutions (Plechkova & Seddon, 2008). This makes hydrophobic ILs suitable for extraction of substances from aqueous solutions. Consequently, ionic liquids have also been widely investigated as extractants for metals from leach solutions. Imidazolium, ammonium, phosphonium as well as pyridinium ILs have been used by different researchers in extraction studies of different metals with significant successes reported (Park *et al.*, 2014; Hernández-fernández *et al.*, 2010; Alguacil, 2017; Shen *et al.*, 2016)

Shen et al. (2016) investigated the use of bi-functional ILs for the extraction of rare earth metals from acidic media. From their study, the researchers determined that pH, extractant concentration and temperature have a significant effect on the extraction

efficiency of metals. This observation necessitated the consideration of these parameters for measurement and control in this research project. The study also observed that the salting out effects decreased efficiency with the increase of Na_2SO_4 but enhanced efficiency with NaCl and $NaNO_3$ in agreement with earlier researchers in ion adsorption studies. The study concluded that ILs may be successfully used in the extraction of metals from aqueous sulphate solutions.

In a related field of application, Fischer *et al.* (2011) in their study of ionic liquids in the extraction of metals from industrial effluent, concluded that this class of extractants may be used for the treatment of metal contaminated waste water. The study focused on the use of ILs based on quaternary, ammonium and phosphonium cations and thiol-, thioether-, hydroxyl-, carboxylate and thiocyanate functionalized anions. Of the total metal species extracted, the findings showed that the efficiency of ILs extraction reached 95% for Ag, Cu, Hg, and Pt. The sections below present a concise review of literature on the ILs investigated as extractants for PMs from different leach solutions. Focus is on the ILs which have been selected for investigation in this research.

[Bmim][PF_6]: 1-Butyl-3-methylimidazolium hexafluorophosphate

[Bmim][PF_6] is an imidazolium based fluorophosphate ionic liquid with the structural formula shown in Figure 2.21 (Sigma Aldrich, 2016). This IL has been investigated by a number of researchers in different applications which include extraction of precious metals from leach solutions (Park *et al.*, 2014). Katsula et al. (2015) investigated the application of different ionic liquids in the extraction of Au (III) from acidic chloride aqueous solutions. [Bmim][PF_6] was among the ILs which was investigated and the authors concluded that the IL is effective in the selective extraction of gold from chloride solutions.

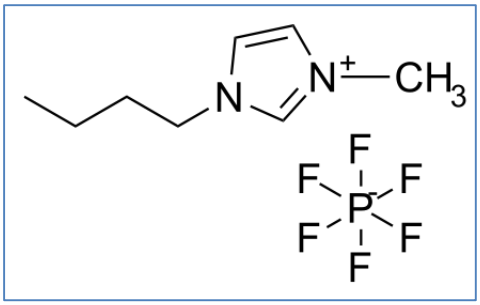


Figure 2.21: [Bmim][PF_6]

[Bmim][Tf_2N]: 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide

Similar to [Bmim][PF_6], [Bmim][Tf_2N] (Figure 2.22) is also a hydrophobic imidazolium IL (Sigma Aldrich, 2016). Due to its hydrophobicity, the IL is ideal for extraction as it forms a biphasic system when mixed with aqueous media. Consequently, the IL has been investigated by different researchers for its application in solvent extraction of different metals from aqueous media (Hernández-fernández *et al.*, 2010; Park *et al.*, 2014). Katsuta *et al.* (2016) investigated the use of eleven different aprotic ionic liquids for the extraction of Au(III) from chloride solution at room temperature. Among these ILs was [Bmim][Tf_2N], which is an imidazolium base IL. From their study, the researchers concluded that [Bmim][Tf_2N] was an effective IL for the selective extraction of gold from chloride solutions.

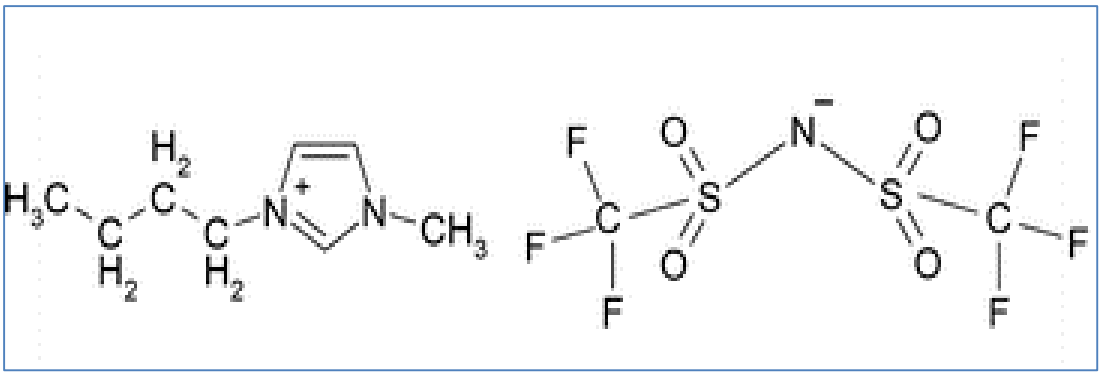


Figure 2.22: [Bmim][Tf_2N]

Cyphos 101 IL: Trihexyl(tetradecyl)phosphonium chloride

Cyphos 101 (Figure 2.23) is a phosphonium-based chloride ionic liquid. The IL is hydrophobic with a high chemical and thermal stability (Sigma Aldrich, 2016), which are some of the properties that make Cyphos 101 IL suitable for extraction of metals from aqueous media. The IL has been investigated by different researchers for its use in the extraction of Au(III) from leach solutions with significant successes reported (Alguacil, 2017; Makertihartha *et al.*, 2017)

Navarro *et al.*, (2012) investigated the recovery of gold (III) from chloride solutions using Cyphos 101 IL immobilized on Amberlite AXD-7. From their study, the researchers concluded that Cyphos 101 IL was effective as an extractant for Au (III) from chloride solutions. Au (III) was extracted from the aqueous solution by an ion exchange mechanism which involved the binding of the Au (III) chloro-complex to the phosphonium cation on the IL. The sorption on the system was favourable with capacities of 160 mg of Au per gram in a 0.01 M of HCl solution. These findings show that Cyphos 101 IL can be used for the extraction of gold complexes from aqueous solutions and they inform the selection of Cyphos 101 as an extractant in this research.

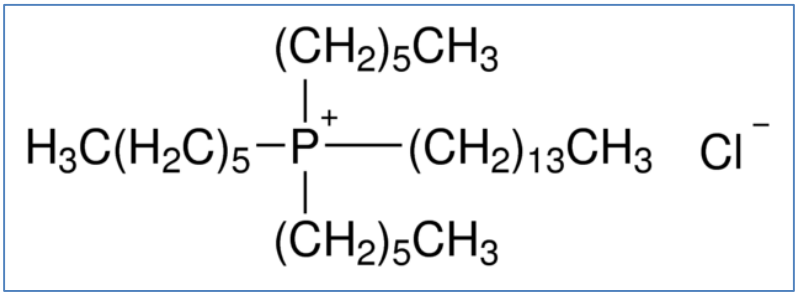


Figure 2.23: Cyphos 101 IL

Similar to the study by Navarro *et al.* (2012), (Campos *et al.*, 2008) conducted a study to investigate the use of IL Cyphos 101for the extraction of Au(III) from chloride solutions. The IL was immobilized on biopolymer capsules. In their study, the researchers conducted liquid/liquid extraction experiments as a first set of experiments followed by

experiments of the IL immobilized on the biopolymer capsules. The sorption of Au (III) reached 140 mg/g of Au in 1 M HCl solutions. These findings also show that the IL is effective in the selective extraction of gold from leach solutions as other base metals did not interfere in the selective extraction of Au.

2.8 Conclusion

The literature presented in this dissertation is adequate evidence that electronic waste is a considerable secondary source of metals which may be recovered. This is substantiated by the volumes of metals which have been reported to be found in e-waste as well the metal demand by the electronic industry. While there are a number of methods which are used in the recovery of metals from electronic waste, these have considerable limitations which include low efficiencies, high costs as well as environmental and health impacts. The environmental and health impacts associated with electronic waste as well as some recycling technologies are a critical drive towards the investigation into more efficient and environmentally benign processes. The description of ionic liquids and their favourable physicochemical properties show that these reagents may be used as alternatives to a number of toxic and environmentally damaging reagents used in hydrometallurgy – in particular for the recycling of metals from electronic waste. This conclusion supports the rationale of this research, which is to investigate the applicability of these novel reagents in leaching and extraction of metals from electronic waste. The experiments conducted, and results obtained are presented in the next chapter.

Chapter 3

EXPERIMENTAL PROCEDURE

3.1 Introduction

This chapter presents and discusses the experimental phase of this research. Sections covered include the experimental design, reagents and materials, experimental set-up and analytical methods which were used in this study.

3.2 Materials and Reagents

This section gives a comprehensive description of the materials as well as reagents which were used in this study.

3.2.1 Sample – high grade PCB powder:

The sample was a high grade crushed PCB powder and was sourced from Desco Electronic Recyclers, an electronic waste dealer in Kempton Park, Johannesburg, Republic of South Africa. This sample was selected based on the fact that a high grade PCB sample is typically rich in a wide range of metals including precious metals (Desco Electronic Recyclers, 2016). The sample came mainly from ICT electronic waste which includes computer circuit boards and mobile phones. E-waste was dismantled and PCBs sorted separately for further crushing by the supplier. PCB sorting involves the classification of PCBs into high grade, medium, and low grade PCBs based on their metal content, with high grade PCBs having the highest metal content. The sample was shredded and ground to 1mm particle size of ~40% metal and 60% other material.

For characterization, the sample was analysed by Mintek laboratories in Randburg, Johannesburg. The ICP results for the metal composition of the sample are presented in Tables 3.1 and 3.2.

Table 3.1: Concentration of different metals in PCB sample (1mm particle size)

Metal	Al	Ca	Cr	Cu	Fe	Mg	Mn	Ni	Pb	Si	Ti	Zn
Composition (%)	4.7	6.1	0.1	26.7	6.7	0.2	0.6	0.6	1.2	11.2	0.5	0.8

Table 3.2: Precious metal content in the PCB sample (1mm particle size)

Metal	Ag	Au	Pd	Pt
Content (ppm)	618	162	55.5	0.44

The results in Tables 3.1 and 3.2 are in consensus with literature which states that copper is the most abundant metal in PCBs (Dimitrijevi *et al.*, 2013; Khaliq *et al.*, 2014). In the sample, copper had the highest composition at 26.7%. Other metals of abundance include iron, calcium and aluminium as shown in Table 3.1. The precious metals under investigation are also found in considerable amounts in the sample. Gold was at 162 g/t while silver was at 618 g/t (Table 3.2), which falls within the ranges reported by different researchers studying e-waste and PCBs (Dimitrijevi *et al.*, 2013; Cui & Anderson, 2016; Chehade *et al.*, 2012). Other precious metals which were detected during the analysis were Pd and Pt.

3.2.2 Reagents

All reagents used in the experiments were of analytical grade and were purchased from Merck and Sigma Aldrich. Unlike technical or laboratory grade reagents, analytical grade reagents are reagents of high purity and are ideal for use in a wide range of analytical assessments (Sigma Aldrich, 2016). This is because analytical grade

reagents have extremely low levels of impurities, typically less than 1% while technical grade reagents may have higher levels of impurities. A summary of the reagents used in the study is given in Table 3.3.

Table 3.3: List of reagents

Experimental Phase	Leaching/Extraction system	Reagent	Purpose	Source
Leaching	Aqua Regia	32% Aqua HCl	Lixiviant for acid leaching	Sigma Aldrich
		55% HNO_3	Oxidant for acid leaching	Merck
	Organic Acid	Glycine	Lixiviant	Merck
		Histidine	Lixiviant	Sigma Aldrich
		H_2O_2	Oxidant	Merck
		NaOH pellets	NaOH solution pH regulator	Sigma Aldrich
	IL Leaching	[Bmim][HSO_4]	Leaching IL & pH regulator	Sigma Aldrich
		Fe_2O_3	Oxidant	Sigma Aldrich
		Thiourea	Complexing agent	Merck
Extraction	IL Extraction	[Bmim][Tf_2N]	Extractant IL	Sigma Aldrich
	IL Extraction	[Bmim][PF_6]	Extractant IL	Sigma Aldrich
	IL Extraction	Cyphos IL 101	Extractant IL	Sigma Aldrich

3.3 Experimental Plan

The experiment was conducted as a series of steps which included crushing, pulverization, leaching, extraction and analysis. Three different leaching systems were used as summarized in Figure 3.1 and 3.2.

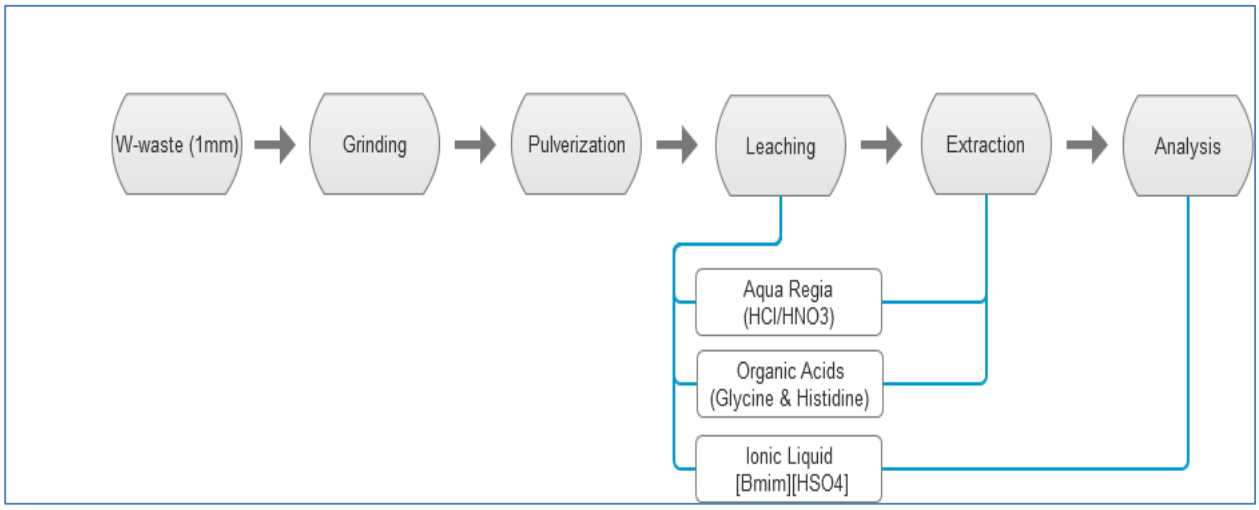


Figure 3.1: Experimental Flow Chart

As previously stated, three leaching systems were used in the experiments. In the aqua regia system, HCl provided the Cl^- ion which acts as a lixiviant and HNO_3 yielded the NO^- ion, which acts as the oxidant in the aqua regia system (Dimitrijevi *et al.*, 2013). The aqua regia system was selected because of its well-studied leaching kinetics and efficiency in the leaching of different metals including precious metals. It was used as a baseline for the leaching experiments with the main objective of getting chloride leach liquor, which will be then used in the subsequent extraction experiments to investigate the applicability and efficiency of ionic liquids for precious metal extraction from chloride leach liquor obtained from leaching PCBs.

