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Gold recovery from waste mobile phones PCBs using ammonia thiosulphate leaching and copper cementation process

by

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DECLARATION

I, **Ramphagane Frank Nchabeleng**, declare that the contents of this dissertation/thesis represent my own unaided work and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

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ABSTRACT

The rate of waste electrical and electronic equipment (WEEE) is growing at an alarming rate, especially in countries where markets are saturated with huge quantities of new electronic goods. Printed circuit boards (PCBs) are a substantial portion of the value contained in waste from WEEE although they are only 6% of the total weight. It is reported that WEEE is currently the fastest growing waste stream in South Africa as the general population’s access to electronic goods in the last decade has increased, especially access to mobile phones. PCBs are found in any piece of electrical or electronic equipment and consist of various metals including precious metals such as gold (Au), silver (Ag) and palladium (Pd). It is reported that gold has the highest economic incentive at 15,200 $ per ton of PCBs.

The rapid introduction of new and advanced technology into mobile phones has caused mobile phones to have a relatively short life span, 1 to 2 years to be exact. Mobile phones printed circuit boards (MPPCBs) have more Au content compared to computer circuit boards. They contain 350 g/ton Au whereas computer (PC) PCBs contains 250 g/ton. This research project will recover gold from waste mobile phones PCBs pregnant ammonia thiosulphate leach solution using copper cementation. The cementation process is preferred to all the other technologies of metals extraction from solution due to ultrahigh purity metals that can be obtained and to the less consumption of materials and energy.

Electronic parts on the PCBs were manually removed using pliers and screwdrivers. PCBs were then cut to smaller pieces of about 2 x 2 m. The pieces were crushed and milled respectively. Some of the particles were recycled back to the crusher to get finer particles. The particles were separated to particles of sizes between 0 and 1350 µm using a shaker. The comminuted fractions of the PCBs were then used in the leaching step.

Batch cementation experiments were performed by bubbling N_2 in glass reaction vessel with a working volume of 0.5 L. The reactor was connected to a circulating water bath for temperature control. The recovery percentage of gold at various temperatures, agitation speeds and different amounts of copper powder used, was determined while pH was monitored. The temperature was varied at 30 ℃, 40 ℃, and 50 ℃ and the agitation speeds at 300 RPM and 900 RPM. Copper powder was added at 0.5 g/L, 1 g/L, and 1.5 g/L.

Gold concentrations were measured by atomic adsorption spectrophotometer (AAS). Scanning electron microscope (SEM) and Energy-dispersive x-ray spectrometry (EDS) analyses of the copper powder after cementation (precipitates) were used to determine the surface morphology and to evaluate the quantitative aspect of the precipitate.

It was found that the recovery of gold from ammonia thiosulphate leach solution was greatly affected by agitation speed. At an agitation speed of 900 rpm, 40 °C and 0.5 g of Copper powder, 96% of the gold was recovered from the leach solution. The cementation rate increased as temperature was elevated from 30 to 40 °C, but slightly decreased as the temperature reached 50 °C. The change in experimental conditions affected the gold concentration on the precipitate recovered.

This study will provide a possible solution to the WEEE problem and more specifically mobile cell phones, in South Africa.

RESEARCH OUTPUTS

Nchabeleng F, Aziz M & Kasongo G; Copper cementation of gold from leach solutions of waste mobile phones printed circuit boards (PCB's), SAIMM Journal, Student Edition (In press)

F. Nchabeleng & M. Aziz, The recovery of gold from waste printed circuit boards using a cementation process (PCB's), CPUT Annual Post Graduate Conference, SARETEC, Cape Town, South Africa, 7 November 2018

F. Nchabeleng & M. Aziz, Copper cementation of gold from leach solutions of waste mobile phones printed circuit boards (PCB's), SAIMM 15th Annual Student Colloquium, MINTEK, Johannesburg, South Africa, 24 October 2018

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DEDICATION

My late father Mr Magabe and my mother Mrs Lesiba Nchabeleng

Table of Contents

List of Figures

List of Tables

Clarification basic terms

Cementation: The electrochemical precipitation of one metal by using another metal, the precipitant as the reducing agent (Guerra & Dreisinger, 1999)

Recovery: Removal of gold from solution into a concentrated and purified form (Lee, 2003).

Leaching: The process of extracting a soluble constituent from a solid by means of a solvent (Luda, 2011)

Printed circuit boards (PCBs): These are found in any piece of electrical or electronic equipment: nearly all electronic items, including calculators and remote control units (Luda, 2011).

WEEE: End of life computers, entertainment electronics, mobile phones and household appliances that have been discarded by their original users (Ghosh et al., 2015; Cui & Forssberg, 2003)

White goods: Large electrical goods used domestically such as refrigerators and washing machines, typically white in colour.

List of Symbols

A	Area (m^2)
A	Frequency factor
a	Specific surface area (m^2/g)
C	Gold concentration (mg/L)
℃	Celsius Degrees
D	Mass transfer coefficient
dAu	Change in Au concentration (mg/L)
dt	Change in temperature (K)
E	Activation energy (J/mol)
J	Flux
k	rate constant (m/min)
M_w	Molecular weight (g/m)
R	Universal gas constant
T	Temperature (K)
t	Time (min)
V	Volume (L)
V	Volts
W	Amount of copper powder (g)

Subscripts

b	Bulk solution
0	zero
t	time

List of Abbreviations

Abbreviations	**Meaning**
AAS	Atomic Absorption Spectroscopy
Ag	Silver
Au	Gold
As	Arsenic
Ba	Barium
Be	Beryllium
BFR	Brominated Flame Retardants
Cd	Cadmium
CFC	Chlorofluorocarbons
CIL	Carbon-in-leach
CIP	Carbon-in-pulp
CIS	Commonwealth of Independent States
CPUT	Cape Peninsula University of Technology
Cr	Chromium
CRT	Cathode Ray Tube
Cu	Copper
EDS	Energy-dispersive X-ray spectroscopy
EIA	Environmental Impact Assessment
eWASA	e-Waste Association of South Africa
Eh	Oxidation/Reduction Potential
Hg	Mercury
Ga	Gallium
Ge	Germanium
IT	Information Technology
ICT	Information and communications technology
In	Indium
LCD	Crystal liquid display
MPPCBs	Mobile phones printed circuit boards
Ni	Nickel

OECD	Organisation for Economic Cooperation and Development
WEEE/e-Waste	Waste from electrical and electronic equipment
PBBs	Polybrominated biphenyls
PBDE	Polybrominated diphenyl ethers
PCBs	Printed circuit boards
PCBs*	Polychlorinated biphenyls
Pd	Palladium
Pb	Lead
PVC	Polyvinyl Chloride
ppm	Parts per million
RIL	Resin-in-leach
RIP	Resin-in-pulp
Sb	Antimony
Se	Selenium
Si	Silicon
SHE	Standard hydrogen electrode
Sn	Tin
Ta	Tantalum
TBBPA	Tetrabromobisphenol
Te	Tellurium
Ti	Titanium
XRD	X-ray powder diffraction (XRD)
Zn	Zinc

CHAPTER 1

1 Introduction

1.1 Background of the research problem

Huge volumes of Waste from electrical and electronic equipment (WEEE) are generated worldwide annually. WEEE is the fastest growing waste stream in the modern world. Currently, printed circuit boards (PCBs) are only 2% of the total weight of WEEE but are a significant portion of the value contained in WEEE as represented by figure 1-1 (Behnamfard et al., 2013). It has been reported that 2 million tonnes of electrical or electronic equipment (EEE) in South African homes will likely enter the waste stream between 2013 and 2018 (Finlay & Liechti, 2008; Ongondo et al., 2011). The use of electronic goods, particularly mobile phones in the last decade has expanded resulting in the rapid growth of WEEE in South Africa (Ongondo et al., 2011).

Conventional disposal methods of WEEE such as landfill and incineration cause environmental pollution and pose health risks (Alzate et al., 2016). Since the precious metal content in WEEE is higher than the ores metal content, recycling the waste is advantageous for the environment and the economic incentive (Behnamfard et al., 2013; Alzate et al., 2016). WEEE has become a matter of concern because of the hazardous material contents such as mercury, lead, and antimony (Cui & Zhang, 2008; Tuncuk et al., 2012). However, as indicated by Li et al. (2004) WEEE also contains valuable metals, for example, gold, copper, zinc, and palladium that can be recovered for reuse.

The process of leaching, commonly used as the first step in gold recovery, involves the use of acid or alkaline solutions to solubilize a solid material. Leaching is especially important during the precious metal recovery from WEEE printed circuit boards (PCBs) (Zhang et al., 2012; Syed, 2012). PCBs are found in any piece of EEE (Khaliq et al., 2014). The most common leaching agents used in the recovery of gold are cyanide, halide, thiourea, aqua regia and thiosulphate (Behnamfard et al., 2013; Petter et al., 2014). Various studies (Abbruzzese et al., 1995; Grosse et al., 2003; Hiskey & Lee, 2003; Karavasteva, 2005; Cui & Zhang, 2008) have shown that thiosulphate leaching method is a non-toxic alternative to the conventional cyanide leaching process. Leach solutions obtained from PCBs contain a variety of base and precious metals with different concentrations due to the diverse PCBs composition (Deveci et al., 2016). Therefore choosing a suitable non-polluting method is important for the recovery of the metal after extraction (Deveci et al., 2016; Alzate et al., 2016). Principal methods used for gold recovery from leach solutions include precipitation, electrowinning, solvent extraction, carbon adsorption, and resin adsorption techniques (Grosse et al., 2003).

According to Akcil et al. (2015), the Au content in WEE is 35-50 times more compared to ores/concentrates. Behnamfard et al. (2013), reported that gold has the highest economic incentive (15,200 $ per ton of PCB), followed by palladium (1850 $ per ton of PCB) and copper (1400 $ per ton of PCB), respectively. Furthermore, it is reported that mobile phones PCBs have more Au content compared to computer circuit boards. They contain about 350 g/ton of Au (Tuncuk et al., 2012; Alzate et al., 2016). Since the precious metal content in Waste PCB's is higher than the ores/concentrates it would be worth to recycle the waste for environmental advantage and for the economic incentive (Akcil et al., 2015).

Cyanide leaching has been widely used to recover gold from gold minerals and secondary sources because of its high efficiency and relatively low cost. The main drawback of this method is the production of a huge amount of cyanide-contaminated wastewaters, which can lead to a serious damage to people and the environment, so this method is gradually replaced by the other methods. Thiosulfate is a favorable lixiviant replacement of cyanide for gold extraction since there are fewer environmental impacts and less interference from foreign cations associated with this process (Behnamfard et al., 2013).

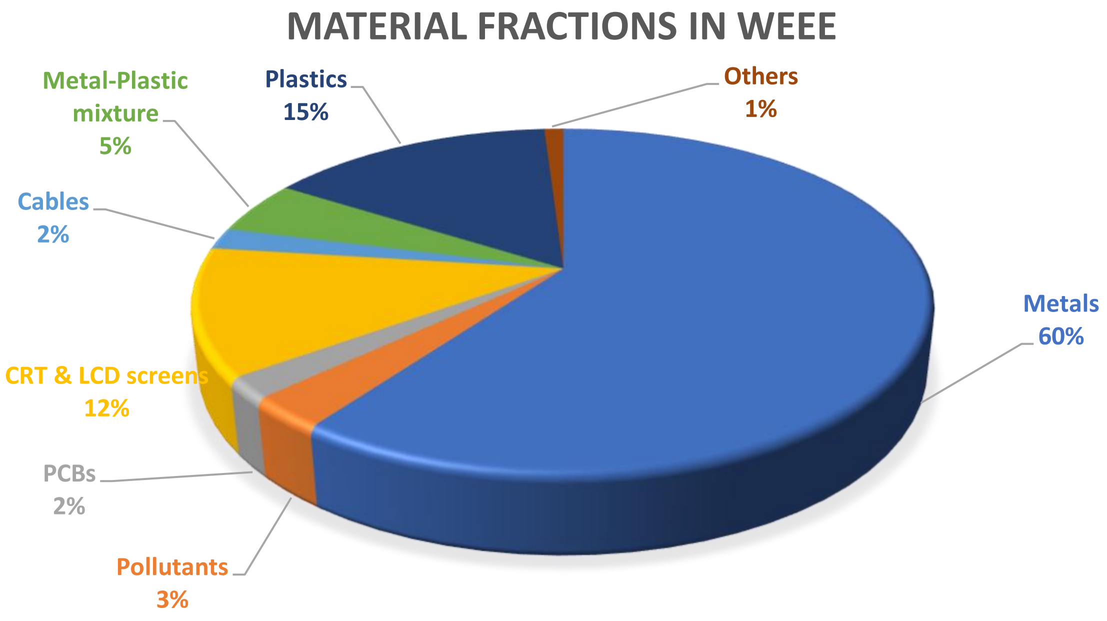


Figure 1-1: Typical material fractions in WEEE. Adapted from Ongondo et al. (2011).

Thiosulphate as a leaching agent is unstable, requires high reagent consumption compared to cyanide, has complex chemistry, and it is difficult to recover dissolved gold from pregnant thiosulphate leach solution (O'Malley, 2002). Gold recovery from leach solutions includes the following: cementation, solvent extraction, ion exchange, adsorption, biosorption, electro-wining, coagulation (Syed, 2012).

The cementation process is preferred to all the other technologies of metals extraction from solution due to ultrahigh purity metals that can be obtained and to the less consumption of materials and energy (Birloaga & Vegliò, 2016).

1.2 Problem Statement of research

The rate of waste electrical and electronic equipment (WEEE) is growing at an alarming rate, especially in developed and developing countries. The recovery of precious metals such as gold, from mobile phones, printed circuit boards is an alternative way to reduce WEEE. However, the leach solutions contain a wide range of base and precious metals with different concentrations due to the heterogeneity of these wastes in a composition which renders downstream processing of the pregnant leach solutions difficult. Therefore the selection of a suitable metal recovery technique is of practical importance for downstream processing.

1.3 Research questions

- What effects do the process variables (i) Temperature (ii) the amount of cementation agent and (iii) stirring speed have on gold precipitation from pregnant ammonia thiosulphate leach solution and hence, on the percentage recovery of gold?
- What effects do the above-mentioned process variables have on the gold concentration of the precipitates produced?

1.4 Aims and objectives

The aim of this study is to recover gold from mobile phones PCBs (printed circuit boards) thiosulphate leach liquor using a copper cementation process and hence minimize WEEE.

The research objectives are:

- To evaluate the effect of temperature, the quantity of cementation agent and stirring speed on the gold percentage recovery.
- To determine the concentration of gold on the precipitates obtained from copper cementation process using Scanning Electron Microscope (SEM) equipped with an Oxford X-Max Energy-dispersive x-ray spectrography (EDS) detector.

1.5 The scope of the study

During this study, the recovery of gold from thiosulphate leach solution was examined through copper cementation process. This research consisted of three stages, namely ammonia thiosulphate leaching, copper cementation and analysis methods of gold concentration. Mobile phones PCBs were used as raw material to extract gold during leaching. Cementation was investigated at temperatures ranging from 30 to 50 ℃, stirring speed of 300 and 900 rpm and the amount of copper powder varying from 0,25 to 0,75 g. Atomic Adsorption Spectrophotometer (AAS) and SEM-EDS were used to measure gold concentration. All other variables were delineated.

1.6 The significance of the research

The recovery of gold from waste mobile phones PCBs will provide a possible solution to the WEEE problem and offer a valuable and sustainable alternative method for gold recovery.

1.7 Thesis Structure

Chapter 1	Provides the introduction of the study
Chapter 2	Gives a detailed literature review
Chapter 3	Gives experimental design and experimental procedure
Chapter 4	Discuss the results that summaries the work done
Chapter 5	Conclusion and Recommendation

CHAPTER 2

2 Literature review

2.1 Introduction

This chapter presents a review of the literature on waste electrical and electronic equipment (WEEE), including composition, hazards and benefits, gold, including its characteristics, Properties, history, and recovery. The focus, however, is on the thiosulphate leaching process and cementation process.

2.2 Waste electrical and electronic waste

2.2.1 Introduction

Waste electrical and electronic equipment (WEEE) also known as electronic waste (e-waste) generation and disposal are becoming issues of concern to solid waste management professionals, environmentalists, international agencies and governments around the world (Stephen E. Musson et al., 2000; Cui & Forssberg, 2003). WEE comprises end-of-life computers, entertainment electronics, mobile phones and household appliances that have been discarded by their original users (Ghosh et al., 2015; Cui & Zhang, 2008). (EEE) electric and electronic equipment includes any device using electricity for power. Such devices are very common and widespread in modern life. However, they often have a short lifespan and as a result, a large fraction (if not all) ends up sooner or later as waste. This type of waste is referred to as WEEE (Bindschedler et al., 2017). EEE consists of six categories:

1. Temperature exchange equipment
2. Screens and monitors,
3. Lamps,
4. Large equipment (e.g., washing machines),
5. Small equipment (e.g., vacuum cleaners), and
6. IT and telecommunication equipment

Electrical and electronic equipment may be televisions, telephones, radios, computers, printers, fax machines, DVDs, CDs, Washing machines, refrigerators, dryers, vacuum cleaners, etc. (Kaya, 2016). The composition distribution of WEEE is represented in figure 2.1.

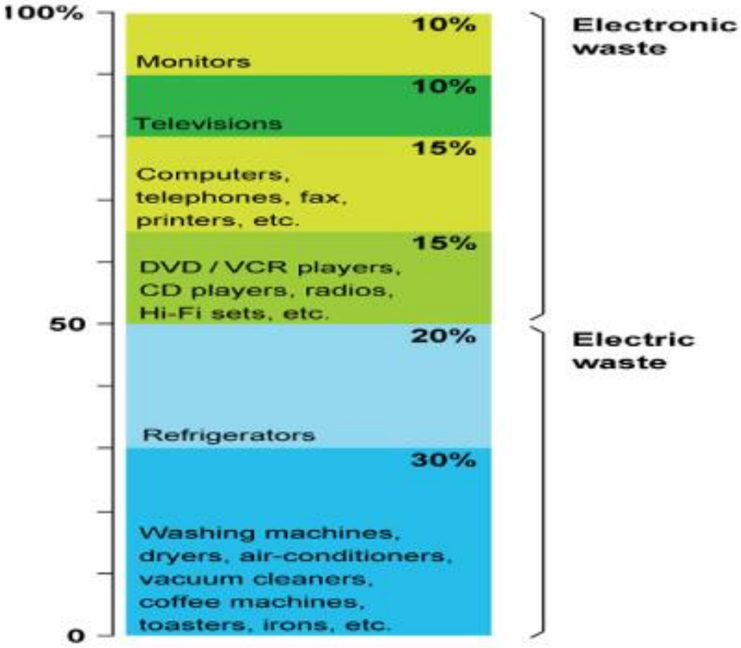


Figure 2-1: Composition distribution of WEEE (Kaya, 2016)

Over time the metal content of WEEE has remained the dominant fraction (Ongondo et al., 2011). WEEE contains hazardous material contents which may cause environmental problems during the waste management phase if it is not properly treated (Nnorom et al., 2008). Moreover, WEEE also contains valuable materials (Li et al., 2004). The following are numerous economic incentives and environmental advantages of precious metals recovery from WEEE (Akcil et al., 2015):

- Conservation of primary metal resources.
- The decrease in the amount of solid waste generated.
- Recovery of non-metal material (plastic, etc.).
- Recovery of Ferrous metals, Non-ferrous metals, and precious metals.
- Energy savings at a greater than the primary metal resources.
- Prevention of environmental pollution caused by heavy metals, solvent-based flame retardant, plastics and toxic gas released from E-waste.

The gold content of a desktop computer is about 0.0016% and 1 ton of electronic scrap of a computer contains more gold than 17 tons of gold ore (Li et al., 2004). According to Nnorom et al. (2008), WEEE can be regarded as a high grade 'ore'. Therefore, secondary gold can be recovered by recycling WEEE (Yamane & Moraes, 2011). Table 2-1 shows that a metal's concentration in WEEE can be about four orders of magnitude higher in comparison to its ore. This makes WEEE a very valuable resource for the recovery of precious metals (Ebin & Isik, 2016).