The second system used amino acids (glycine and histidine) as lixiviants and H_2O_2 as the oxidant (Oraby & Eksteen, 2015). The corrosive nature and toxicity of mineral acids as well as other leaching reagents such as cyanide remains one of the major challenges facing their applications in metallurgy (Perkins *et al.*, 2014; Cui & Anderson,

2016). As a result, the organic acid system was selected as an alternative leaching system for precious metals in this study. Organic acids are less toxic and have a lower environmental footprint compared to their inorganic counterparts (Oraby & Eksteen, 2015). Organic acids thus, remain as one of the key potential lixiviants in the leaching of precious metals from solid sources.

The third leaching system used an Ionic liquid [Bmim][HSO_4], thiourea as a lixiviant and Fe_2O_3 as an oxidant (Whitehead *et al.*, 2007). The ionic liquid [Bmim][HSO_4] acts as the leaching solvent and pH regulator in the acidic thiourea leaching system. It also acts as an alternative to H_2SO_4 in the conventional acidic thiourea system. This eliminates the use of toxic and corrosive H_2SO_4 as a mineral acid. The other main advantage of using the IL is that [Bmim][HSO_4] is recyclable as an ionic liquid and has other benefits which include higher leaching efficiency of silver in gold-silver ores compared to the H_2SO_4 system (Whitehead, Lawrence & McCluskey, 2004). Consequently, ionic liquids are at the centre of research for different applications because of their distinct properties as discussed in preceding sections. The leaching and extraction experiments are summarized in Figure 3.2 (page 73).

While the solid: liquid ratio in the experiments above was kept constant, the leaching time used for leaching experiments was varied as informed by previous experiments and knowledge found in literature. Different researchers used different time durations for the leaching of PMs in the three different leaching systems under study; aqua regia, organic acids, and ionic liquids [Bmim][HSO_4], and ultimately recommended optimum leaching times for each of these systems (Whitehead *et al.*, 2007; Oraby & Eksteen, 2015; Sheng & Etsell, 2007).

3.3.1 *Experimental parameters*

The sections below describe the parameters which were selected for investigation in both the leaching and extraction experiments. The leaching parameters are discussed according to the three different leaching systems used.

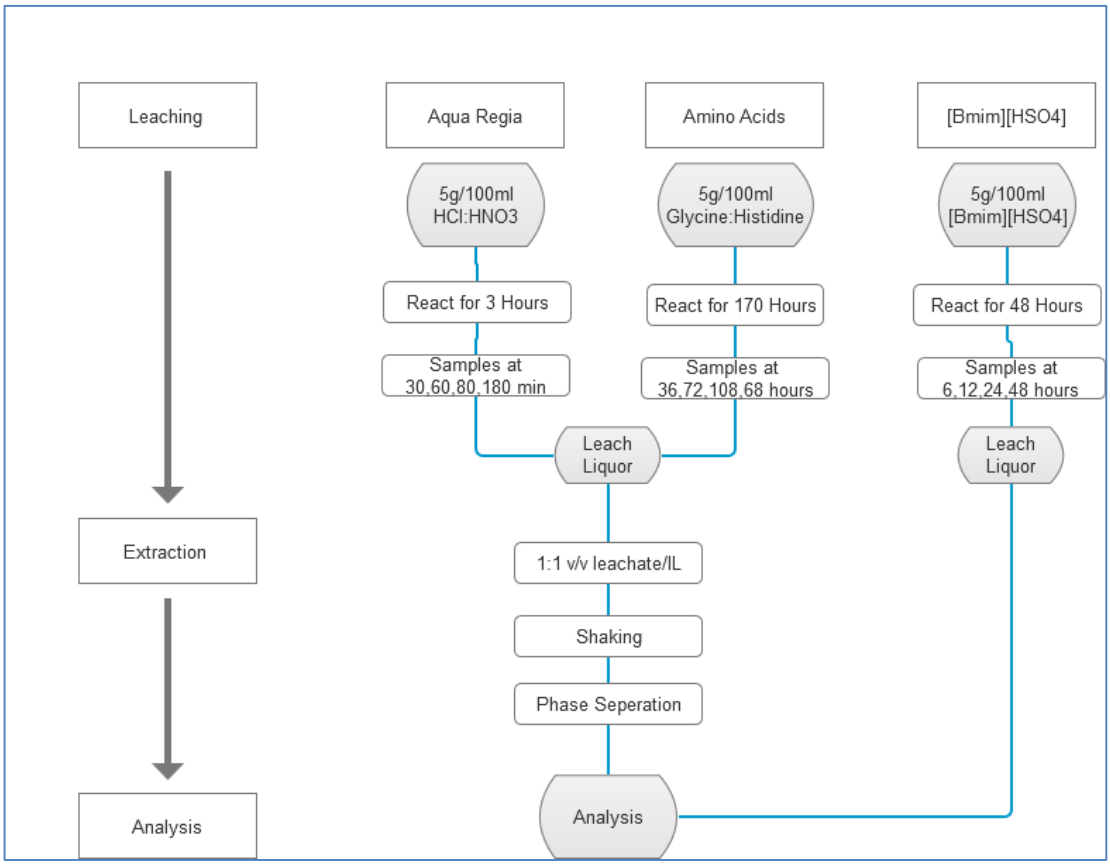


Figure 3.2: Leaching and Extraction Flow Sheet

3.3.2 *Aqua regia leaching*

Leaching with aqua regia was performed as a baseline leaching experiment since aqua regia is a common leaching system for precious metals. For this reason, there was no research need to vary leaching conditions with aqua regia and optimal conditions as these are found in literature (Sheng and Etsell, 2007; Dimitrijevi *et al.*, 2013) The

leaching experiments were only aimed at investigating the reaction kinetics of aqua regia under ambient conditions and also attaining chloride leach liquor which would be used in the investigation of solvent extraction with ionic liquid, which is the basis of this study. The leaching conditions which were used with aqua regia during the leaching experiments are shown in Table 3.4, and the solid:liquid ratio used was 5 g/100 ml.

Table 3.4: The leaching conditions for aqua regia leach experiments

Exp	Fixed	Variable	Rationale	Replicates	Sampling time (mins)
1	Temp: 25^0C Acid Conc. 32%HCl:55%HNO_3	Time	Investigate the reaction kinetics for aqua regia	2	30,60,120,180

This experimental set-up sought to analyse the concentration of precious metals in samples taken at the stated times for the two replicates. This would allow the plotting of the concentration time graph for aqua regia leaching, which would make it possible to verify that the reaction reached equilibrium at three hours as anticipated. This experiment would also yield the leach liquor for extraction studies. The sample at time (180 min) was expected to be the highest concentration of PMs assuming that the concentration of PMs in solution increased with time; hence it was selected as the sample time to be used for extraction experiments with the different ionic liquids.

3.3.3 Organic acid leaching

The leaching of precious metals using organic acids is a novel technique in hydrometallurgy. The system has only been investigated mainly on a pyrite ore and has not been investigated on e-waste (Oraby & Eksteen, 2015). The chemical composition of e-waste is different from that of pyrite. Consequently, a number of parameters were studied in this experiment to better investigate the efficiency of the organic acid

leaching system as well as the main factors which affect the leaching kinetics in this system. Some of the main factors which affect reaction kinetics as reported by Oraby and Eksteen (2015) included type of acid, concentration, temperature and time. The experimental design for these experiments is summarized in Table 3.5, and the solid;liquid ratio used was 10 g/200 ml.

Table 3.5: Experimental conditions for organic acid leaching

Exp. #	Fixed	Variable	Conditions	Rationale	Replicates	Total samples
1		Concentration	0.1 M glycine 0.5 M glycine 1.0 M glycine	Investigate the effect of concentration of acid on leaching	2	6
2		Acid combination	0.1 M glycine 0.1 M of 1:1 Glycine: Histidine	Investigate the synergistic effect of histidine on glycine	2	4
3		Temperature	25^0C 40^0C 65^0C	Investigate the effect of temperature on leaching	2	6
	pH		12			
	H_2O_2		5% wt/wt			
	Agitation		100 rpm			

All the experiments in 1 and 2 as shown in Table 3.5 were conducted at constant temperatures of 25^0C. Experiments in 3, where the effect of temperature variability was investigated were conducted at different temperatures; 40^0C and 65^0C as informed by the findings of Oraby & Eksteen (2015) that higher temperatures enhance the leaching of PMs in organic acids. 5% H_2O_2 was also used on all experiments as an oxidizing agent. To enhance the oxidizing capacity of H_2O_2 in the system, the pH of the leaching

system was also kept constant at pH 12 by adding NaOH solution. The glycine and peroxide leach medium is sensitive to the pH and the presence of hydroxide ions in solution (Oraby & Eksteen, 2015). NaOH activated the peroxide, and as H_2O_2 decays, it forms more hydroxide ions, hydroxide radicals and oxygen. Besides the oxidizing conditions which result from the decomposition of the activated peroxide, the hydroxide radicals further enhance gold dissolution as gold forms the gold-glycine complex (Nowicka et al. 2010) as cited by Oraby and Eksteen (2015).

3.3.4 Ionic liquid leaching

The use of ionic liquids such as [Bmim][HSO_4] in leaching experiments is a new development in leaching sciences (Whitehead *et al.*, 2007). For ionic liquid leaching, the parameters which were investigated were; time and ionic liquid concentration. Temperature was kept constant at 25^0C as Whitehead *et al.*, (2009) reported that increasing the leaching temperature has no effect on gold leaching and only a 10% increase in leaching efficiency is achieved for silver, from 60 to 70%. For thiourea and Fe_2O_3, constant quantities of 20 g/kg thiourea/ sample, and 0.4 g Fe_2O_3/sample were used as noted by Whitehead *et al* (2007). The leaching conditions for ionic liquid samples are summarized in Table 3.6.

Table 3.6: Experimental conditions for IL leaching experiments

Ex.#	*Fixed*	*Variable*	*Conditions*	*Rationale*
1	Temp. 25^0C	Concentration	10% IL solution 20% IL solution 50% IL solution	Investigate the effect of concentration of IL on leaching

For each of the experiments, samples were taken at 6, 12, 24 and 48 hours to investigate the reaction kinetics for the leaching of PMs in the IL-thiourea system.

3.3.5 Ionic liquid extraction

For extraction by IL from the leach solution, aliquot samples with the highest concentration of PMs (those taken at the last sampling time with the assumption that concentration increased with time) were used for extraction experiments. Parameters which were investigated were as follows;

- Type of ionic liquid: Different ionic liquids perform differently in the extraction of different metals from different aqueous media. Varying the type of ionic liquids would lead to understanding the efficiencies of the different ionic liquids when used as extractants for PMs.

- Type of aqueous media: Leach liquors for the PMs in these experiments are chloride based, glycine and glycine-histidine based. Using these different leach liquors would lead us to understand if the type of leach liquor used affects the action of the ionic liquid during extraction from aqueous media.

- Volume ratio of IL and sample: The volume ratio of the ionic liquid to the aqueous leach liquor (IL:A) were varied from 1:3, 1:2, 1:1, to 2:1 in order to investigate the effect of the volume ratio of the IL in extracting the PMs from the leach liquor.

- Extraction temperature: Ionic liquids are viscous, which may affect the mobility of their molecules and hence their ability to extract PMs from the leach solutions. Varying the temperature would affect the viscosities of the ILs and hence their mobility which may in turn, affect the action of the ILs in extraction.

The extraction time was kept constant at 15 minutes. This was in line with Tong *et al.* (2013) who investigated the effect of time of extraction efficiency of ILs from chloride leach solutions. The researchers varied the extraction times from 1 to 28 minutes and recorded 98.5% extraction within the first minute. Consequently, the researchers concluded that 5 minutes was the best adequate time for complete extraction. Since the extraction

experiments are from different leach solutions in this research, a longer extraction period of 15 minutes was preferred.

3.4 Experimental methods

The section below summarizes the methodology used in the leaching of metals from PCB powder as well as their extraction from leach liquor.

3.4.1 Crushing and grinding:

The 1 mm PCB sample as sought was ground in a ball mill to reduce the particle size from 1 mm to the desired particle size. The sample was then screened using a vibrating screen to separate the fraction -106 µm to +45 µm, which was used in all the experiments in the following sections. This is because this fraction has the highest distribution of gold (Whitehead *et al.*, 2007) and a large surface area for leaching.

3.4.2 Leaching:

All leaching experiments were performed under fume hood as toxic gases are evolved during the leaching processes.

3.4.2.1 *Aqua Regia:*

Using the ratio 1g:20ml (Sheng and Etsell, 2007), two replicate samples of 10 g sample powder and 200 ml aqua regia ($3HCl:1HNO_3$) were added into a 500 ml Erlenmeyer flask. The reaction was run under the fume hood for 3 hours at room temperature (25^0C). No heating or agitation was done to the reaction. The reaction is exothermic hence there was no need for further heating. Agitation was natural and caused by the evolution of nitrous gases. Four samples per replicate were drawn during the progression of the reaction using a glass pipette at 30, 60, 120, and 180 min. These were filtered through a 0.22 µm

PES syringe filter and transferred to glass sample bottles for extraction and analysis. The pH and Eh of the reaction was measured and recorded throughout the duration of the experiment.