Table 2-1: Concentration of main elements recovered from WEEE with a comparison to average content in their ores (Ebin & Isik, 2016)

Element	**Average minimum content in ore (%)**	**Average Minimum and maximum content in WEEE (%)**
Copper (Cu)	0.5	10-20
Iron (Fe)	30	1-5
Aluminium (Al)	30	2-6
Zinc (Zn)	4	0.5-6
Nickel (Ni)	1	1.5-8
Tin (Sn)	0.5	0.3-5
Lead (Pb)	4	0.3-1.8
Antimony (Sb)	3	0.2-1.8
Gold (Au)	0.0001	0.002-0.03
Silver (Ag)	0.01	0.03-0.3
Palladium (Pd)	0.0001	0.001-0.02
Indium (In)	0.001 (in zinc ores)	0.02-0.04

Kaithari & Al Balushi (2016) made a comparison between different metals present in the various type of WEEE, as shown in figure 2.2. it can be seen that there is a considerable amount of gold present in computers and mobile phones

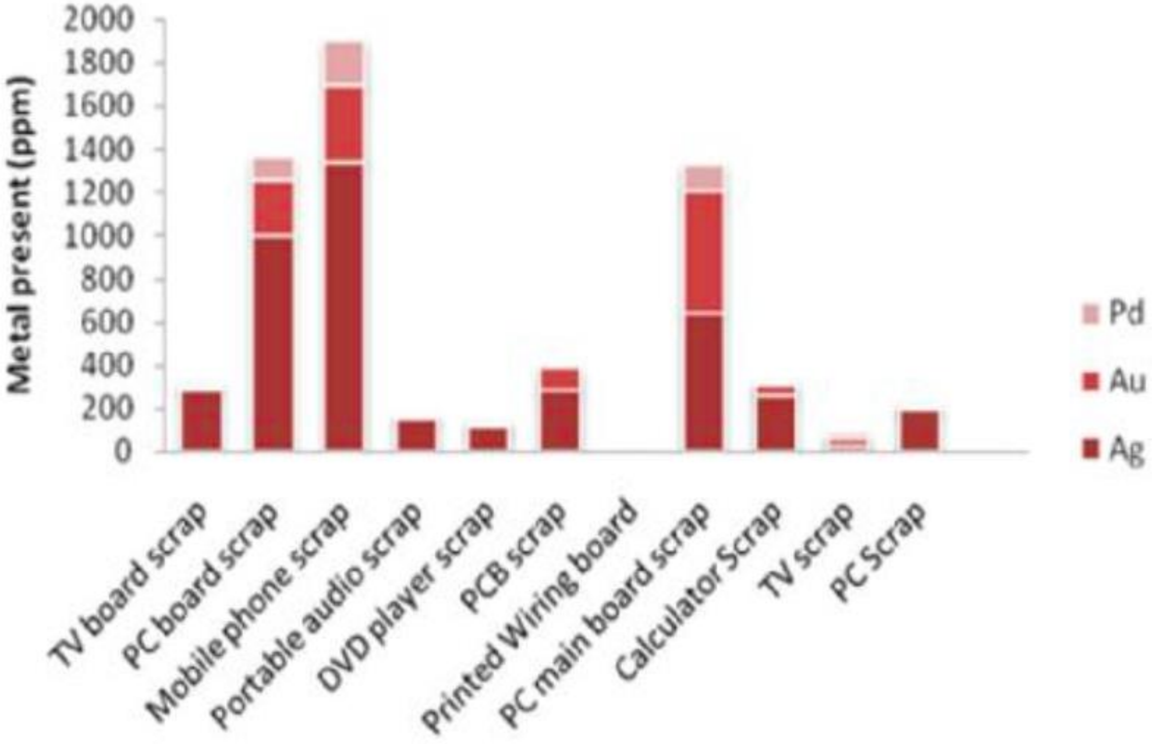


Figure 2-2: Concentration of main elements recovered from WEEE with a comparison to average content in their ores (Kaithari & Al Balushi, 2016).

According to Khaliq et al. (2014), metals in WEEE can be grouped into precious metals (PMs), platinum group metals (PGMs), base metals (BMs), metals of concern (MCs), and scarce elements (SEs), as shown in table 2-2. The extraction of PMs and BMs from WEEE is a major economic drive due to their associated value. According to Alzate et al. (2016), WEEE is the main secondary sources to recover precious metals (PMs) and base metals (BMs).

Table 2-2: Types of metals found in WEEE (Khaliq et al., 2014).

PMs:	Au, Ag;
PGM:	Pd, Pt, Rh, Ir, and Ru;
BMs:	Cu, Al, Ni, Sn, Zn, and Fe;
MCs (Hazardous):	Hg, Be, In, Pb, Cd, As and Sb;
S:	Te, Ga, Se, Ta, and Ge.

2.2.2 Global electronic waste

The global production of e-waste/WEEE is increasing rapidly and is expected to accelerate in the near future. Global e-waste generation was estimated to be 41.8 million tonnes in 2014 and was expected to increase to 65.4 million tonnes in 2017 with the majority of WEEE generated by Europe, USA, and Australasia. However, China, Eastern Europe, and Latin America are expected to become significant e-waste producers in the next decade (Heacock et al., 2016; Khaliq et al., 2014).

2.2.3 Electronic waste in South Africa

E-waste volumes are expected to increase considerably is the country in the near future. As a country, South Africa faces challenges at the level of consumer awareness, recycling processes, and the collection and disposal of e-waste. These concerns call for action, from all stakeholders, to deal with the e-waste challenge in the country. Plan of action may include developing appropriate policy and legislation, and a practical e-waste management solution which benefits all stakeholders (Finlay & Liechti, 2008).

South Africa is one of the top three African countries with the highest e-waste generation in absolute quantities. Other countries include Egypt and Nigeria. In 2014 it was estimated that 0.35 Megatonnes of e-waste were produced in South Africa (Baldé et al., 2015; Basson et al., 2016) and approximately 6.6 kilograms of e-waste was generated per individual (Baldé et al., 2015).

There is an increase in material recovery activity for electronic scrap in South Africa. Presently there is mechanical processing of obsolete computers, photocopiers, telephones, printers, faxes, telex machines, calculators, cell phones and other post-consumer goods in the country. More than 4000 tons of electronic waste is processed each year by recyclers in the country (Nnorom et al., 2008).

According to Finlay & Liechti (2008), about 70% of the country’s e-waste is thought to be in storage, and most of it is held by the government. The 70% represents about 10-20 thousand tons of e-waste, which is expected to double in 10 years’ time. Basson et al., (2016) only 12% (45 000 tonnes) is being recycled currently. Table 2-3 shows the tonnages of total waste, as classified by EWASA.

Table 2-3: E-Waste total waste (Basson et al., 2016).

E-Waste classification	Tonnes	Percentage recycled
Large appliances stoves and fridges.	125 000	39%
Consumer equipment	78 000	24%
Information technology equipment	77 000	24%
Small household appliances	40 000	13%

The National Environmental Management: Waste Act (Act 59 of 2008) includes WEEE within the definition of hazardous waste due to its potentially hazardous nature (when improperly handled or when not handled at all). Therefore, certain activities in managing WEEE require a special waste management license. Thus, one must ensure that no harm is caused to people or the environment in the process (Jeffares & Green (Pty) Ltd & Envirosense, 2013)

According to Jeffares & Green (Pty) Ltd & Envirosense (2013), no one is allowed, by Law, to store more than 35 m^3 waste at any time or sort more than 500 kg per day without a license.
Obtaining a waste management license is a costly and lengthy process which is a barrier for business as most recyclers are medium-sized enterprises and can therefore not afford the associated environmental impact assessment (EIA) (Basson et al., 2016).

2.2.4 WEEE management

All components of WEEE represent a potential environmental hazard when not properly disposed of. As a result, several options are available for the treatment of WEEE. They are either landfilled or incinerated. Alternatively, they can be reused, recycled or remanufactured. Landfilling and incineration are not desired as they pose environmental concerns through emissions of hazardous compounds such as dioxins and heavy metals (Bindschedler et al., 2017). Reuse and recycling are preferred as they have a few impactful effects (Canda et al., 2018):

1. Technologically – using waste on current production flows as raw materials thus replacing the depleting reserves of natural raw materials
2. Economically – can substantially reduce manufacturing costs by recycling waste
3. Ecologically – removing waste that is currently produced or currently stored as it poses a threat to the health of the population and a threat to the environment

2.2.5 Hazards associated with E-waste

E-waste is made up of a large range of materials, some of which contain a variety of toxic substances that can contaminate the environment and threaten human health if not correctly managed. Table 2-4 shows common toxic substances associated with WEEE and their health implications (Kiddee et al., 2013).

According to The Constitution of the Republic of South Africa (Act 106 of 1996), it is illegal for anyone to burn any part of e-waste (such as cables, plastic casings), as this creates very toxic smoke.

Table 2-4: Common toxic substances associated with e-waste and their health impacts adapted from (Kiddee et al., 2013).

Substance	**Health impact**
Antimony (Sb)	Antimony has been classified as a carcinogen. It can cause stomach pain, vomiting, diarrhea and stomach ulcers through inhalation of high antimony levels over a long time period
Arsenic (As)	It has chronic effects that cause skin disease and lung cancer and impaired nerve signaling
Barium (Ba)	Causes brain swelling, muscle weakness, damage to the heart, liver, and spleen through short-term exposure
Beryllium (Be)	Exposure to beryllium can lead to berylliosis, lung cancer, and skin disease. Beryllium is a carcinogen
Brominated flame retardants (BFRs): (polybrominated biphenyls (PBBs), polybrominated diphenyl ethers (PBDEs) and tetrabromobisphenol (TBBPA))	During combustion, printed circuit boards and plastic housings emit toxic vapors known to cause hormonal disorders
Cadmium (Cd)	Cadmium compound pose a risk of irreversible impacts on human health, particularly the kidneys

Chlorofluorocarbons (CFCs)	These substances impact the ozone layer which can lead to a greater incidence of skin cancer
Hexavalent chromium/chromium VI (Cr VI)	Is extremely toxic in the environment, causing DNA damage and permanent eye impairment
Lead (Pb)	Can damage the brain, nervous system, kidney, and reproductive system and cause blood disorders.
Mercury (Hg)	Mercury can damage the brain, kidneys, and fetuses
Nickel (Ni)	Can cause allergic reactions, bronchitis, reduced lung function, and lung cancers
Polychlorinated biphenyls (PCBs)	PCBs cause cancer in animals and can lead to liver damage in humans
Polyvinyl chloride (PVC)	May lead to respiratory problems.
Selenium (Se)	High concentrations cause selenosis

Although the materials found in mobile phones do not present immediate environmental or human health hazard in ordinary use, if their disposal is not properly managed, it may involve processes and conditions that could lead to the release of these substances or toxic by-products. The disposal of mobile phones thus needs to be managed in an environmentally sound way to minimize releases into the environment and threat to human health (Nnorom et al., 2008).

Thus, Ongondo et al., (2011) and Finlay & Liechti, (2000) emphasize the importance of WEEE recycling. Different methods are applied to recycle WEEE. Pyrometallurgy, electrochemical processes, and hydrometallurgy are methods usually employed to recover valuable metals from WEEE (Tunsu & Retegan, 2016).

Hydrometallurgy and recycling WEEE

Hydrometallurgical treatment of WEEE has received interest due to their potential for relatively low environmental impact (e.g no hazardous gases or dust), small-scale applications and for low-grade WEEE (i.e., 100 g/t Au) (Tuncuk et al., 2012; Deveci et al., 2016).

Hydrometallurgical processes are now being usefully applied to the treatment of obsolete electronic components, spent catalysts, and reactive process residues, to recovering metals from effluents generated in many manufacturing activities, including the manufacturing of integrated circuits and printed circuits boards. Hydrometallurgical processes can also be used to recycle water (Doyle, 2005).

Tunsu & Retegan (2016) report that the two main steps required in any hydrometallurgical process are:

1. The transfer of metals from the solid matrix into an aqueous phase. This step is called leaching or lixiviation and often brings into solution not only the metals of interest but undesired constituents present in the material as well.

2. Separation of the metals of interest from the undesired elements present in solution.

Alongside the two aforementioned steps, additional processing steps are often required. These steps usually comprise a leaching solution pre-concentration of metals in the case of low- grade materials and a purification of the products (Tunsu & Retegan, 2016).

The hydrometallurgical process is associated with acid or alkaline solutions to solubilize a solid material (Petter et al., 2014). The process also involves the mechanical pre-treatment of WEEE, leaching of metals by a proper lixiviant, purification of pregnant leach solution and recovery of metals. The pre-treatment (i.e. size reduction) process is especially needed to expose metals of interest that are covered with or encapsulated by various plastic or ceramic materials on printed circuit boards. Furthermore, the size reduction process is required to facilitate the efficient extraction of metals of interest (Tuncuk et al., 2012).

The most common leaching agents tested for recovery of precious metals include cyanide, halide, thiourea, and thiosulphate (Petter et al., 2014)

The efficiency of the leaching process is influenced by many factors namely; the type of leaching agent, its concentration, pH, temperature, leaching time, stirring, solid-to-liquid ratio, particle size, distribution of elements in the material, entrapment of soluble species into less soluble/insoluble particles, and others (Tunsu & Retegan, 2016).

Cui & Zhang (2008) declare that several substitutes for cyanide have been proposed because a series of environmental accidents at various gold mines that caused severe contamination of rivers and groundwater and that has caused widespread concern over the use of cyanide as a leaching reagent. Generally, the non-cyanide lixiviants thiourea and thiosulfate are regarded as being the most realistic substitutes. Table 2-5 shows alternative substitutions for cyanide.

Table 2-5: Suggested alternatives for leaching of gold to cyanide (Cui & Zhang, 2008)

Reagent type	**Concentration range**	**pH range**	**Basic chemistry**	**Research level**	**Extent of commercialization**
Ammonia	High	8-10	Simple	Low	Pilot tests
Ammonia/cyanide	Low	9-11	Simple	Extensive	Applied to Cu/Au ores
Ammonia thiosulphate	High	8.5-9.5	Complex	Extensive	Semi- commercial
Slurry CN-electrolysis	Low	9-11	Simple	Historical	Limited historical
Sodium sulfide	High	8-10	Simple	Low	Geological interest only
Alpha-hydroxynitriles	Moderate	7-8	Fairly simple	Fairly popular	None
Malononitrile	Moderate	8-9	Fairly complex	Low	None
Alkali cyanoform	Poorly defined	~9	Poorly defined	Low	None
Calcium cyanide	Poorly defined	~9	Poorly defined	Low	None
Alkaline polysulfides	High	8–9	Poorly defined	Low	None
Hypochlorite/chloride	High chloride	6–6.5	Well defined	Extensive	Historical and modern
Bromocyanide	High	6–7	Poorly defined	Historical	Historical

Iodine	High	3–10	Poorly defined	Low	None
Bisulfate/sulfur dioxide	High	4–5	Fairly simple	Low	None
Bacteria	High	7–10	Fairly complex	Low, growing	None
Natural organic acids	High	5–6	Fairly complex	Low	None
DMSO, DMF	Poorly defined	7	Poorly defined	Very low	None
Bromine/bromide	High	1–3	Well defined	Low	Historical
Thiourea	High	1–2	Well defined	Fairly popular	Some concentrates
Thiocyanate	Low	1–3	Well defined	Low	None
Aqua regia	High	Below 1	Well defined	Low	Analytical and refining
Acid ferric chloride	High	Below 1	Well defined	Low	Electrolytic Cu slimes
Ethylene thiourea	High	1–2	Poorly defined	Very low	None
Haber process	Poorly defined		Proprietary	One entity	None
“Bio-D leachant”	Poorly defined		Proprietary	One entity	None
High-temperature chlorination	High	6–7	Simple	Historical	Historical

2.2.6 Pre-processing

Tuncuk et al. (2012), states, that to recycle valuable metals from WEEE by a hydrometallurgical process, a mechanical pre-treatment step will be needed. Disassembly of WEEE is a systematic approach that allows removal of a component or part, or a group of parts or separation a product into all its parts for a given purpose (Cui & Forssberg, 2003). After the removal of components, metal bearing components such as PCBs are subjected to size reduction prior to the metal recovery process. (Tuncuk et al., 2012). Petter et al. (2014) declare that the precious metals are often encapsulated by a polymer or ceramic materials, so it is necessary to decrease the size of the particles to improve the extraction. According to Havlik et al. (2014), the reason for pre-treatment in WEEE is that metals in WEEE are present in a metallic form or as alloys whereas in ores they occur in form of chemical compounds. This makes them especially suitable for mechanical–physical pre-treatment before metallurgical processing. PCBs in WEEE is the richest source of base and precious metals promoting economic drive for metal recover (Arora & Dikshit, 2014).

2.3 Printed circuit boards (PCBs)

Printed circuit boards (PCBs) are found in any piece of electrical or electronic equipment. Almost all electronic items contain circuit boards. An increasing number of white goods, like washing machines, contain circuit boards in electronic timers. PCBs contain a variety of materials like metals, polymers, and ceramics (Luda, 2011).

PCBs are used to mechanically support and connect electronic components electrically using conductive pathways, tracks or signal traces. PCBs are essentially the base of electronics. PCBs, contain Cu sheets laminated onto a non-conductive substrate. PCBs make up no less than 3% of the total electronic scraps by weight (Kaya, 2016). According to Arshadi & Mousavi (2015), the purity of precious metals has been found to be 10 times greater than that of rich-content minerals. Table 2-6 below illustrates material compositions of printed circuit boards. According to Kaya (2016), PCBs essentially consists of the following three basic parts:

- a non-conducting substrate or laminate,
- conducting Cu substrate printed on or inside the laminate and
- the components attached to the substrate (chips (Ga, In, Ti, Si, Ge, As, Sb, Se, and Te), connectors (Au, Ag), capacitors (Ta, Al), etc.).

Table 2-6: Representative material compositions of printed circuit boards (wt%) adapted from (Ogunniyi et al., 2009).

Materials	**%**
Metals (Max. 40%)	
Cu	20
Al	2
Pb	2
Zn	1
Ni	1
Fe	8
Sn	4
Sb	0.4
Au/ppm	1000
Pt/ppm	-
Ag/ppm	2000
Pd/ppm	50

Ceramic (Max 30%)	
SiO_2	15
Al_2O_3	6
Alkaline and Alkaline earth oxides	6
Titanates, Mica, etc.	3
Plastics (Max 30%)	
Polyethylene	9.9
Polypropylene	4.8
Polyesters	4.8
Epoxies	4.8
Polyvinyl-chloride	2.4
Polytetra-chloroethane	2.4
Nylon	0.9

2.3.1 Characterization of PCBs

Characterization of PCBs in terms of types, structure, components, and composition is important to establish the route and process for recycling. Table 2.9 shows different types of PCBs with contents and properties (kaya, 2016). There are two types of PCBs normally used in personal computers and mobile phones, FR-4, and FR-2 (FR = Flame Retardant). The FR-4 type is used in small devices such as mobile phones and the FR-2 type is used in televisions and household appliances such as personal computers. The FR-4 type is composed of a multilayer of epoxy resin, fiberglass coated with a copper layer, however, the FR-2 type is a single layer of fiberglass or cellulose paper and phenolic coated with a copper later (Yamane & Moraes, 2011).

Table 2-7: PCBs types, contents and properties (Kaya, 2016).

Board/substrate	**Single Sided**	**Double Sided**	**Multiple layered**
Resın	**Type**	**Color**	**Value**
FR-2 (reinforcement)	Phenolic cellulose paper	Yellow/brown	Low-value EEE (TV, home electronics)
FR-4 (reinforcement)	Epoxy glass fiber	Green	High-value EEE (PC, phones)
Glass fiber/cellulose	FR-4	FR-4	FR-4
	FR-2	FR-2	FR-2
Cu substrate			
Solder	Sn, Pb		
Electronic components (IC)	Chips, ICs, relays	Connectors, capacitors	Resistors, switches

2.3.2 Mobile phones PCBs (MPPCBs)

Mobile phones are the most used general electronic product on the globe. They generally have relatively short life-cycles because of rapid changes in equipment features and capabilities. Furthermore, the rapid introduction of new and improved technology into mobile phones, coupled with increasing functionality such as cameras and music players, means that mobile phones have relatively short life cycles. Discarded mobile phones represent a significant and growing problem with respect to WEEE. Mobile phones probably represent one of the most valuable electronic products that are currently found in large numbers in the waste stream, in terms of mass and volume (Nnorom et al., 2008; Ongondo et al., 2011)

Yamane & Moraes, (2011) indicate that the lifetime of mobile phones is approximately one year whereas the lifetime of a computer is two to five years. It is estimated that about 100 million mobile phones are discarded annually in the world due to malfunctioning equipment or because technologies become obsolete.

Mobile phone subscribers worldwide are anticipated to reach 8.2 billion as presented in figure 2-3. The life of mobile phones is drastically getting reduced; it is less than two years in developed countries and three in developing countries. Hence an enormous mobile phone waste of more than 8.2 billion mobile phones is expected to be accumulated worldwide in the coming years (Vats & Singh, 2015).