Figure 3.3 shows aliquots of aqua regia samples after leaching of the printed circuit board sample.

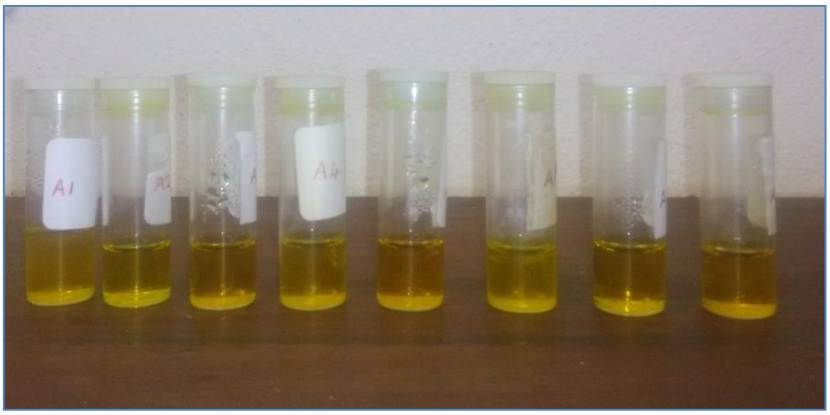


Figure 3.3: Aqua regia leach liquor samples

3.4.2.2 Amino Acids:

Leaching with amino acids used different combinations, concentrations and temperatures to investigate the effects of these on the reaction kinetics and efficiencies.

- To investigate the effect of acid combination, one experiment was undertaken with glycine while the other was leached with a mixture of 1:1 of 0.1M glycine and 0.1M histidine.
- To investigate the effect of concentration, 0.1M, 0.5M, and 1M glycine solutions were used in the leaching tests.
- To investigate the effect of temperature, experiments were run at 25^0C, 40^0C and 65^0C.

For each of the experiments above, 10 g: 200 ml of solid: liquid ratio was added to a 500 ml Erlenmeyer flask. The solid was the PCB sample while the liquid was the leaching solvent. The leaching solvent was prepared by dissolving the organic acid in

deionized water in volumetric flasks with 5% H_2O_2 as described below. The pH of the solutions was measured then adjusted to alkaline pH of 12 using NaOH solution. These were then shaken in a shaker for 160 hours with samples taken through the duration of the experiments. The samples were then filtered through a 0.22 µm PES syringe filter and transferred to glass sample bottles for subsequent extraction studies and analysis. The pH and Eh of the reaction was measured and recorded throughout the duration of the reaction.

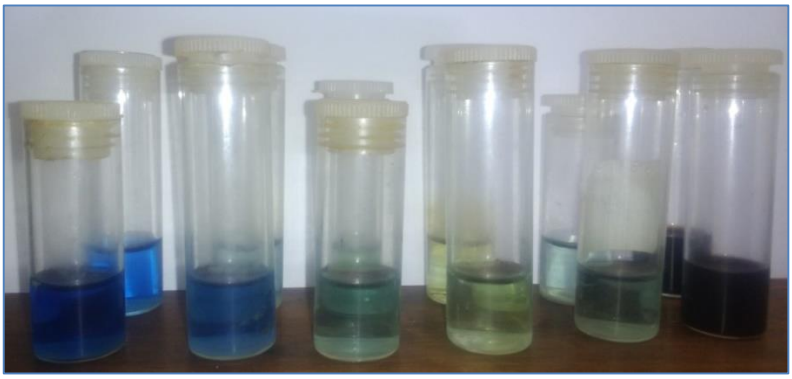


Figure 3.4: Glycine & histidine leach liquor samples

Figure 3.4 shows aliquots of glycine and histidine samples after leaching of the printed circuit board sample. The blue coloured (light blue to navy blue) are glycine leach liquors of different concentrations while the black liquor on the far right is a glycine - histidine leach liquor.

The experimental reagents were prepared as below;

Glycine: 1M glycine was prepared by accurately weighing 75.07 g of glycine granules and transferring it to a 1000 ml volumetric flask. This was filled to volume with deionized water. Lower molarities were prepared by proportionally diluting 1 M glycine with deionized water to the desired concentrations.

Histidine: 1 M histidine was prepared by accurately weighing 15.52 g of histidine granules and transferring it into a 100 ml volumetric flask. This was then filled to volume with deionized water.

Sodium hydroxide: 16 M NaOH solution was prepared by accurately weighing 320 g of NaOH pellets and transferring it into a 500 ml volumetric flask. This was then filled to volume with deionized water.

3.4.2.3 [Bmim][HSO_4] and thiourea:

For the ionic liquid leaching approach, the concentration of the ionic liquid was varied and the concentrations, 10%, 20%, and 50% of the ionic liquid in water was used to investigate the effect of the concentration on reaction kinetics and leaching efficiency.

10 g of the PCB sample was added into a 500 ml Erlenmeyer flask followed by 200 ml of ionic liquid solution of different concentration per experiment. 0.01 grams Fe_2O_3 and 0.5 grams of thiourea were then added. The mass for Fe_2O_3 and thiourea should be kept constant at 0.5 g/kg ore, Fe_2O_3, and 0.5 g/100 ml IL, thiourea. The reaction was agitated using a magnetic stirrer for a period of 48 hours at 25^0C with samples taken at 6, 12, 24, and 48 hours. The Eh and pH were measured and recorded throughout the duration of the experiments.

Figure 3.5 shows aliquots of [Bmim][HSO_4] leach liquor samples after leaching of the printed circuit board sample.



Figure 3.5: [Bmim][HSO_4] leach liquor samples

The experiment reagents were prepared as below;

[Bmim][HSO_4] solutions:

The following solutions were prepared with the assumption that the ILs were 100% pure.

10% solution: 10 g [Bmim][HSO_4] was weighed into a 100 ml volumetric flask and diluted to volume with deionized water. This was shaken until the IL completely dissolved in the deionized water.

20% solution: 20 g [Bmim][HSO_4] was weighed into a 100 ml volumetric flask and diluted to volume with deionized water. This was shaken until the IL completely dissolved in the deionized water.

30% solution: 30 g [Bmim][HSO_4] was weighed into a 100 ml volumetric flask and diluted to volume with deionized water. This was shaken until the IL completely dissolved in the deionized water.

3.4.3 Extraction with Ionic Liquids:

For ionic liquid extraction experiments, a volume ratio between the sample and the ionic liquid was used (IL:A). For the ratio 1:1, 2 ml of the sample and 2 ml of the IL were mixed in 15 ml centrifuge tubes. These were shaken in a shaker for 15 minutes to reach

equilibrium. They were then centrifuged at 3000 rpm for 5 minutes to attain complete phase separation. The two phases were then separated; the aqueous phase transferred into a glass sample bottle ready for analysis. Three different ionic liquids were used as extractants in the solvent extraction experiments. These were; [Bmim][Tf_2N], [Bmim][PF_6], and Cyphos IL 101. In a separate experiment, the volume of the IL to the sample was varied to investigate the effect of the IL to leach liquor ratio. The following ratios of IL to leach liquor were used; keeping the volume of the leach liquor constant at 2 ml; 1:2, 1:1 and 2:1.

To investigate the effect of temperature on the efficiency of the IL, three experiments were carried out; one at 25^0C, 50^0C and at 70^0C where Cyphos 101 was used as the extracting IL.

3.4.4 Analysis:

The samples were analysed using Flame Atomic Absorption Spectrometer (FAAS). The instrument conditions are summarized in Table 3.7 (page 84). The metals which were analysed were Ag and Au as these were the metals under study. The base metal Cu was also analysed due to its abundance in the sample. This was done to investigate the selectivity of the ILs used in the experiments in consideration of the quantities of Cu found in the sample, which is about 27% of the total sample weight. These findings are important in determining whether pre-extraction of base metals such as Cu is fundamental for the efficient recovery process of the Ag and Au from e-waste.

Table 3.7: Instrument Working Conditions

Parameter	Condition
Lamp Current	4mA
Fuel	Acetylene
Support	Air
Flame Stoichiometry	Oxidizing

Data Processing

The data collected from measurements carried out during experiments as well as results from the analysis of samples was used to calculate the efficiencies of the reagents used in both leaching and extraction. The methods used for calculating efficiencies are given in the sections below.

Leaching efficiency

To determine the leaching efficiency of a system, the total amount of the metal leached into solution should be calculated using the concentration readings from the instrument and equation 3.1. This equation converts the solution concentration in mg/L (equivalent to µg/ml) to the solid sample concentration (µg/g). The amount of leached metal in µg/g can then be compared to the initial concentration of the metal in the solid sample to determine the fraction that was leached.

$$C_f = \frac{C_i x V x D}{W} \qquad \text{Equation 3.1}$$

Where;

C_f = Final concentration of analyte in (µg/g)

C_i = AAS concentration reading in (µg/ml)

V= Volume of sample in (ml)

D = Dilution factor

W = Weight of sample in (g)

Calculating Dilution factor (D)

$$\mathbf{D} = \frac{\mathbf{V_{dil}}}{\mathbf{V_{conc}}} \qquad \textbf{Equation 3.2}$$

Where;

V_{dil} = Final volume of solution after dilution

V_{conc} = Initial volume of solution (before dilution)

After determining [C_f] for each sample from equation 3.1, the leaching efficiency may then the calculated using equation 3.3.

$$\%\mathbf{L} = \frac{\mathbf{C_f}}{\mathbf{C_T}} \mathbf{x\ 100}\% \qquad \textbf{Equation 3.3}$$

Where;

C_f = Concentration of sample after leaching in ppm (obtained from equation 3.1)

C_T = Total concentration of the metal as reported in Table 3.1 and Table 3.2

Extraction efficiency

The extraction efficiency (%E) was used to determine the efficiency of the IL in extracting the PMs from the aqueous phase. The %E of the IL was calculated using equation 3.4;

$$\%E = 100\ x\ \frac{C_x - C_y}{C_x}$$ Equation 3.4

Where C_x is PM concentration in the aqueous phase before IL extraction and C_y is PM concentration after IL extraction.

Where dilutions were conducted, concentrations before dilution for all the samples would be computed by equation 3.5. C_{dil} would be the concentration reported by the instrument, while the required concentration for calculations is the undiluted concentration (C_{conc})

$$\mathbf{C_{conc} = C_{dil} x D}$$ Equation 3.5

Where;

C_{con} = Concentration without dilution

C_{dil} = Concentration with dilution

D = Dilution factor (equation 3.2)

Chapter 4

RESULTS AND DISCUSSION

This chapter presents the results from experiments conducted in this research. It further discusses the observed results with an aim of providing solutions to the research questions. The results are presented and discussed according to the three different approaches which were taken in the experiments in an attempt to leach and extract Ag and Au from PCBs. These are leaching and extraction of the PMs through; aqua regia, Ionic liquid [Bmim][HSO_4], and organic acids – glycine and histidine. The results are presented and discussed below.

4.1 Aqua regia and ionic liquids

This section presents and discusses the results obtained from the leaching and extraction experiments based on aqua regia as a leaching system and the different hydrophobic ILs; [Bmim][Tf_2N], [Bmim][PF_6] and Cyphos 101, which were used as extractants for the PMs from the aqueous aqua regia leach liquors.

4.1.1 Leaching experiments

The leaching of Ag and Au from crushed PCBs in aqua regia at ambient temperatures proved to be an effective leaching system for both metals; Ag and Au, with leaching reaching completion within three hours of reaction time. The maximum concentration of Ag which was attained was 650 ppm and that of Au was 180 ppm after a leaching period of three hours. These values are slightly higher than the 618 ppm reported for Ag and 162 ppm reported for Au in chapter 3 as the concentration of Ag and Au in the sample. This difference may be attributed to the fact that sample characterization was

done on a sample of -1mm in particle size, while for these experiments, the -1 mm sample was further pulverized and the fraction; -106 µm to +45 µm was separated and used in the experiments. For the purpose of this research, the Ag, Au, and Cu concentrations in the solid sample obtained by leaching the -106 µm to +45 µm fraction in aqua regia were taken as sample characterization results for the sample. This is because, the fraction (-106 µm to +45 µm), according to Whitehead *et al.* (2007), has the highest distribution of PMs and an increased surface area for leaching compared to the -1 mm sample size fraction which was used at characterization. Consequently, the reason for the higher concentrations of PMs observed in the leaching experiments may be a result of the differences in particle sizes of the samples.

Figure 4.1 (page 89) shows the leaching kinetics in terms of percentage PM extracted during the leaching process in aqua regia. From the results obtained, it was observed that aqua regia is an effective reagent in the dissolution of PMs from e-waste. This may be attributed to the acidic and oxidative characteristics of aqua regia as well as the relatively low concentrations of the PMs in the PCB sample. According to Martines *et al.* (1993), an Ag-Au sample with more than 15% Ag cannot be leached in aqua regia. This is because of the passivation of the sample by the formation of AgCl. The AgCl coat formed retards further leaching of the metals, thus limiting the efficiency of extraction if the Ag concentration is greater than 15%. However, if the Ag concentration is below 15% as in the PCB sample, Ag reacts with the HNO_3 to form a soluble $[Ag]^+[NO_3]^-$ thus the leaching reaction proceeds efficiently. Au, on the other hand, complexes with free chloride ions in solution to form a stable aqueous gold-tetrachloroaurate complex $[AuCl_4]^-$.

The Au^{3+} (tetrachloroaurate complex) is the most stable complex compared to the Au^+ complex in aqua regia (Nicol, Fleming & Paul, 1987). Consequently, an Au^+ complex formed disproportionates to form the more stable Au^{3+} complex. The tetrachloroaurate complex forms under very acidic and oxidative conditions. The acidic nature of HCl and HNO_3, as well as the reaction between HCl and HNO_3 which yields NOCl and free Cl atoms are ideal for Au dissolution. NOCl and Cl atoms are strong oxidants which are

favourable for Au dissolution and the Cl atom further acts as a ligand for the formation of tetrachloroaurate complexes.