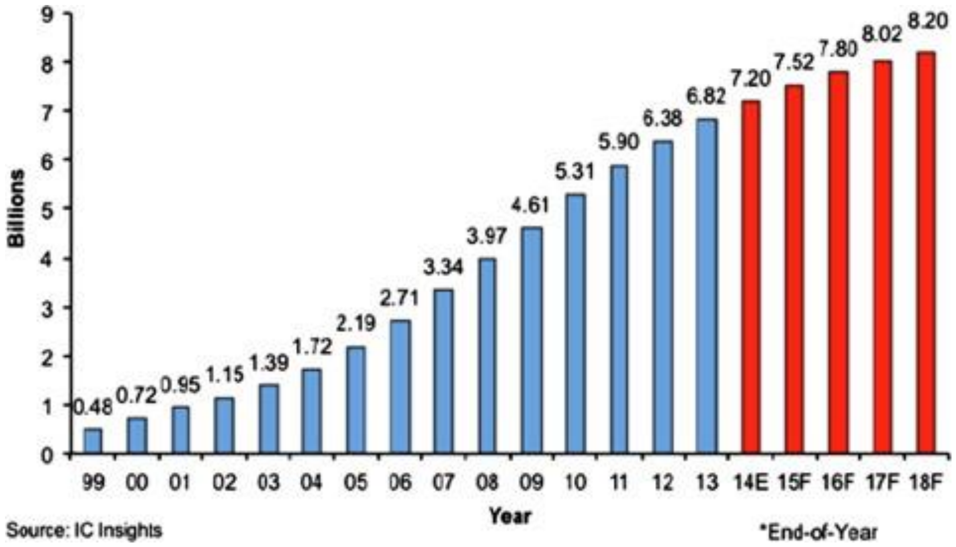


Figure 2-3: Total worldwide cellular subscription from 1999 to 2018 (Vats & Singh, 2015).

According to Nnorom et al. (2008), mobile phones are similar in composition to other electronic devices. Figure 2-4 shows the characteristics composition of a mobile phone. They are made up of plastics, metals, ceramics, and trace other substances. A mobile phone typically consists of the following:

1. electronic circuitry — a PCB, containing a microprocessor, digital signal processor, read-only-memory and flash memory chips, to which are attached connectors, a small microphone, and a small speaker,
2. an antenna, sometimes contained inside with circuitry
3. a screen–liquid crystal display (LCD) technology and glass,
4. a battery — sealed within its own case, using one of the three technologies: nickel–cadmium, nickel metal hydride, or lithium ion/polymer
5. a case — plastic, holding the components described above, sometimes with a metal coating or liner,
6. a charger base or connector — a small transformer to low-voltage direct current, wire, plastic, with copper connecting points, used for recharging the battery and,
7. accessories such as an earphone or connecting cable to a computer

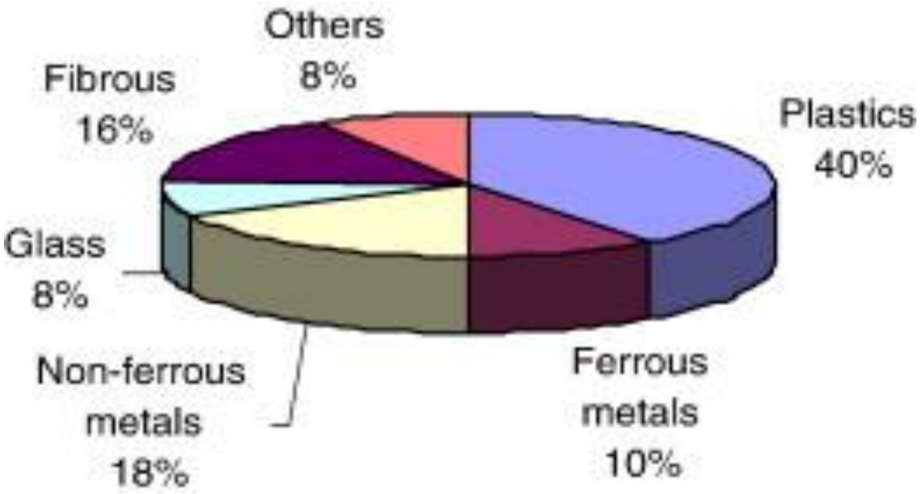


Figure 2-4: Composition of a typical cell phone (Nnorom et al., 2008)

Mobile phones contain toxic elements, such as lead (Pb), mercury (Hg), chromium (Cr), nickel (Ni), beryllium (Br), antimony (Sb) and Arsenic (As). Hence, recycling waste mobile phones are required for both environmental protection and resource conservation (Ha et al., 2010; Vats & Singh, 2015). Furthermore, Waste mobile phones can be regarded as an important source of metals for the recovery of precious metal such as gold and silver, which will help to protect the environment by decreasing the accumulation of WEEE (Jing-ying et al., 2012).

Jing-ying et al. (2012), used Atomic absorption spectrophotometer (AAS) to determine copper, zinc, nickel, gold and silver contents present in the digestion solution, and the results are shown in Table 2-7.

Table 2.7: Average metal content and value ratios of typical mobile phones, Adapted from Jing-ying et al. (2012).

Element	Cu	Zn	Ni	Au	Ag
Content (mg/g)	398.6	4.56	3.96	0.043	0.54
Value ratio (%)	39.86	0.456	0.396	0.0043	0.054

Mobile phone printed circuit boards (MPPCBs) are the main carrier of metals in which precious metals make up more than 70% of their weight. Figure 2-5 shows the metal content of MPPCBs determined via the inductively coupled plasma emission spectrometry (Arshadi & Mousavi, 2015). MPPCBs is special due to the high content of precious metals (PMs). They can contain up to 40 different elements (Szalatkiewicz Jakub, 2014).

According to Petter et al. (2014), PCBs of mobile phones are made of polymers, ceramics, and metals. The metallic fraction consists of several metals, such as copper (Cu), tin (Sn), zinc (Zn), nickel (Ni), gold (Au), silver (Ag), and palladium (Pd). From an economic perspective, recycling mobile phones are very attractive because each ton has on average 130 kg of Cu, 3.5 kg of Ag, 0.34 kg of Au, and 0.14 kg of Pd.

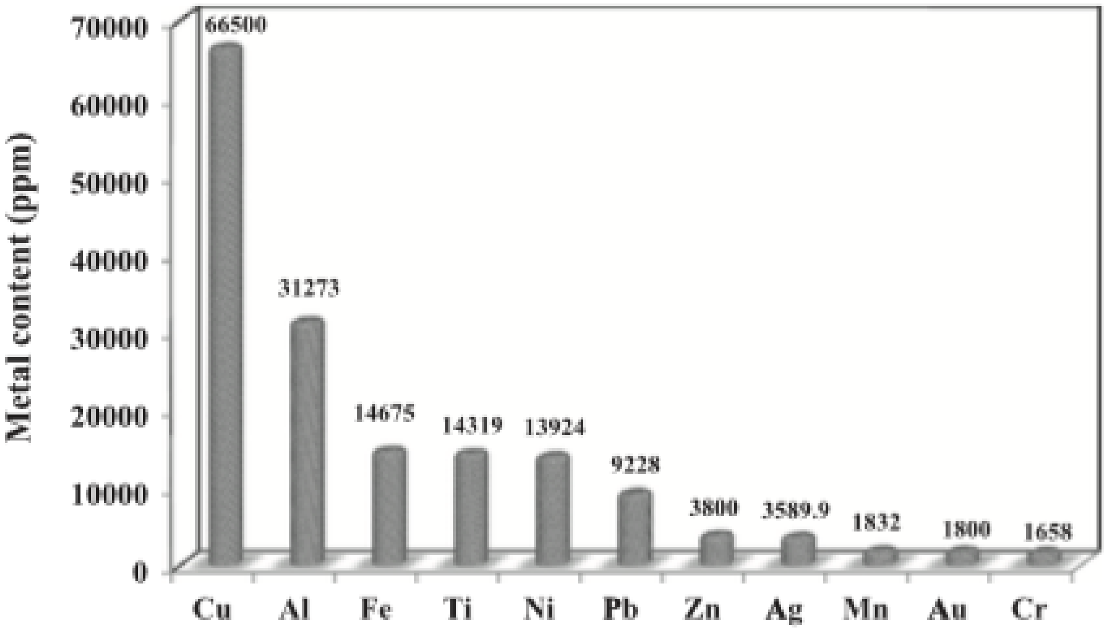


Figure 2-5: The Metal content of mobile phones printed circuit boards (Arshadi & Mousavi, 2015)

Printed circuit boards (PCBs) of a PC can contain 250 g/ton of gold, which is 25-250-fold when compared with gold ores (~1– 10 g/ton Au). However, MPPCBs have more Au content compared to computer circuit boards. They contain 350 g/ton Au (Tuncuk et al., 2012; Akcil et al., 2015).

2.4 Gold

Lee, (2003) indicates that Gold is a highly valued and attractive metal. It is sometimes found free in nature but it is usually found in conjunction with silver, quartz ($Si0_2$), calcite (CaCOs), lead, tellurium, zinc or copper. Arshadi & Mousavi, (2015) say that a significant portion of gold has been used in electrical instruments during the last four decades because of its high electrical conductivity.

Gold recovery is remarkable due to its huge industrial applications, high market prices and extensive use as a precious metal. Gold is an essential precious metal with a singular beauty. Furthermore, it is treasured because of its color. It has a massive demand in the jewelry, high-tech industries, and medical applications. Considerable quantities of gold have been used by the electronic and electric industries due to its excellent electrical conductivity, low contact electrical resistance for inserting connections and outstanding corrosion resistance (Syed, 2012).

Gold recovery from WEEE is crucial because of its growing demand. According to Vats & Singh (2015), 267.3 Megatons of gold is being consumed per year for the manufacturing of mobile phones, laptops, and other electronic equipment.

Bindschedler et al., (2017) point out that Gold is a precious metal and represents a non-renewable resource. It is extremely rare in the environment and occurs in the following three states:

1. 0 (Au(0))
2. Aurous gold: +1 (Au(I))
3. Auric gold: +3 (Au(III))

Au ions are unstable in aqueous solutions under surface conditions (Pressure and temperature). Consequently, Au(0) will form metal colloids, whereas Au(I) and Au(III) form complexes with available anions. Au complexes are usually toxic to organisms (Bindschedler et al., 2017).

2.4.1 History of gold

The history of gold begins in ancient times. Bits of gold were found in Spanish caves where Palaeolithic people live around 40 00 BC. Gold was called aurum by the Romans, means being “shinning dawn”. Gold is the first element and the first metal mentioned in the Bible, where it appears in more than 400 references (Lee, 2003).

2.4.2 Background

According to Bouwer (1999), the metal is characterized by certain physical properties, which include the following:

- gold metal has a bright yellow color;
- conducts heat and electricity;
- is nonmagnetic;
- has a high ductility (can be drawn into a thin wire without breaking);
- has a high malleability (where one ounce [31,3 g] can be beaten into a sheet of 9 m^2);
- is a very soft metal, rating 2 on Moh's scale;
- has a melting point of 1063 ^oC and a boiling point of 2660 ^oC; and
- is a very heavy metal, having a specific gravity ranging from 15-19 g/cm^3, depending on the silver content and declines with increasing silver content.

2.4.3 Gold recovery

Mechanical separation, pyro-metallurgical, bio-hydrometallurgical and hydrometallurgical technologies have been extensively used to recover gold from secondary sources (Cui & Zhang, 2008; Syed, 2012).