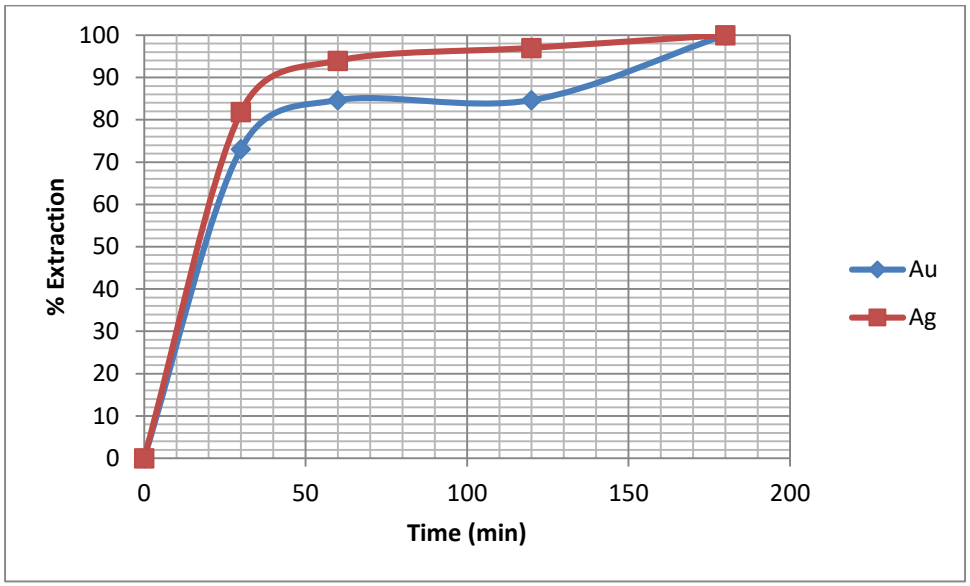


Figure 4.1: Percentage extraction of gold and silver in aqua regia

The other observation made in this experiment is the difference in dissolution rates between the two metals in the sample. The rate of Ag dissolution was faster than that of Au. After an hour into the reaction time, 94% of the Ag had already been leached while only 85% had been recorded for Au (Figure 4.1). This observation is in line with the conclusion made by Senanayake (2004) and Jeffrey, Breuer and Choo (2001) in their studies of Ag-Au leaching kinetics. The researchers state that Ag dissolution is faster than Au dissolution. Further to that, the researchers also conclude that the presence of Ag in an Au sample further enhances the rate of dissolution of Au. Jeffrey, Breuer and Choo (2001) state that the dissolution rate of pure Au in a chloride system is $1.4x10^{-5}$ mol m^{-2} s^{-1} while the rate of Au in an Ag-Au sample is $1.64x10^{-5}$ mol m^{-2} s^{-1}.

With the very high leaching efficiencies observed in Au chlorination in the form of aqua regia as well as Ag leaching, this system is effectively one of the oldest Au leaching processes with faster kinetics than the widely used cyanidation (Hilson & Monhemius, 2006). However, the invention of cyanidation in 1887 (Fleming *et al*.,1992) led to the

replacement of chlorination. The high costs associated with high chlorine consumption in the chlorination leach processes was instrumental in its replacement by cyanidation in industrial gold leaching processes, as the latter has lower costs associated with reagent consumption (Yen *et al.,* 1990; Fleming, 1992; Norman and Raforth, 1994). However, in present day, the toxicological as well as health and environmental consideration of these reagents are the critical prohibitors of their application in Au processing (U.S. Department of Health and Human Services, 2006; Hilson & Monhemius, 2006)

4.1.2 Extraction experiments

The ionic liquids used for the extraction of Ag and Au from aqueous solutions in this study displayed very high efficiencies for Au extraction compared to Ag. The results obtained from extraction experiments are discussed in the section below.

4.1.2.1 Gold Extraction

The three ionic liquids; [Bmim][PF_6], [Bmim][Tf_2N] and Cyphos 101 used in the experiments in this research as extractants displayed very high extraction efficiencies for Au. Extraction experiments were conducted on leach liquor which contained 180 ppm Au and 650 ppm Ag. The results obtained for Au in these experiments are presented and discussed in subsections below.

Type of ionic liquid and extraction efficiency

The three ILs; Cyphos 101, [Bmim][Tf_2N] and [Bmim][PF_6] were used as extractants for Ag and Au at ambient conditions. The results from the extraction experiments are presented in Figure 4.2 (page 91). Figure 4.2 shows that all three ionic liquids were efficient for Au extraction, with different percentage efficiencies recorded however.

Cyphos 101 IL was the most efficient IL for Au extraction, with the extraction efficiency of about 97%. [Bmim][Tf_2N] had the second highest extraction efficiency which was recorded at 95%, and the least efficient IL being [Bmim][PF_6] with 92% extraction efficiency. Although there are differences in extraction efficiencies between these ILs, it is important to note that the efficiencies are all above 90%. This shows that these ionic liquids may be successfully employed as extractants for Au from aqueous PCB leach liquors.

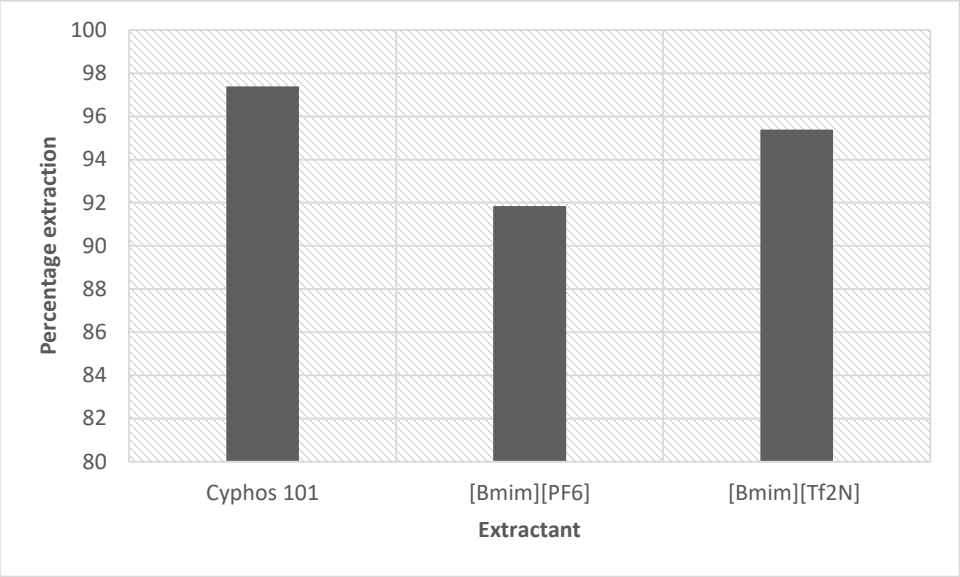


Figure 4.2: Extraction efficiency of ILs for gold in aqua regia at 25 ^oC

As already stated, Cyphos 101 shows the highest affinity for Au in chloride media. The 97% extraction recorded in this study is very close to the 95% recorded by Makertihartha *et al.* (2017) who was also investigating the use of the IL in Au extraction from chloride media. It is also important to note that immobilization of the IL on supports such as amberlite XAD-7 increases the extraction efficiency of this IL to over 99% for Au as reported by the same author. Extraction reactions of phosphonium-based ILs such as Cyphos 101 proceed through mainly anion exchange (Regel-rosocka & Wisniewski, 2011). The chloride ion of the IL is displaced by the metal chloro-complex from the aqueous phase as [$PC_{38}H_{68}^+$][$AuCl_4^-$] where $AuCl_4^-$ displaces the original Cl^- anion of the IL [$PC_{38}H_{68}^+$][Cl^-]. While Cyphos 101 shows such higher affinities for Au, it

should also be noted however that the IL has similar affinity to Pd in chloride solutions (Cieszyńska, Regel-Rosocka & Wiśniewski, 2007; Navarro *et al.*, 2012) hence the IL may not be effectively used for selective extraction from a leach solution with Pd.

The two imidazolium ILs [Bmim][PF_6] and [Bmim][Tf_2N] have the same cation and different anions which show the effect of the type of an anion on the properties of ILs as discussed in the review chapter. The [Tf_2N] IL has a higher affinity for Au^{3+} in chloride solution compared to the [PF_6] IL. The hydrophobicity as well as chemical stability of the ILs, which is largely influenced by the type of the anion may explain this observation. If the high hydrophobicity of [Tf_2N] compared to [PF_6] is considered (Cieszyńska, Regel-Rosocka & Wiśniewski, 2007), it should be expected that [Bmim][PF_6] has a higher extraction as it mixes better with the aqueous phase compared to [Bmim][Tf_2N] (Yang et al., 2014). However, the opposite was observed here as [Tf_2N] had a higher extraction compared to [PF_6]. This may further be explained by the poor chemical stability of the [PF_6]- ion in very acidic conditions (Freire et al., 2010). The $[PF_6]^-$ ion decomposes through hydrolysis of the anion thus decreasing the amount of the IL which leads to lower performance.

Temperature and extraction efficiency

Since Cyphos 101 IL showed the highest affinity for Au in chloride solutions, the effects of temperature as well as IL volume ratio was further investigated for Au extraction in chloride solutions. The effect of temperature on the efficiency of Cyphos 101 IL on extraction of Au from aqueous chloride solutions is presented in Figure 4.3 (page 93). From the Figure, it can be concluded that temperature has no significant effect on the efficiency of Cyphos 101 for the extraction of Au from aqueous solutions. There is only a difference of 1% in average between the extraction efficiency of the IL over the different temperatures used. This observation implies that the IL is adequately efficient as an extractant at ambient temperatures. Consequently, there is no significant requirement for the addition of energy to enhance the extraction process.

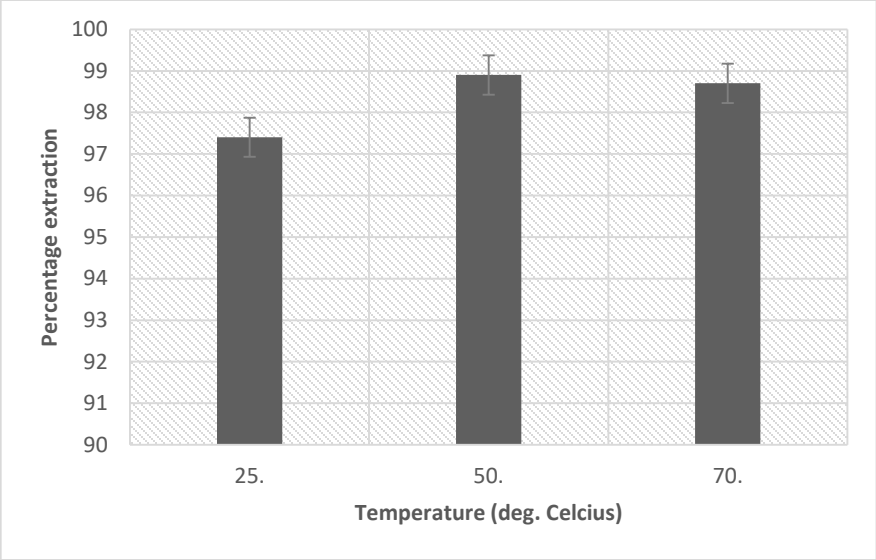


Figure 4.3: Extraction efficiency of Cyphos 101 for gold in aqua regia at different temperatures

IL: Aqueous volume ratio and extraction efficiency

The effect of the IL: aqueous sample volume ratio for Cyphos 101 in gold extraction was also investigated. Varying the IL volume ratios (Figure 4.4) shows a slight percentage increase in extraction efficiency.

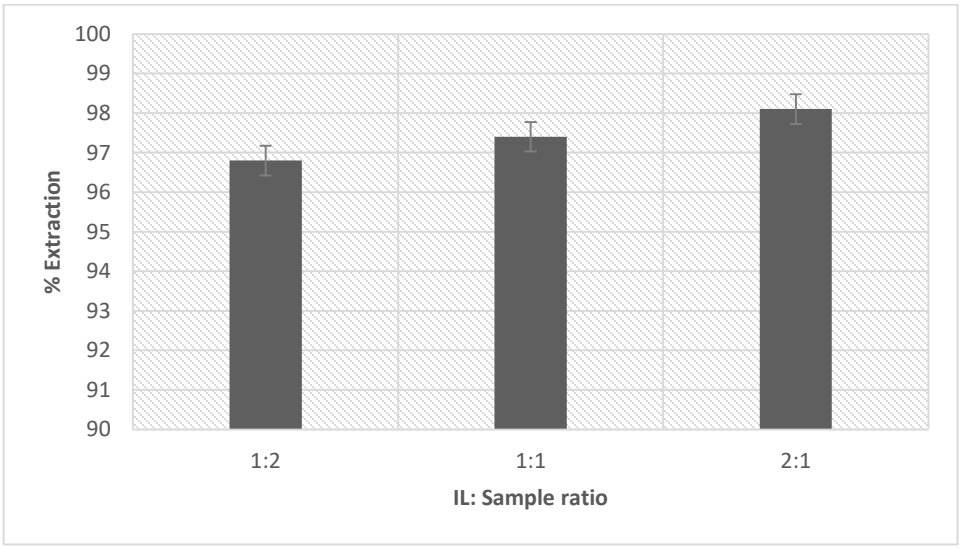


Figure 4.4: Extraction efficiency of Cyphos 101 for gold in aqua regia at different IL: aqueous ratio

When the volume ratio was 1:2, the percentage extraction of Au from aqueous solution was 96.8%. At the ratio of 1:1, the percentage extraction slightly increased to 97.4% while at the ratio of 2:1, it peaked at 98.1%. With these observations, and considering the costs of the IL, it becomes ideal to use the ratio with the lowest IL volume as the difference in extraction efficiencies between these ratios is quite minimal and may be traded for a lower volume of the IL required.

From the results of Au extraction presented above, it can be concluded that Cyphos 101 is an effective extractant for Au from chloride solutions. It is also important to note that, as already stated in previous sections, the efficiency of IL on Au extraction may further be enhanced by the immobilization of the IL on solid supports such as amberlite XAD-7.

4.1.2.2 Silver Extraction

While the ionic liquids used in the experiments in this research as extractants displayed very high extraction efficiencies for Au, Ag extraction was not as efficient. Ag was only extracted in some experiments and the extraction efficiencies were considerably lower than those for Au. The results obtained in these experiments are subsequently presented and discussed.

Type of ionic liquid and extraction efficiency

From the ionic liquids used in the experiments, only two ILs extracted Ag from the leach solutions. These were Cyphos 101 and [Bmim][PF_6]. [Bmim][Tf_2N] did not extract any silver from the leach solutions as shown in Figure 4.5 (page 95). The extraction efficiency for [Bmim][PF_6] was ~94% while that of Cyphos 101 was ~95%. These results suggest that, unlike Au where any of the three ILs may be effectively used for extraction, only [Bmim][PF_6] and Cyphos 101 may be used for Ag extraction.