2.4.3.1 Pyrometallurgy

Pyrometallurgical techniques for recovering metals from various waste materials have been used during the last two decades (Khaliq et al., 2014). Smelting in furnaces, incineration, combustion, and pyrolysis are typical e-waste recycling processes. The technique is practiced at high temperatures, and therefore require a high amount of energy input (Cui & Zhang, 2008; Khaliq et al., 2014; Ebin & Isik, 2016).

2.4.3.2 Biohydrometallurgy

Biohydrometallurgy process such as cyanogenic leaching is commercially exploitable technology applicable for metal extraction from electronic waste and low-grade ores (Sahni et al., 2016). A variety of microorganisms such as *Chromobacterium violaceum*, *Pseudomonas fluorescens*, *Pseudomonas aeruginosa,* and *Bacillus megaterium* are that in the presence of various metals are able to form cyanide as secondary metabolite and consequently mobilize some stable metals like platinum and gold (Arshadi & Mousavi, 2015). Although having huge potential, bioleaching of metals involves the use of live microorganisms, which takes significant time to finish the process (Bhat et al., 2012). In addition, as reported by Sahni et al. (2016), bioleaching proved to be an inefficient way to leach out gold from SIMW in the presence of a high proportion of other metals like copper.

2.4.3.3 Hydrometallurgy

Hydrometallurgy is an ancient technique (Ehrlich, 2001). Hydrometallurgical techniques are associated with acid or alkaline solutions to solubilize a solid material (Petter et al., 2014). Solvents such as halides, cyanides, thiourea, and thiosulphate are used for the leaching of WEEE (Khaliq et al., 2014).

When compared to conventional pyrometallurgical techniques, hydrometallurgical techniques are more accurate, predictable, and can be controlled easily (Cui & Zhang, 2008). Although simple in nature and rather straightforward, effective hydrometallurgical processing of WEEE requires pre-treatment of the material (Tunsu & Retegan, 2016).

2.4.4 Gold mining in South Africa

Naicker & Cukrowska, (2003) reported that gold mining in South Africa commenced in the Johannesburg area in 1886. Gold was initially extracted using a mercury amalgam method, but as mining operations became deeper, an unoxidized ore containing pyrite (FeS_2) was encountered, which interfered with the extraction. During that time, the MacArthur-Forrest process of gold extraction, using cyanide, was developed, and was successfully applied to Witwatersrand ores. This was phased in during the 1890s.

Gold has been mined in South Africa for more than 120 years, producing a cumulative total of about 51 200 tons and about 30 percent of the 157 000 to 180 000 tons cumulative world production in 2010. About 85% of this production remains in circulation. For several decades, South Africa was the largest gold producer in the world, with production peaking at about 1000 tons in 1975, although declining to less than 200 tons/year in recent years (Cairncross & Kisting, 2016).

2.4.5 Uses of gold

Gold is used in electronics mainly in the form of electroplating chemicals, gold bonding wire, and sputter targets. Smaller quantities are used in hybrid inks and solders. Goodman, (2002) indicates that the use of gold as an electroplated coating on connectors and contacts is largest in electronics. According to Lee (2003), gold alloys are used to make jewelry, decorative items, dental fillings, and coins.

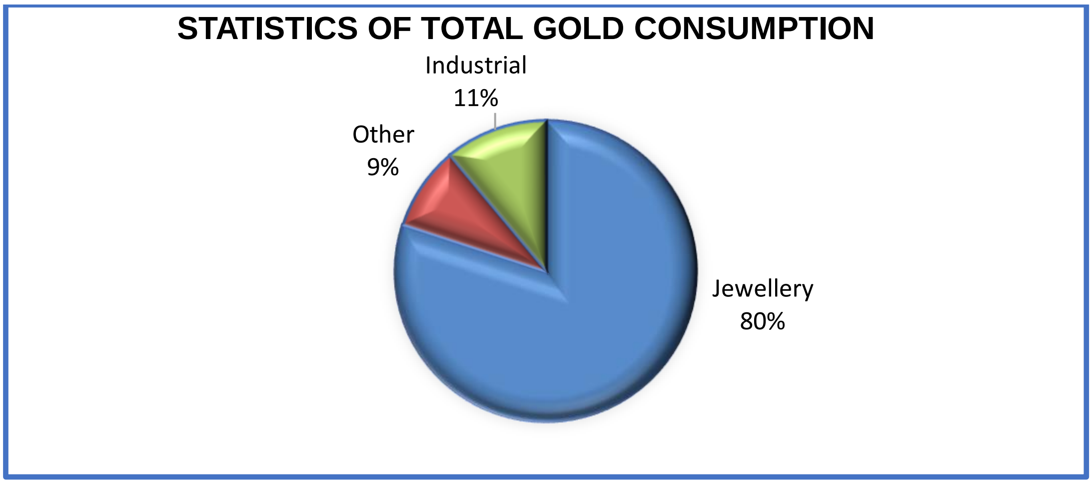


Figure 2-6: Total consumption of gold. Adapted from (Lee, 2003)

In jewelry production, pure metal is alloyed with other metals, usually copper, to increase the hardness, as the pure metal is too soft (Bouwer, 1999).

Figure 2-6 and 2-7 illustrate the world consumption of gold (Lee, 2003). Jewelry consumes 80 % of gold and industrial usage is only 11 %. Electronics usage is 54 % of industrial usage and dentistry uses 18 % as shown in Figure 2.7.

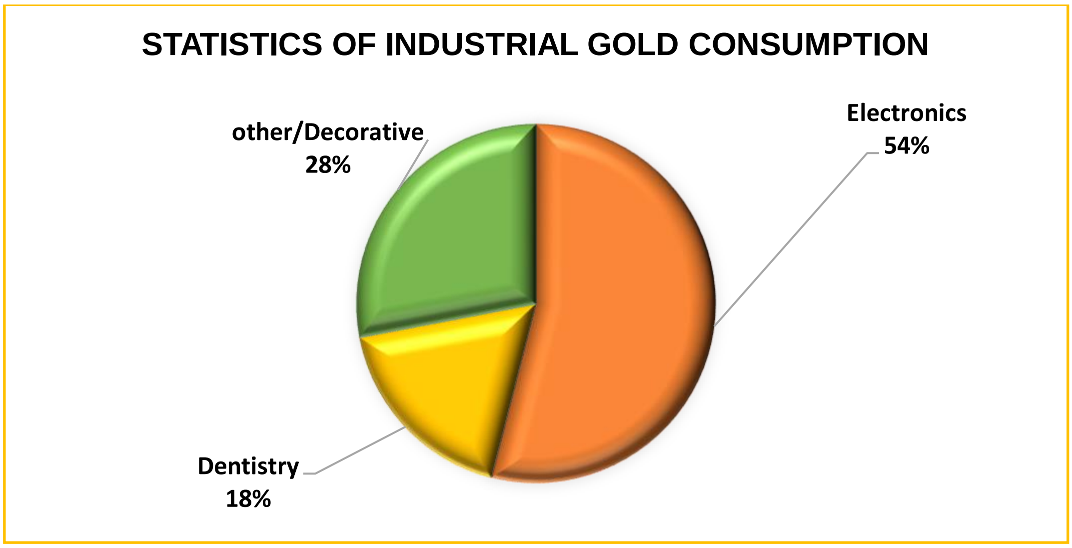
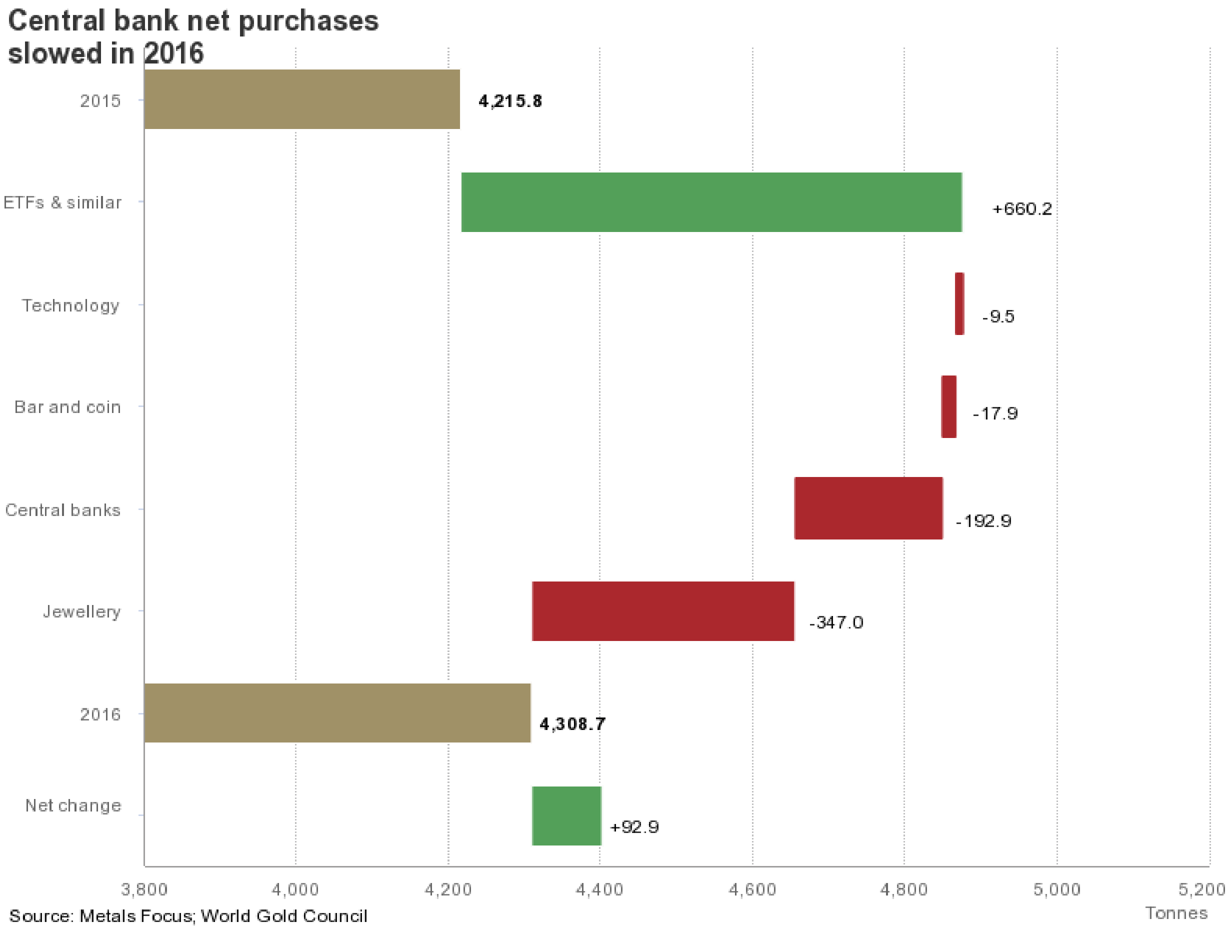


Figure 2-7: Industrial consumption of gold. Adapted from (Lee, 2003)

2.4.6 Gold demand

In 2016, gold demand gained 2% to reach a 3-year high of 4308.7 tonnes as shown in figure 2-8. Declines in jewelry production and central bank purchases counter weighed this growth. Annual bar and coin demand were broadly stable at 1029.2 tonnes (World Gold Council, 2017)



Source: Metals Focus; World Gold Council

Figure 2-8: Change in annual gold demand, 2016 vs 2015. Adapted from (World Gold Council, 2017)

2.4.7 Gold prices

According to (Zhang & Wei, 2010) gold plays a special role as a store of value especially in times of political and economic uncertainties. Hence, compared with other metals in the large commodity market, gold registers an evident advantage and outstanding position.