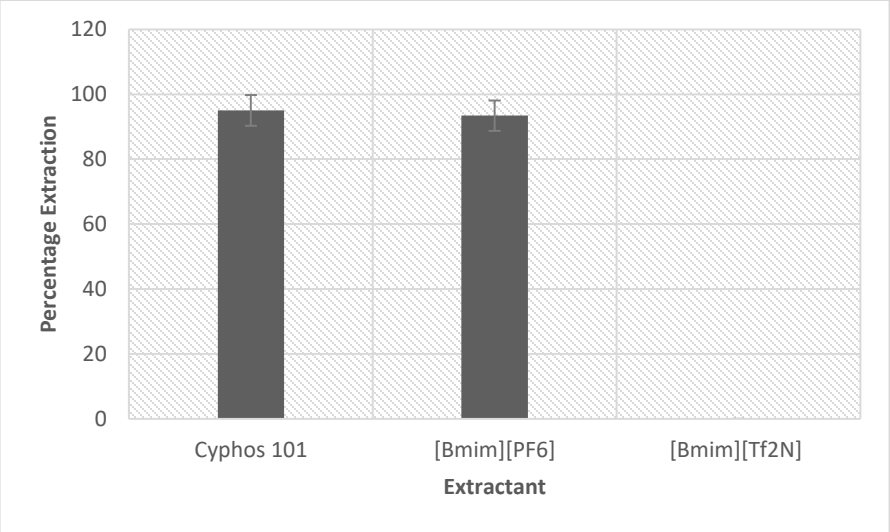


Figure 4.5: Extraction efficiency of ILs for silver in aqua regia at 25 ^{o}C

The existence of metal ions in solutions as hydrated ions or aqua-complexes (Domańska & Rękawek, 2009; Guo-cai, Jian & Yi-xin, 2010) leads to the inefficient extraction of these metals from solutions using hydrophobic ILs. Soluble Ag^{+} ions (from $AgNO_3$ formed in aqua regia) exists as $[Ag(H_20)_n]^{+}$ in aqueous solutions (Persson, 2010; Senanayake, 2004). This nature of the ion may explain why the extraction of Ag was lower compared to that of Au. The ILs used in the extraction experiments, in particular [Bmim][Tf_2N], are hydrophobic. Consequently, they would have lower affinities for hydro-complexes due to their hydrophobicity. The more hydrophobic the ionic liquid is, the lower the affinity of the IL towards hydro-complexes in aqueous solutions. To enhance extraction of hydrated metal complexes using ILs, a complexing agent which dissolves in the IL may be added. This agent dehydrates the metal ion and forms a new complex which is then extracted by the IL (Regel-rosocka & Wisniewski, 2011; Joskowska & Hupka, 2008). Au, on the other hand, exists as a soluble chloro-complex in the system hence the hydrophobicity of the IL does not affect its affinity toward the Au chloro-complex while AgCl is generally precipitated from solution and not available for solvent extraction.

In order to enhance the affinity of hydrophobic ILs towards metals which form hydro-complexes, a special type of ligand may be added to the aqueous solution. The ligand dehydrates the metal hydro-complex forming a new non-hydrous complex which the IL

would have a higher affinity to. Alternatively, a less hydrophobic IL may be employed. However, the latter option compromises the desired property of hydrophobic ILs in separation processes where the extractant must be immiscible with the aqueous phase to facilitate complete phase separation after extraction. Consequently, addition of a ligand in aqueous solutions for the extraction of metals such as Ag is the most preferred option. The extraction of Ag from solution in the presence of a ligand reaches 99% as reported by Domańska and Ręka wek (2009).

The extraction efficiencies of the ILs Cyphos 101 and [Bmim][PF_6] are a breakthrough in replacing organic extractants in hydrometallurgy for e-waste. However, the non-selectivity of the ILs Cyphos 101 and [Bmim][PF_6] between Ag and Au is of concern as these metals may not be selectively extracted because the two ILs extract them simultaneously from solution. The complete failure of [Bmim][Tf_2N] to extract Ag from the leach liquor (Figure 4.5, page 95) comes as a solution to this limitation. Since [Bmim][Tf_2N] was able to extract ~96% Au at ambient temperature (Figure 4.2, page 91) and no extraction was recorded for Ag (Figure 4.5), this IL, due to its selectivity for Au, may be used to selectively extract Au from solution leaving the Ag in solution. The other IL, [Bmim][PF_6] may then be used to extract the remaining Ag in solution due to its affinity for Ag ~94% at ambient conditions (Figure 4.5). Through this process, the selective extraction of Ag and Au from leach liquor would have been achieved.

Temperature and extraction efficiency

The effect of temperature on the efficiency of Cyphos 101IL and [Bmim][PF_6] on the extraction of Ag from aqueous solutions was also investigated. The results from the experiments are presented on Figure 4.6 (page 97).

From the results, it may be concluded that for Ag extraction, temperature again, has an insignificant effect on the efficiency of the ILs on the extraction of Ag from aqueous

solutions. This is evident in that there is no considerable change in extraction efficiency at elevated temperatures. The efficiency only increases slightly over the ranges of temperatures which were investigated. Consequently, with the excellent efficiencies displayed by Cyphos 101 and [Bmim][PF_6] at ambient temperatures, the ILs are recommended for extraction at ambient temperatures. This is of significant importance as processes which are efficient at ambient temperatures mean that there are no additional energy costs on them.

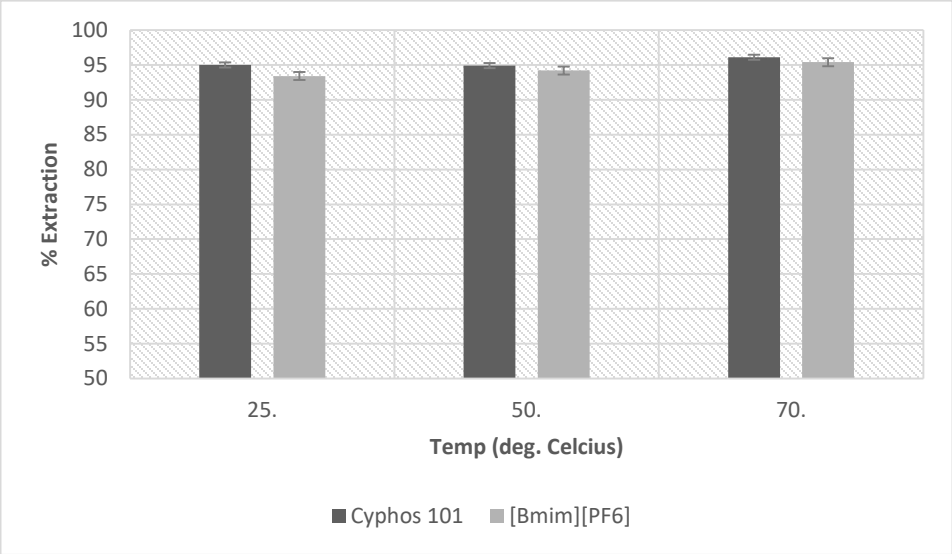


Figure 4.6: Extraction efficiency of Cyphos 101 for silver in aqua regia at different temperatures

IL: Aqueous volume ratio and extraction efficiency

The IL: Aqueous ratio was also investigated for Cyphos 101 to determine the minimal IL volume which gives the desired extraction efficiency. Only Cyphos 101 was investigated as the two ILs (Cyphos 101 and [Bmim][PF_6]) had comparable efficiencies for Ag extraction. When the IL: Aqueous volume ratio was varied, there were significant differences in extraction of Ag by the IL. When the volume ratio was 1:2, the percentage extraction of Ag from aqueous solution was 0% as there was no extraction detected.

However, at a ratio of 1:1, the percentage extraction sharply increased to 95%, while at a ratio of 2:1, it peaked at 97% (Figure 4.7).

With these observations, it may be concluded that the IL: Aqueous volume ratio has a significant effect on Ag extraction unlike in Au extraction. However, a 1:1 volume ratio between the sample and the IL is recommended based on these results. There is only an insignificant difference in the extraction efficiency between these two ratios, hence the ratio requiring the least volume of the IL is preferred. The effect on the concentration of the metals on the volume of the IL required for efficient extraction was however not investigated. This opens another avenue for further research in the field in order to ascertain if the concentrations of Au and Ag in solution affect the volume of the IL required for total extraction.

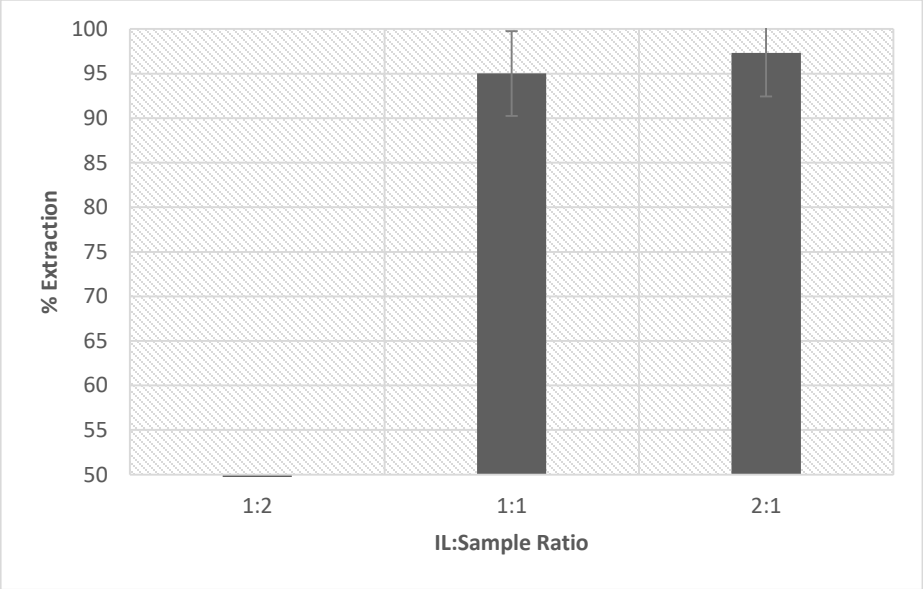


Figure 4.7: Extraction efficiency of Cyphos 101 for silver in aqua regia at different IL: Aqueous ratio

4.1.2.3 Extraction of Copper

Since the PCB sample was found to have a high concentration of Cu (~26% wt/wt), the investigation into the extraction of Cu by the ILs used in the experiments was fundamental. Extraction of Cu was conducted using a volume ratio of 1:1 between the sample and the IL at ambient conditions. The initial Cu concentration in the sample was 200 ppm Cu. The results from the analysis of Cu extraction from different ILs are presented in Figure 4.8.

The observations made from these experiments (Figure 4.8) show that Cu is directly loaded on to the ILs with Cyphos 101 having the highest loading. These observations show that the three ILs (Cyphos 101, [Bmim][PF_6], and [Bmim][Tf_2N]) proposed for Ag and Au extraction from aqua regia leach solutions are not adequately selective for these metals as they displayed high affinities for Cu as well.

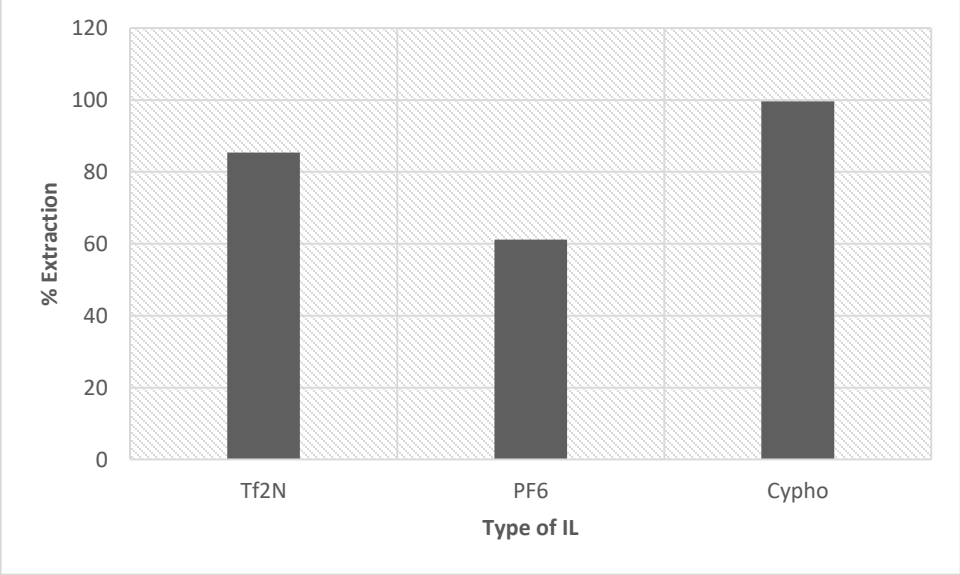


Figure 4.8: Extraction of Cu in different ILs

The comparison between the performances of these ILs is thus presented below with an aim of identifying a suitable IL for each application in the extraction of the metals; Ag and Au from leach solutions. Figure 4.9 (page 100) shows the different extractions

of these ILs for the three metals; Ag, Au, and Cu at ambient conditions using a sample:IL ratio of 1:1.

Figure 4.9 shows that of the three ILs investigated, Cyphos 101 has the highest affinity for all three metals which were investigated, with more that 90% efficiency for all three metals; Ag, Au and Cu. This means that even though the IL is effective in Ag and Au extraction as desired, of the three ILs, Cyphos 101 has the lowest selectivity for Au and Ag due to its very high affinity for Cu, which is 99%. Consequently, the IL may not be recommended for use in the selective extraction of Au and Ag from e-waste leach solutions in aqua regia.

Pre-removal of other metals such as Cu from the sample before Ag and Au extraction would thus, be fundamental if Cyphos 101 was to be used as an extractant for Ag and Au from the leach solution.

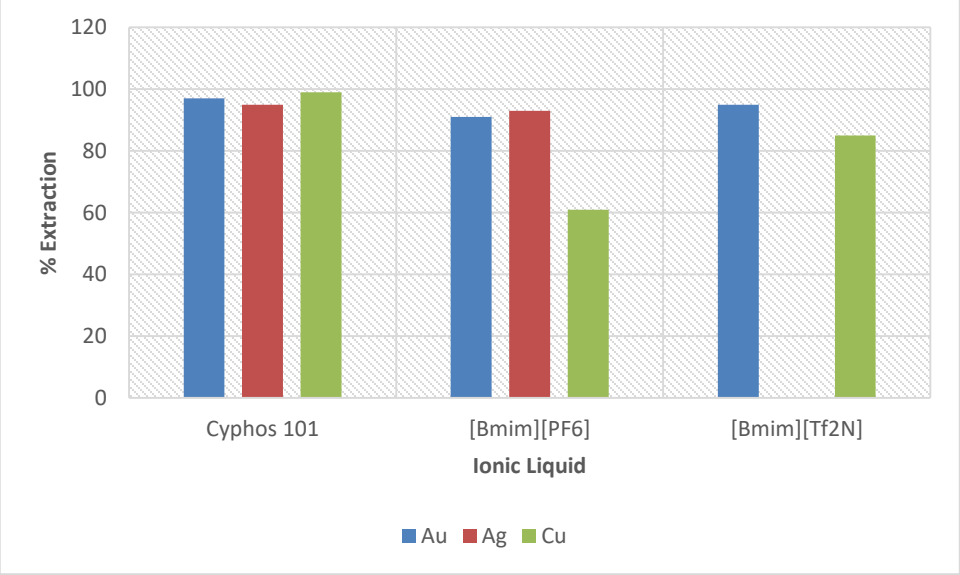


Figure 4.9: Comparison of extraction efficiencies of different ionic liquids in aqua regia

The 85% Cu extraction for [Bmim][Tf_2N] and 61% Cu extraction for [Bmim][PF_6] show that these two ILs also have low selectivity for the sought PMs; Ag and Au and hence,

pre-treatment of the sample to eliminate the other metals would be necessary. The findings made on Cu open another research need which would focus on the affinities of these ILs towards the metals found in the samples as listed in Table 3.1 and Table 3.2 in order to determine those metals which would be extracted along with Ag and Au. The investigation of Fe and Al would also be important since these have a high content of 6.7% and 4.7% respectively in the sample.

Cyphos 101 has also been investigated for the extraction of other PGMs such as Pd and Pt, and it has also shown very high affinities for these metals (Cieszyńska, Regel-Rosocka & Wiśniewski, 2007; Kumar, Choi & Lee, 2017). Consequently, the IL may not be an effective selective extractant for Ag and Au in leach liquors which have these PGMs, as these will also be extracted along with Ag and Au.

As discussed under the section on Ag extraction, [Bmim][Tf_2N] as shown in Figure 4.9 fails to extract Ag from aqua regia leach solutions, and it shows selectivity for Au and Cu. With Cu removed before leaching of PMs, the IL [Bmim][Tf_2N] may be used for selective extraction of Au leaving Ag in solution. Ag may then be extracted separately with Cyphos 101 which has an Ag extraction efficiency of 95% as seen in Figure 4.9.

The use of ionic liquids in the extraction of Ag and Au from PCB – Aqua regia leach solutions as discussed above, shows that ionic liquids are ideal extractants for these metals from acid leach solutions. As a result, these reagents may be used as alternatives to organic reagents which have a number of limitations as discussed in preceding chapters. These findings are a breakthrough for the recovery of these precious metals from e-waste using aqua regia as a leaching system and ionic liquids as extractants. Ionic liquids used in metal extraction from leach solutions are recyclable and may be used in several extraction cycles after regeneration. The recycling of ILs after extraction cycles further enhances the financial viability as well as the environmental compatibility of ILs as used in hydrometallurgy, while economic sustainability and environmental performance are at the centre of this research.

4.2 Gold and silver leaching using Ionic liquid [Bmim][HSO_4]

This section presents and discusses the results obtained from the leaching experiments based on the use of the IL, [Bmim][HSO_4], thiourea as a complexing agent and Fe^{3+} as an oxidant. It should be noted that for this system, extraction was not part of the experimental set-up as PMs may be directly stripped from the IL pregnant solutions. In this system, thiourea acts as the complexing agent while the IL acts as the leaching solvent and a pH regulator as an analogue to H_2SO_4 in the conventional acidic thiourea leaching system, where thiourea acts as a complexing agent and H_2SO_4 as a leaching solvent and pH regulator. Replacing H_2SO_4 with [Bmim][HSO_4] in this system eliminates the use of concentrated and toxic mineral acids and replaces them with a more environmentally benign and recyclable solvent, [Bmim][HSO_4], thus enhancing the environmental performance and sustainability of acidic thiourea as an Au leaching system.

4.2.1 Eh and pH Studies

Leaching of PMs in thiourea-[Bmim][HSO_4] was carried out at ambient conditions. Aqueous solutions of 10%, 20% and 30% IL (w/w) were used. The pH and redox potential for the reactions were measured and recorded during leaching in order to attain a better understanding of the process. The pH and Eh curves are shown in Figures 4.10 and 4.11 (pages 103 and 104 respectively).

The pH values for the IL solutions were initially recorded at about 1, with the 10% IL at pH of 1.2, the 20% solution at pH 1.1, and the 30% IL solution at pH 1. The pH levels of the leaching solutions increased slightly as the reaction progressed as shown in Figure 4.10, with the 10% IL solution reaching the pH of 1.7 while the 30% IL solution only reached the pH of 1.36 after 48 hours. This indicates that the lower the IL concentration, the higher the change in pH during the course of the reaction. The optimum pH conditions for acidic thiourea leaching system are between pH 1 and 2 (Hilson & Monhemius, 2006), and the readings in Figure 4.10 are within this range. However, the solution with the

lowest IL concentration has the fastest rate of pH increase, which approached the threshold of pH 2 by the end of the experiment. This may be attributed to the fact that the concentration of the pH regulator, which is the IL is lowest in the 10% IL solution, hence the pH for that solution would rise rapidly compared to solutions where the concentration of the IL as the pH regulator is higher. As a number of properties of ILs have not been adequately studied, the causes for the pH stability within the desired range in the IL system may consequently not be adequately explained. However, Kilicarslan *et al.* (2014) discovered that the addition of an oxidizing agent such as H_2O_2 and $KHSO_5$ as used in their research, lowers the pH of the IL solution when added to the IL. The researchers however, only report their observations without postulating the mechanism for the reactions which lead to the decrease in pH when the oxidants are added.

The redox potential for the leaching solutions was also measured throughout the leaching process as gold dissolution is governed by both pH and the redox potential of the system. The curves for the changes in the redox potential values are shown in Figure 4.11 (page 104). The results obtained show that the redox potential for the leaching solutions decreases during the reaction.

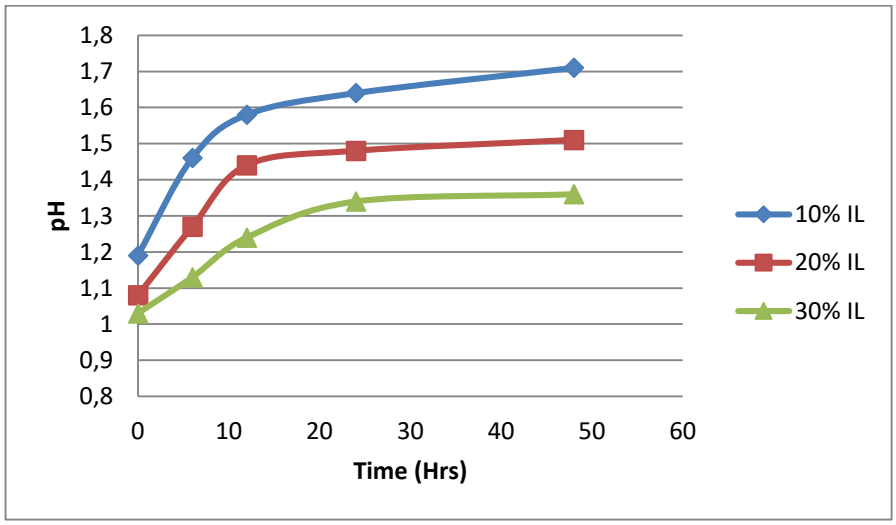


Figure 4.10: pH curves for leaching experiment

As observed on the pH values, the concentration of the IL also has an effect on the redox potential of the solution. From the results, it can be concluded that the higher the IL concentration, the lower the redox potential drop of the solution during the leaching period.

The redox potential values shown in Figure 4.11 show that even though the main role of the IL [Bmim][HSO_4] in the leaching system is to act as a pH regulator and reaction solvent, the IL also has an effect on the redox potential of the solution. This view is supported by the fact that although the quantity of the oxidant used ($Fe_2(SO_4)_3$) was the same in all the experiments, the redox potentials recorded were different. Figure 4.11 shows that there is a direct relationship between the concentration of the IL in the leaching solution and the observed potential. This behaviour may in part be explained by the fact that [Bmim][HSO_4] has been found to enhance the stability of thiourea in the leach solution (Fang *et al.*, 2014).

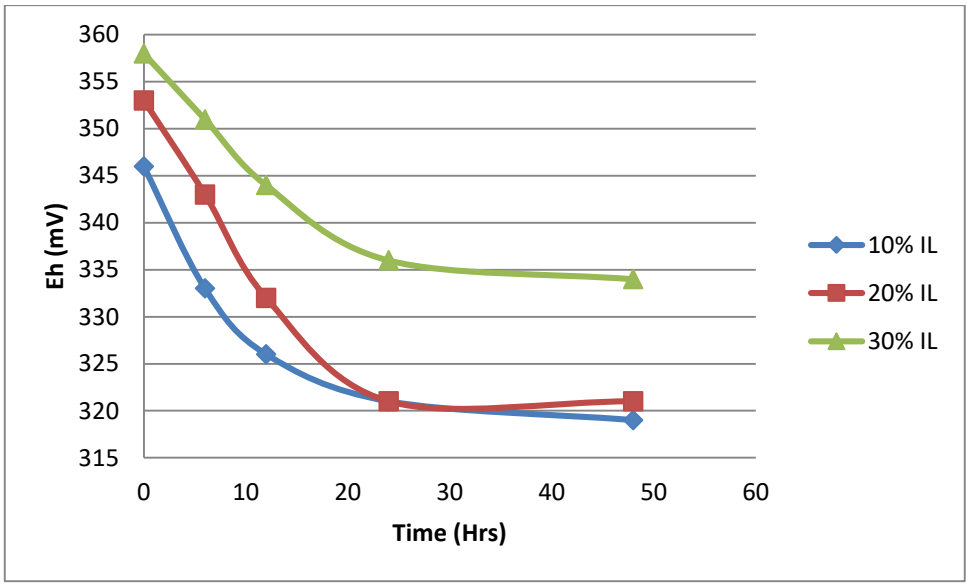


Figure 4.11: Redox potential curves for leaching experiment

The IL inhibits the oxidative decomposition of thiourea, thus both thiourea and the oxidant are conserved during the process, unlike in aqueous solutions where the

oxidative decomposition is rapid, hence a rapid decrease in redox potential. Furthermore, the non-decomposition of thiourea means that the products of the decomposition of thiourea which include reducing chemicals such as sulphur will be minimal in solutions with higher IL concentration (Gašpar *et al.*, 1994).

When considering both the pH and Eh changes through the reactions, it can be concluded that the higher the concentration of the IL in the leaching solvent, the more favourable the conditions are for leaching the metals; Ag and Au. According to Nicol, Fleming and Paul (1992), thiourea works well in oxidative conditions with Fe^{3+} being the most preferred oxidant. The researchers, along with Gašpar *et al.* (1994) state that the suitable range for the redox potential for Au dissolution in thiourea is between 300 mV and 600 mV, with an optimum around 400 mV. Below 300 mV, dissolution is retarded, and above 600 mV, thiourea tends to decompose more rapidly, thus inhibiting the dissolution of Au due to the lack of the oxidant as well as the production of the sulphur which is unfavourable for Au dissolution.

The redox potential for the system was slightly lower than the optimum potential of 400 mV. This may have been as a result of the presence of high quantities of other materials in the sample such as Cu, which has been reported to be 26% of the sample. Such assertions emphasize the need for pre-treatment of the sample before experiments in future research in order to ascertain if the sample composition, due to other active metals, has a negative contribution towards Au dissolution. On the other hand, the dissolution of Ag is governed by the redox potential and the pH has no effect on the system's ability to dissolve silver (Figure 2.17 in chapter 2). The required potential for Ag dissolution ranges at about 250 mV to over 1000 mV. The readings recorded in Figure 4.11 show that the redox potential of the IL system was within the required range for the dissolution of silver.

4.2.2 Leaching Studies

The results from the analysis of the ionic liquid leach liquor are presented in this section. Figure 4.12 shows the kinetics for the leaching of the PCB sample in a 30% [Bmim][HSO_4] solution at 25^{0}C within 48 hours of leaching. Thiourea was used as a complexing agent and $Fe_2(SO_4)_3$ as an oxidant. From the results presented here, it can be seen that the IL leach system has a higher affinity for Au than it has for Ag.

The results shown in Figure 4.12 are in agreement with studies of [Bmim][HSO_4] on leaching of Ag and Au ores (Whitehead *et al.*, 2007; Whitehead, Lawrence & McCluskey, 2004; Whitehead *et al.*, 2009).The leaching system has a higher affinity for Au compared to Ag. The redox potential of the system of about 350 mV was near the optimum potential for Au dissolution (400 mV) while it was way below the dissolution threshold for Ag, which is 1000 mV. The extraction efficiency for the IL is discussed in the subsequent sections, where the total metal leached is compared with the total amount of metal that was present in the PCB sample. Similar to the experiments on aqua regia in the preceding section, the leaching rates of Cu in the IL system were also investigated due to the high Cu content in the PCB sample. The results are presented and discussed below.