Source: Reuters Datastream, LBMA, World Gold Council

Figure 2-9: Gold price in US Dollars Adapted from (World Gold Council, 2017)

The price and production behavior of gold differs from most other mineral commodities. In the 2008 financial crisis, the gold price increased by 6% while many key mineral prices fell and other equities dropped by around 40% as indicated in figure 2-9 (Shafiee & Topal, 2010).

Białkowski et al., (2015) say that since 2001 the price of gold has increased rapidly from US$ 250 per troy ounce to an all-time high of US$ 1900 in August 2011, before dropping substantially to around US$ 1200 at the end of June 2013.

2.4.8 Gold extraction from its ores

Since the discovery of gold, various techniques have been tested to separate the precious metal from its the ores. The type of techniques utilized to extract gold from the ore body is determined by the mineralogy of the ore and the degree of liberation of gold particles. The raw ore body is crushed and ground in the attempt to free as much gold, which could be separated either by a chemical, physical or surface based process (Bouwer, 1999).

Wan & LeVier (2003) indicate that most gold production from primary resources is still achieved by cyanidation although several research activities have been focused on alternative processes using non-cyanide lixiviants.

Cyanidation and recovery by the Carbon-in-Pulp/Carbon-in-Leach process (CIP/CIL) is the primary and proven treatment process for free milling ores (Brooy et al., 1994).

Generally, gold ores can be classified as "free milling', "complex" or "refractory", as illustrated in Figure 2-10.

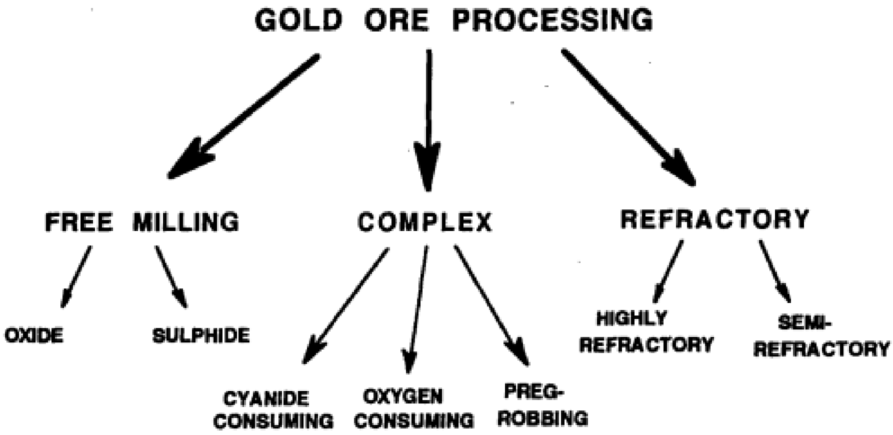


Figure 2-10: Choice of gold processing route (Brooy et al., 1994)

2.5 Leaching

This is the first step in the gold recovery process in which all accessible soluble metals in the feedstock are dissolved. The most common leaching agents used in the recovery of gold include cyanide, halide, thiourea, and thiosulphate (Syed, 2012). It is a hydrometallurgical process associated with acid or alkaline solutions to solubilize a solid material (Petter et al., 2014).

Factors affecting the rate of extraction

According to Backhurst & Harker, (1999), there are four important factors to be considered:

Particle size: The smaller the size, the greater is the interfacial area between the solid and the liquid, and therefore the higher is the rate of transfer of material and the smaller is the distance the solute must diffuse within the solid.

Solvent: The liquid chosen should be a good selective solvent and its viscosity should be sufficiently low for it to circulate freely. Generally, a relatively pure solvent would be used initially, as the extraction proceeds, the concentration of the solute increases while the rate of extraction progressively decreases. Firstly, this is because the concentration gradient is reduced, and secondly the solution generally becomes more viscous.

Temperature: The solubility of the metal being extracted increases with temperature to give a higher rate of extraction in most cases.

Agitation of the fluid: Agitation of the solvent is important because this increases the eddy diffusion and therefore the transfer of material from the surface of the particles to the bulk of the solution.

2.5.1 Aqua regia

Aqua regia is a traditional medium for dissolving gold and the platinum group metals. It is a mixture of three parts concentrated hydrochloric acid to one part concentrated nitric acid. The reactions (equation (1)-(3)) involved in the process are as follows (Sheng & Etsell, 2007):

$$2HN0_3 + 6HCl \rightarrow 2NO + 4H_2O + 3Cl_2 \quad (1)$$

$$2Au + 9HCl + 3HN0_3 \rightarrow 2AuCl_3 + 3NOCl + 6H_2O \quad (2)$$

$$3HCl + HN0_3 \rightarrow Cl_2 + NOCl + 2H_2O \quad (3)$$

Gold forms the stable tetrachloroaurate (III) complex anion upon dissolution in this media as shown in equation (4) below (Geoffroy & Cardarelli, 2005).

$$Au + 4HCl + HN0_3 \rightarrow HAuCl_3 + NO + 2H_2O \quad (4)$$

Previous studies have reported successful gold extraction using aqua regia. Cyganowski et al. (2017) recovered up to 86% of gold from aqua regia leachate of WEEE using a core-shell type anion exchange resin. Park & Fray (2009) used aqua regia as a leachant and gold of about 97 wt.% was recovered. Sheng & Etsell (2007) used a three-stage process that involves aqua regia to recover gold from computer PCBs. 550 mg/L of gold from computer circuit boards was leached.

According to Geoffroy & Cardarelli (2005), the main drawback of the treatment with aqua regia is the nitric oxide (NO) gas that evolves when the metal is digested. NO gas is noxious and poses a major threat to the health of personnel and the overall safety in the workplace. In addition, the presence of silver chloride in the residue decreases the purity of the precipitated gold. Metastannic acid furthermore hinders the dissolution of gold (Sheng & Etsell, 2007). Aqua regia is usually applied in the laboratory scale because of aqua regia’s strong-oxidation and high-corrosion to the equipment (Behnamfard et al., 2013).

2.5.2 Cyanide leaching

According to Jing-ying et al., (2012), cyanide leaching has been widely used to recycle gold, however, this method can produce a lot of cyanide wastewater, which can lead to a serious damage to people and the environment, so this method is gradually replaced. Syed, (2012) reports that a progression of environmental accidents at different gold mines the world over has led to a widespread concern over the use of cyanide as a leaching reagent.

The overall reaction is given by equation (5) below (Syed, 2012):

$$4Au + 8CN^{-} + O_2 + 2H_2O \rightarrow 4Au(CN)_2^{-} + 4OH^{-} \qquad (5)$$

Over the last century, cyanide leaching has been widely used to recover gold from gold minerals and also secondary sources because of its high efficiency and relatively low cost. The main disadvantage of this method is the production of a huge amount of cyanide-contaminated wastewater, which can lead to serious damage to people and the environment (Behnamfard et al., 2013).

2.5.3 Halide leaching

The use of halide (fluorine, chlorine, bromine, iodine, and astatine) systems for gold dissolution pre-dates cyanidation. All halogens have been tested and/or used for the extraction of gold with the exceptions of fluorine and astatine. Gold forms both Au(I) and Au(III) complexes with chloride, bromide, and iodide depending on the solution chemistry conditions. However, of the halides, only chlorine/chloride has been applied industrially on a significant scale. The drawback of the process is that gold halide complexes are generally unstable (Hilson & Monhemius, 2006; Cui & Zhang, 2008).

2.5.4 Thiosulphate leaching

Thiosulphate was the main competitor to cyanide in the 1880s when there was an increase in research to improve gold leaching and recovery from existing gravity and mercury amalgamation (O'Malley, 2002). Thiosulfate leaching is widely considered to be the most promising alternative method owing to its reduced environmental risk, high reaction selectivity, low corrosivity of leach solution, cheap reagents, etc. (Xu et al., 2017). Acceptable gold leaching rates using thiosulphate are achieved in the presence of ammonia with copper(II) acting as the oxidant (Breuer & Jeffrey, 2000).

2.5.5 Thiourea leaching

Thiourea is a selective and less hazardous agent. It is another alternative to the conventional and toxic cyanide (Jing-ying et al., 2012). The leaching is carried out in acidic medium because the separation of metals in an alkali solution is difficult and unstable. Thiourea leaching can result with a recovery percentage above 90% in a short duration of leaching time, but the thiourea consumption is too high and therefore it is an expensive process compared to cyanide and thiosulphate lixiviant (Akcil et al., 2015)

2.6 Thiosulphate leaching

2.6.1 Introduction

Russel and Von Patera both developed processes that used thiosulphate to leach gold and silver (O'Malley, 2002). Thiosulphate leaching was first proposed as part of the Von Patera process, where the leaching was implemented after chloridizing roasting (Xu et al., 2017).

Thiosulphate ($S_2O_3^{2-}$) is a chemical used widely in photography and in the pharmaceutical industries hence it was proposed as a substitute for cyanide by researches (Cui & Zhang, 2008).
According to Abbruzzese et al. (1995), the thiosulphate leaching method is considered as the non-toxic alternative to the conventional cyanide leaching process, the method permits a decreasing interference from foreign cations and hence lowers environmental effects.
Thiosulphate is regarded as being environmentally friendly because when exposed to air or the environment, it decomposes by disproportion, oxidation, and through decomposition by sulfur-consuming microorganisms (O'Malley, 2002).
High thiosulphate consumption is one of the blockades for the wide industrialization of thiosulphate leaching. The main reasons for excessive thiosulphate consumption are as follows (Xu et al., 2017):

(i) Thiosulphate is metastable and easily oxidized by Cu(II)
(ii) And, moreover, certain associated minerals can accelerate its oxidation

Tuncuk et al. (2012) claimed that 95% of gold can be recovered from printed circuits boards using thiosulphate leaching. Ficeriová et al. (2011) reported excellent recoveries of all the metals that were of interest. In the case of Au, Ag and Pd, the recoveries were 98 %, 93 %, and 90 % respectively.
The thiosulphate process has a more complex chemistry compared to the cyanide process, which could be expected to pose considerable control problems. Variables that must be considered are the thiosulphate, ammonia, copper and oxygen concentrations, pH and temperature (O'Malley, 2002).