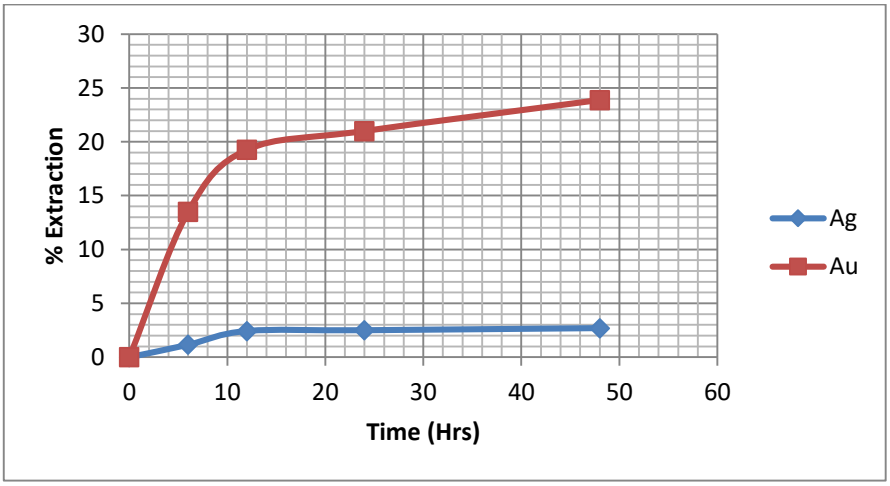


Figure 4.12: Gold and silver leaching in 30% [Bmim][HSO_4] at 25 ^{0}C

Figure 4.13 shows the extraction efficiency for aqueous [Bmim][HSO_4] at different concentrations at 25^0C over a period of 48 hours. From the results presented in the figure, it can be seen that the difference in extraction efficiencies of aqueous [Bmim][HSO_4] between the three concentrations used is marginal. The efficiency for Au extraction increases from 18.5% in 10% IL solution to ~24% in a 30% IL solution. Again, these findings are in agreement with Whitehead *et al.* (2007) who reported that there were insignificant changes in gold extraction when they varied the volume ratio of the IL and water from 0% to 50%. The researchers further state that when a neat (undiluted) IL was used however, the rate of dissolution of Au decreased due the high viscosity of the IL but conversely, Cu dissolution was enhanced. The extraction of both Ag and Cu in the IL in this research were found to be very low, with Ag at about 3% and Cu at about 2%.

The percentage extractions observed in this research however (Figure 4.13), are considerably lower when compared to those reported by Whitehead, Lawrence and McCluskey (2004), Whitehead *et al.* (2007) and Whitehead *et al.* (2009).

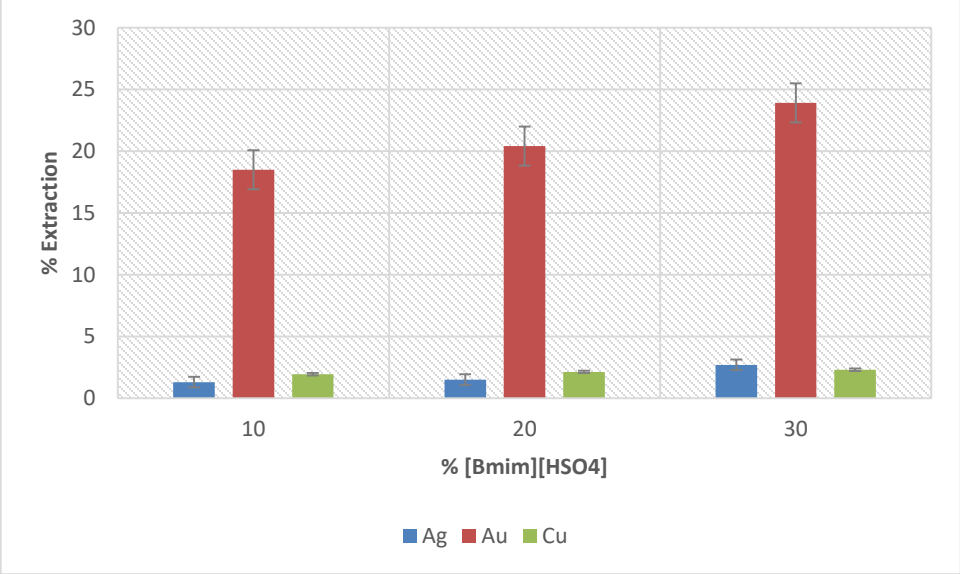


Figure 4.13: Leaching of Ag, Au, and Cu in different concentrations of [Bmim][HSO_4] in 48 Hrs and 25 ^{0}C

The researchers reported extraction efficiency of about 85% for Au and 60% for Ag at room temperature using [Bmim][HSO_4], compared to the 25% for Au and 3% for Ag observed in this research in the leach solution of 30% [Bmim][HSO_4]. While at initial consideration, these results seem to be way too low compared to those reported by the researchers above, the results are actually comparable when one investigates the stoichiometric relations between these studies. The difference between the 85% and 25% extraction efficiencies may be explained by the fact that, although similar leaching conditions may have been used in these experiments, the nature and composition of the two samples used in these studies were different. This and other possible contributors to the observed differences are discussed below.

A number of factors may have influenced the reduced extraction efficiency observed in this study when compared to those by Whitehead, Lawrence and McCluskey (2004), Whitehead *et al.* (2007) and Whitehead *et al.* (2009). One of the reasons which may explain these observations may be the difference in chemical composition of the samples which were used in these different studies. The researchers above used a 'natural sulphidic gold-bearing ore' while a PCB sample containing metallic Ag and Au was used in this research. From this perspective, the interaction of the IL, thiourea and $Fe_2(SO_4)_3$ with a sulphide material and a metallic material may differ. Consequently, the investigation of the behaviour of the system towards sulphidic Ag and Au against metallic Ag and Au may be recommended. Further to that, the different concentrations of Ag, Au and Cu in the samples used may well be another explanation of these different efficiencies observed. The sample used by the other researchers in their experiments contained Au, Ag and Cu in the following concentrations; Au = 5.65 gt^{-1}, Ag = 18.72 gt^{-1}, and Cu =1.52%. The concentration of Au, Ag and Cu in the PCB sample used in this study was; Au = 160 gt^{-1}, Ag = 618 gt^{-1} and 26% Cu.

The values given above show that the sample which was used by the researchers above had only 3.5% of the Au found in the PCB sample. The PCB sample used in this study was consequently 28 times more concentrated in Au than the natural gold ore used. In consideration of stoichiometry and the huge difference in the concentration of

Au in the samples, the lower efficiency observed may be justified. A larger volume of the solvent and possibly more reaction time in this case may have been required to leach 160 g compared to 5.65 g Au from the sample. The same argument may stand for the low extractions observed for Ag when compared to the previous studies. This argument forms the basis for a recommendation which may be made, that the optimum solid-liquid ratio for the dissolution of concentrated Au-Ag samples such as the PCB sample should be investigated instead of the ratios used in this research (1 g/ 20 ml sample: IL, 0.5 g/Kg Fe_2O_3:sample, and 0.5 g/ 100 ml thiourea: IL).

Another explanation for the lower extraction for Ag and Au in this experiment compared to that of the researchers stated above may be the concentration of Cu in the PCB sample as already stated above. Whitehead *et al.* (2007) investigated the dissolution of Cu in the IL [Bmim][HSO_4]. The researchers reported that high extraction efficiencies for Cu in [Bmim[HSO_4], up to ~86% were observed at different temperatures. Like Au, Cu is leached under acidic and oxidative conditions. In this way, the metal may consume the oxidant which was added for Au dissolution. The PCB sample used in this research was ~ 26% Cu while that used by Whitehead *et al.* (2007) was only 1.52% Cu. Consequently, there was considerably more Cu present in the PCB sample and as a result, more of the reagents may have been required to leach the metals Ag, Au, along with Cu. While the percentage Cu that was extracted was less than 5%, it is important to note that this is a large quantity of the metal considering the fact that the sample was composed of 26% Cu. The amount of Fe in all the studies was comparable, and as a result, the influence of Fe may have not been a cause for the significant differences in the extraction efficiencies of Ag and Au. The sample used in the preceding studies was 9.22% Fe, while in this research, the sample was 6.7% Fe.

While the extraction of Cu recorded in this research was very low, at about 2.3%, this is a large amount of Cu (wt/wt) when considering the fact that Cu has the highest concentration in the sample, which is 26%. The 2.3% extracted is equivalent to 5989 µg/g Cu which is extracted by the IL, thus reagent consumption by Cu dissolution may be considered significant. Consequently, pre-extraction of Cu from the sample before

leaching Ag and Au in [Bmim][HSO_4] may be necessary. This would eliminate the reagent consumption by Cu. This argument forms another basis of a recommendation that the effect of the presence of Cu along with other base metals in the PCB sample on Ag and Au dissolution should be investigated and verified.

However, in an industrial application where the recovery of valuable metals such Ag and Au is sought along with metals such as Cu, the ability of the IL to leach the metals Ag, Au and Cu may be of significant importance. While Cu extraction was very low, Whitehead *et al.* (2007) reported that the dissolution of base metals in the IL is enhanced at elevated temperatures, which was the reason behind keeping the experiments in this research at ambient conditions since Cu dissolution was not desired. The leached metals may then be processed for selective recovery downstream, and a 'green' leaching process for all three metals may be achieved. However, more research on optimization of the process for higher extraction efficiencies of Ag and Au is required.

For the development of an efficient Ag-Au leaching process based on the [Bmim][HSO_4]-thiourea system for PCB samples, there are further factors which need to be considered. These include temperature, IL concentration, pH stabilization, and oxidant among others. Increasing the leaching temperature in the [Bmim][HSO_4]-thiourea system increases the extraction efficiency of other metals such as Cu and Fe if present in the sample. However, at lower temperatures (~25^0C), the extraction of the metals; Cu, Fe and other base metals is minimal while the extraction of the PMs; Ag and Au remains high (Whitehead *et al.*, 2007). The researchers further state that, for Ag and Au, temperature only affects the rate of dissolution, but the effect on total extraction is insignificant. This suggests that there is a trade-off between energy requirements and process time. At elevated temperatures, the process time is shorter but it comes with a cost implication in terms of energy requirements. Further to that, as already stated, elevated temperatures lead to the leaching of other metals. Ultimately, for selective extraction of Ag and Au, leaching at ambient temperatures over longer time periods is thus preferred.

As observed in Figure 4.10, the pH of the leaching solution increases with the reaction time, while leaching is favoured by lower pH, typically pH 1. It may thus be important to stabilize the pH through IL dosing during the course of the reaction. Whitehead *et al.* (2007) used H_2SO_4 as a solvent for [Bmim][HSO_4] instead of water as used in this research, when the 10, 20, and 30% IL solutions were prepared. This suggests that the acid was dosed as a pH regulator to maintain a constant pH favourable for leaching. However, dosing with H_2SO_4 would not be advocated for this study as the rationale behind the use of [Bmim][HSO_4] was to eliminate the use of mineral acids in the acidic thiourea leaching system for Au. As a result, dosing with the IL to regulate the pH during the reaction is recommended. Alternatively, a higher concentration of the IL solution may be used as it is observed in Figure 4.9 that the change in pH in the more concentrated solution is lower than that of the less concentrated solutions. Careful balancing of thiourea and $Fe_2(SO_4)_3$ is also critical for this system. If $Fe_2(SO_4)_3$ is deficient, there may be inadequate oxidant for leaching. On the other hand, excess $Fe_2(SO_4)_3$ leads to the consumption of thiourea by the Fe^{3+} thus leading to deficiency of the complexing agent. Consequently, the investigation of other oxidants such as oxone ($KHSO_5$) for this system may be fundamental.

While Au dissolution has been evident in the IL leaching system, the system could however not be recommended for large scale application at the time, due to the low recoveries recorded in this research. It may still be concluded however, that IL [Bmim][HSO_4] may potentially be a successful reagent for Au dissolution from e-waste samples, but further research in this area focusing on optimization of the process at higher feed grade and with pre-removal of Cu will be fundamental. These findings are a breakthrough towards the ‘green recycling’ of precious metals from e-waste without the use of toxic and environmentally degrading reagents such as strong mineral acids and volatile organic solvents traditionally used in hydrometallurgy.

4.3 Organic acids and ionic liquids

This section presents the results which were obtained from the leaching and extraction experiments of Ag and Au in organic acids; glycine and histidine followed by subsequent extraction of the metals from the leach liquors using the IL; [Bmim][PF_6], [Bmim][Tf_2N], and Cyphos 101 as extractants.

4.3.1 Leaching Experiments

The results obtained from the leaching of Ag and Au from the PCB sample using alkaline glycine and histidine with hydrogen peroxide as an oxidant proved that alkaline glycine may be used for leaching of Au. The extractions recorded showed dependence on the concentration of the organic acid as well as the temperature. The higher the concentration of the organic acid, the higher the extraction recorded. Similarly, an increase in temperature resulted in the enhancement of the extraction of Ag and Au from the sample.

Figure 4.14 shows the extraction efficiency of glycine in different concentrations for Ag and Au. For the same reason as in aqua regia and [Bmim][HSO_4], which is the high content of Cu in the sample, the dissolution of Cu in glycine was also analyzed. The results for Cu dissolution are also included in the Figure 4.14. From Figure 4.14, it is evident that the concentration of glycine has an effect on the extraction efficiency of the metals. More concentrated solutions have higher extraction efficiency than dilute solutions. The results also show that glycine leaches both Ag and Au, along with Cu. Similar to the discussions in the preceding sections, the pre-removal of Cu from sample may also be fundamental for Ag and Au dissolution in glycine since the solution also has an affinity for Cu.

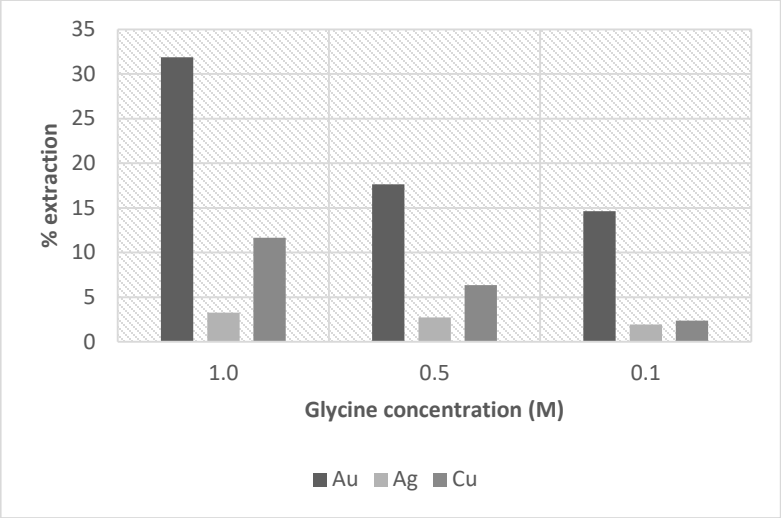


Figure 4.14: Extraction of Ag & Au in different alkaline glycine concentration at 25 ^{0}C

While the extraction efficiency for Au in 1 M glycine solution at 25 ^{0}C is only 32% as observed, it is important to note that the efficiency of glycine is also influenced by temperature. Figure 4.15 shows the temperature dependency of 1 M glycine in the extraction of Ag and Au. The extraction efficiency of Au in 1 M alkaline glycine solution was approximately 31% at 25 ^{0}C. The efficiency increased to about 66% when the experiment was conducted at an elevated temperature of 70 ^{0}C. This observation confirms that Au extraction in alkaline glycine solutions is dependent on temperature as determined by Oraby and Eksteen (2015).

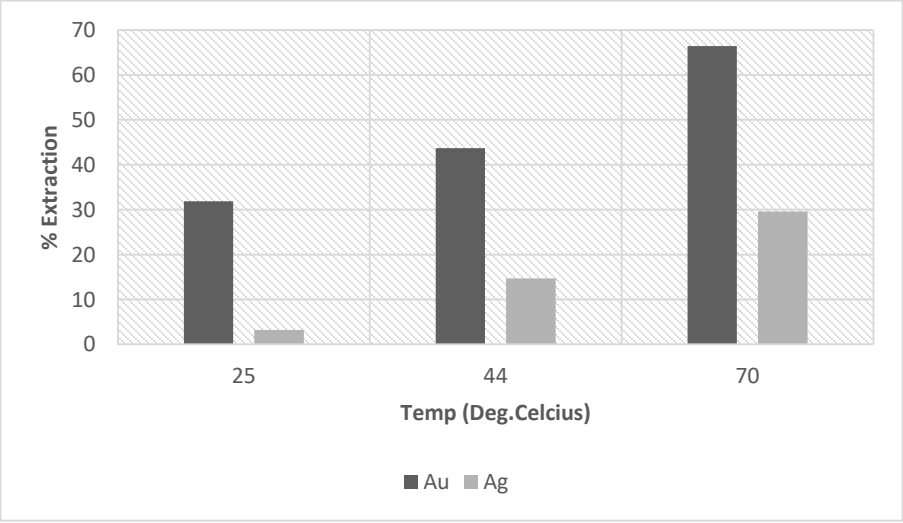


Figure 4.15: Effect of temperature on Ag and Au extraction in 1 M alkaline glycine solution

As suggested by Oraby and Eksteen (2015), the organic acids; glycine and histidine have a synergistic effect on the leaching of Au from solid sources. This has also been observed in this research when the extraction efficiency of 0.1M glycine was compared to that of a combination of 0.1M glycine and histidine. The combined acids showed a stronger extraction efficiency compared to that observed when glycine was the only acid used. Figure 4.16 shows the extraction efficiencies of the acids on the extraction of Ag and Au from the PCB sample.

From Figure 4.16, it is evident that a mixture of glycine and histidine is more superior to glycine alone for Au extraction. In consideration of the observations made in these experiments, it can be concluded that the organic acids; glycine and histidine, may be effectively used for the extraction of Au from PCBs. Furthermore, in an effort to enhance the efficiency of the system, the concentration and temperature are of key importance.

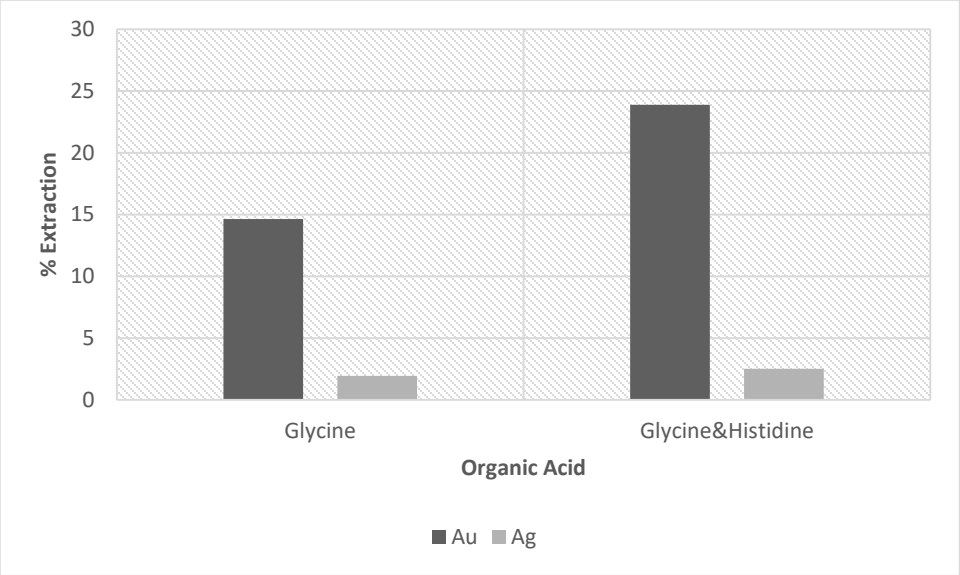


Figure 4.16: Extraction of Ag and Au in 0.1 M Glycine and Histidine at 25 ^{0}C

Leaching should be conducted at elevated temperatures of about 70^{0}C, and a more concentrated solution should be used as supported by the results from this research.

Furthermore, a combination of glycine and histidine as the leaching solution is preferred since the acids showed an enhanced efficiency when mixed.

While the effect of Cu on the leaching of Ag and Au was not investigated in this study, it is recommended that it should also be investigated given the amount of Cu found in the sample. Cu was also leached along with Ag and Au in the glycine-histidine leaching system, and hence its effect on the dissolution of Au and Ag should be investigated to determine if the metal is a significant competitor for reagents in the leaching process. This investigation would inform the decision as to whether Cu should be removed prior to leaching of the PMs in the glycine-histidine leaching system. However, findings already made in this research on Cu dissolution point to the fact that Cu should be excluded from the sample prior to the leaching of Au and Au.

The other main consideration on Au dissolution in glycine-histidine solutions is the pH as discussed in the experimental section. Its effect on Au dissolution was also not investigated in this study as the researchers; Oraby and Eksteen (2015), had already determined that Au dissolution in glycine and histidine as complexing agents is effective under very basic conditions, above pH 11. This is due to the activation of the oxidant (H_2O_2) under basic conditions by NaOH which acts as the pH regulator. Furthermore, the production of OH^- radicals enhances Au dissolution at these pH values. The pH for the experiments was adjusted to pH 12 at the beginning of the experiments and both the pH and Eh were monitored throughout the experiments. The pH and Eh values at the beginning and the end of each of the experiments are given in Table 4.1.

From the values given in the Table 4.1, it can be seen that the pH values stayed within the desired range for Ag and Au dissolution in alkaline glycine-histidine. As a result, there was no further need to regulate the pH since the reaction conditions were well adjusted at the beginning of the reaction.

Table 4.1: Eh pH values for glycine-histidine leach solutions

Sample	*pH (start)*	*pH (end)*	*Eh (start)*	*Eh (end)*
1M glycine	12.3	11.1	-335	-323
0.5M Glycine	12.1	10.8	-327	-319
0.1M Glycine	12.1	10.6	-329	-317
0.1M Glycine (	12.2	10.9	-332	-321
0.1M Glycine	12.0	10.5	-325	-313
0.1M Glycine&Histidine	12.3	11.3	-336	-324

4.3.2 Extraction with ILs

While the ionic liquids used in this research are effective for the extraction of Ag and Au from chloride leach solutions, the ionic liquids were found to be ineffective as extractants of these metals from alkaline glycine and histidine leach liquors. There were no significant differences in the concentration of these metals in the leach liquors and raffinate solutions before and after extraction with the ionic liquids. Figure 4.17 shows the results from the extraction experiments which were carried out using the three ILs as extractants. From Figure 4.17, it can be concluded that this set of ionic liquids is ineffective for Ag and Au extraction from the alkaline glycine-histidine leach liquor. This observation aligns in part with Sheng and Etsell (2007), who state that the pH of a solution is one of the important factors that affects the extraction potential of ionic liquids on different metals from solution.

As a result of the observations made on the extraction experiments carried out, an investigation of a different set of hydrophobic ILs which has high affinities for precious metals in alkaline conditions should be conducted. This would be fundamental as an attempt to find ILs that would be suitable for the extraction of PMs from alkaline leach liquors has ascertained that [Bmim][Tf_2N], [Bmim][PF_6] and Cyphos 101 are only suitable for metal extraction in acidic solutions.

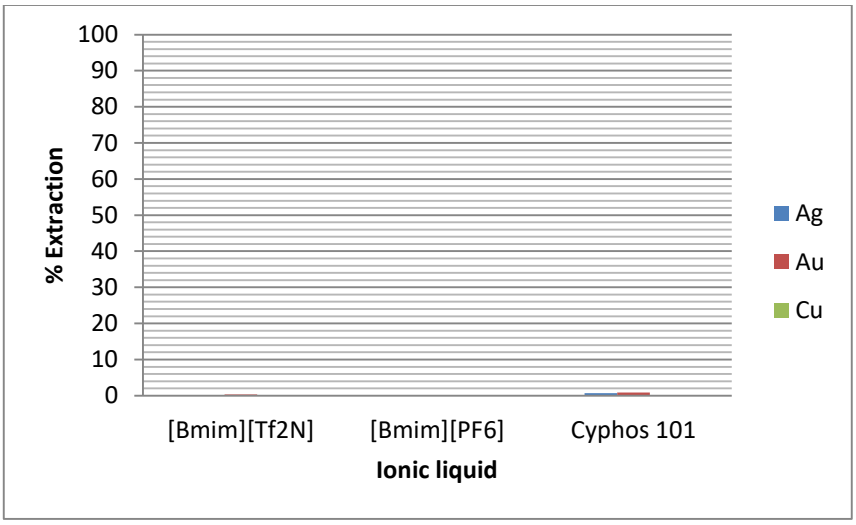


Figure 4.17: Extraction of Ag, Au, and Cu from alkaline glycine solutions

This opens yet another research focus in the application of ILs in metal extraction in an attempt to enhance sustainable hydrometallurgical processes in e-waste recycling.

Chapter 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

The results reported in this research show that ionic liquids are potentially effective alternatives for mineral acids and organic extractants in the recovery of Ag and Au from e-waste through hydrometallurgical processes. This is supported by the observations made when these reagents were used in leaching and extraction of these metals from the PCB sample used in the study. Although the IL, [Bmim][HSO_4] showed low extraction efficiency towards Ag and Au leaching, from the PCB sample, the observed dissolution, especially that of Au shows that the IL is a possible alternative to H_2SO_4 in the conventional acidic thiourea leaching system. This would mean an environmentally benign substitute for the strong mineral acid in thiourea leaching system, thus eliminating the environmental footprint of the process. Direct stripping of PMs on activated carbon from the IL is yet another key point for this system; it eliminates the use of toxic and volatile organic extractants used in Au extraction from pregnant leach solutions.

The hydrophobic ionic liquids [Bmim][PF_6], [Bmim][Tf_2N] and Cyphos 101were also efficient in the extraction of Au and Ag from chloride leach solutions with more than 90% extraction efficiency for Au. Similar to the assertions made about [Bmim][HSO_4], these ionic liquids are effective alternatives to organic solvents used in the solvent extraction of precious metals from acidic chloride leach liquors. This breakthrough opens the possibility of substituting toxic, volatile and highly inflammable organic reagents in solvent extraction of PMs with more stable reagents in the form of ionic liquids as described in literature.

As characteristically environmentally benign reagents, the application of ionic liquids in the hydrometallurgical processes of metal recovery from e-waste will eliminate the use of

their environmentally unfriendly counterparts. This application will to a great extent address some of the environmental concerns associated with the hydrometallurgical processes used in the extraction of noble metals such as Au from their ores and other secondary sources such as e-waste.

While ionic liquids have not been used extensively in industry because of the high costs associated with them (Mai, Ahn & Koo, 2014), there are only marginal differences in costs of ionic liquids compared to their analogues. Moreover, it is asserted that with possible increase in demand for ionic liquids, the costs may lower due to increased volumes of production which may benefit the application of these reagents in a broader scope of fields. The reusability of ionic liquids, especially in hydrometallurgical applications remains one of the cornerstones of their supported application in hydrometallurgy along with other characteristics such as chemical and thermo stabilities. The reusability of the reagents meets both the economic and environmental objectives in the recycling of PMs from e-waste.

With the limited successes reported for the leaching of Ag and Au in an ionic liquid as well as the high extraction of Ag and Au from chloride leach liquors, it should however, be acknowledged that the three ionic liquids investigated as extractants were ineffective in the extraction of the metals from alkaline glycine and histidine leach liquors. This observation is a drawback in the attempt to devise a ‘green’ process for the recycling of Ag and Au using environmentally benign organic acids as leaching agents as well as ionic liquids as extractants. The organic acids were effective as leaching agents as gold and silver were dissolved in their alkaline solutions but the ionic liquids failed in the extraction of these metals from their alkaline liquors. This observation opens another research need which would focus on investigating hydrophobic ionic liquids which would have high affinities for PMs in alkaline conditions.

5.2 Recommendations

The following are recommendations subsequent to this research;

- Further research on this topic should be conducted. The scope of such studies may include the areas which were not considered by this research. This includes the optimization of the sample to ionic liquid solution volume ratio in the [Bmim][HSO_4] thiourea leaching system as well as a comparison of the reagent need and efficiency with acidic thiourea in H_2SO_4 as a leaching solution.
- Pre-extraction of base metals such as Cu and Fe should be conducted before leaching experiments, especially for [Bmim][HSO_4] and glycine-histidine leaching systems in order to understand the effect of these metals on Ag and Au leaching.

- While there are several routes to recycle spent ILs, there has been minimal research in this area - in particular the application of such processes at large scale. This opens up another research focus area in the field of ionic liquids. The recyclability of the ionic liquids should be investigated after use in e-waste leaching or extraction to verify the fact that these may be used multiple times after stripping the metals.

- Ionic liquids which are compatible with alkaline, glycine and histidine should also be investigated as the ILs studied in this research did not work successfully with the alkaline leach liquors.

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