The stability constants for thiosulphate in comparison with several other gold complexes are shown in Table 2-8. The gold thiosulphate complex is fairly stable once formed, as shown in Table 2-8 (Cui & Zhang, 2008).

Table 2-8: The stability constant of gold complexes. Adapted from (Cui & Zhang, 2008)

Gold species	**Stability log *K***
$Au(CN)_2^-$	38.3
$Au(SCN)_2^-$	16.98
$Au(SCN)_4^-$	10
$AuCl_4^-$	25.6
$Au(NH_3)_2^+$	26 13[b]
$Au(S_2O_3)_2^{3-}$	26.5 28

Constant K=$\frac{[AuL_n]}{[Au^{z+}][L]^n}$ for the reaction $Au^{z+} + nL = AuL_n$ at temperature 25 ^oC.

[b] Constant K Calculated from linear free energy relationship, ionic strength = 1.0.

2.6.1.1 Advantages of thiosulphate leaching

Thiosulphate is cheaper than cyanide and has the potential to leach gold more rapidly (Nicol & O'Malley, 2001). According to Abbruzzese et al. (1995), thiosulphate leaching has the oxidant necessary to oxidize metallic gold to gold(I) which is present in solution as copper(II) ions. Lee, (2003) further mentions that thiosulphate is a non-toxic environmentally safe substitute for cyanide.

2.6.1.2 Disadvantages of thiosulphate leaching

Zhang & Dreisinger (2004) noted that it is difficult to recover gold from the thiosulphate pregnant solution. For instance, the gold–thiosulfate complex does not effectively adsorb onto activated carbon and hence the carbon-in-pulp technology is not applicable.

According to O'Malley (2002), thiosulphate as a leaching agent, need high reagent concentrations compared to cyanide as well as the complexity of its chemistry.

2.6.1.3 Factors affecting ammonium thiosulphate leaching

Several factors affect thiosulphate leaching and its kinetics. The most studied variables are thiosulphate, copper(II), ammonia and oxygen concentration, agitations speed, temperature, and pH.

I. Effect of temperature

Abbruzzese et al. (1995) stated that temperature does not have a positive effect on dissolution. It was found an increase in temperature from 25 to 60℃ produces a decrease in gold recoveries. The decreased gold recovery at temperatures higher than 25℃ may be ascribed to the passivation due to cupric sulfide, formed by the thermal reaction between Cu(II) ions and thiosulphate.

However, Rath et al. (2003) found that there is a slight increase in gold leaching with an increase in temperature.

II. Effect of thiosulphate concentration

According to Abbruzzese et al. (1995), leaching at high thiosulphate concentrations, namely 2 M the rate of gold extraction was found to be high, with the recovery of about 60% after the first hour of the attack.

Ha et al. (2010) findings indicated that an increase in thiosulphate concentration increases the leaching of gold and then after reaching maximum leaching, decreased with a further increase in thiosulphate concentration.

III. Effect of ammonia concentration

Ammonia plays an important role in the leaching of gold thiosulphate solutions. It stabilizes copper in the cupric state for the oxidation of gold. Also, an increase in the ammonia concentration increases the leaching efficiency of gold (Ha et al., 2010). According to Abbruzzese et al. (1995), they discovered that the rate of gold dissolution rapidly increased during the first hour of reaction; then the extraction reached steady state. Maximum gold recovery was obtained at 4 M NH_3 concentration.

IV. Effect of rotational speed

Varying the rotation speed of stirrer from 200−600rpm while, thiosulphate, ammonia, and copper concentrations were kept at constant concentrations it was found that gold leaching increases with an increase in rpm from 200−400 rpm. In some cases, a decrease in leaching was observed at higher speeds. It appears that higher rotation creates a turbulence, which may be affecting the leaching performance (Rath et al., 2003).

V. Effect of $CuS0_4$ concentration

Abbruzzese et al. (1995) indicate that the presence of Cu(II) ions has been found to be essential to promote the dissolution of gold in thiosulphate solutions. The initial rate of gold extraction within the first 30 min was enhanced with increasing $CuSO_4$ concentration. However, the ultimate recovery is not prominently influenced.

VI. Effect of oxygen

The amount of oxygen or air in thiosulphate solutions affects thiosulphate stability (Oraby, 2009). Breuer & Jeffrey (2000) reported that the rate of thiosulphate oxidation was fast when the solution was sparked with pure oxygen; the thiosulphate was consumed in less than 25 min, compared to 1 hour for air.

2.6.1.4 Chemistry of the ammonia-thiosulphate

The chemistry of the ammonia-thiosulphate system is very complicated due to the simultaneous presence of complex ligands such as ammonia and thiosulphate. The Cu(II)-Cu(I) redox couple and the oxidative decomposition reactions of thiosulphate involve the formation of additional Sulphur, compounds such as tetrathionate (Breuer & Jeffery, 2000).

According to Navarro et al. (2004), gold dissolves slowly in alkaline or neutral dissolution, as shown in equation (6) below:

$$4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \longleftrightarrow 4Au(S_2O_3)_2^{3-} + 4OH^- \quad (6)$$

The dissolution reaction being catalyzed in the presence of copper(II). The ammonia thiosulphate leaching of gold depends on the simultaneous presence of complexing agents and the Cu(II)–Cu(I) redox couple as well as the stability of thiosulphate in solution.

Equation (7) presents an oxidation reaction, which is promoted by the copper(II) ion (Ha et al., 2010).

$$2Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \longleftrightarrow 2Cu(S_2O_3)3^{5-} + 8NH_3 + S_4O_6^{2-} \quad (7)$$

$[Cu(NH_3)_4]^{2+}$ as a catalyzer boosts gold dissolution dramatically, but it also evidently accelerates thiosulphate decomposition due to its relatively strong oxidizing ability. By maintaining the appropriate concentration of ammonia and thiosulphate, the conversion from the Cu(II) to the Cu(I) state can be controlled to obtain efficient leaching of gold. Copper plays the role of the catalyst due to the redox reaction between the copper(II) and the copper(I) state (Xu et al., 2017).

According to Lee (2003), gold could be present in solution as $[Au(NH_3)_2^+]$ rather than as $[Au(S_2O_3)_2^{3-}]$ according to Eh-pH diagram, especially at high pH. Figure 2-11 shows the Eh-pH diagram for $Au - NH_3 - S_2O_3^{2-}$ system in 1M othe f $[S_2O_3^{2-}]$ and 1M of $[NH_3 + NH_4^+]$. From figure 2-11 it can be deduced that the gold thiosulphate complex is the most stable species in the leaching system up to pH 8.5. Above this pH when NH_4^+ converts to NH_3, the predominant gold compound is gold(I) diamine complex.

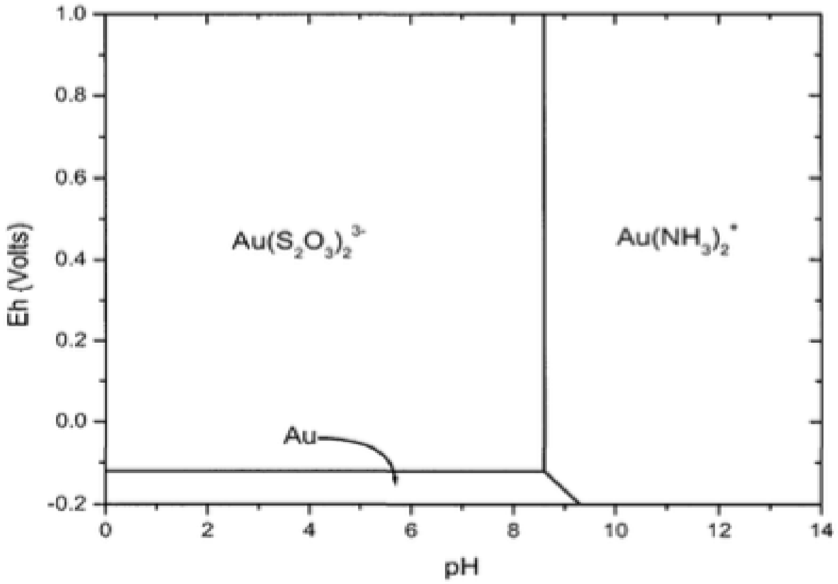


Figure 2-11:Eh-pH diagram for $Au - NH_3 - S_2O_3^{2-} - H_2O$ systeThe m at 25°C (Lee, 2003)

$[Au] = 2.5 \times 10^{-5} M, [S_2O_3^{2-}]$= 1M and $[NH_3 + NH_4^+] = 1M$

According to Xu et al. (2017), NH_3 moves to the gold surface and complexes with Au^+ to generate the complex $[Au(NH_3)_2^+]$in anodic areas. Then NH_3 is substituted by $S_2O_3^{2-}$ and, thus more stable complex $[Au(S_2O_3)_2^{3-}]$ is formed. Hiskey & Lee (2003) reassert that in an ammoniacal thiosulphate solution, gold potentially exists as either $[Au(NH_3)_2^+]$ or $[Au(S_2O_3)_2^{3-}]$ depending on the respective concentrations of ammonia and thiosulphate. The presence of mixed complexes (e.g. $[AuNH_3S_2O_3{}^-]$) has not been verified. Aylmore et al. (2001) have reviewed the thermodynamics and solution chemistry of the gold–ammonia-thiosulphate system and have concluded that $[Au(S_2O_3)_2^{3-}]$ is the predominant species under the conditions used.

Not only does NH_3 stabilize Cu^{2+} in alkaline media forming$[Cu(NH_3)_4]^{2+}$, but it also catalyzes the complex reaction between Au^+ and $S_2O_3^{2-}$. In cathodic areas, $[Cu(NH_3)_4]^{2+}$ is reduced to$[Cu(S_2O_3)_3]^{5-}$, and newly generated $[Cu(S_2O_3)_3]^{5-}$is quickly oxidized back into $[Cu(NH_3)_4]^{2+}$ by dissolved oxygen in solution. Therefore, $[Cu(NH_3)_4]^{2+}$ catalyzes the reaction of oxygen reduction. The electrochemical-catalytic mechanism of thiosulphate leaching of gold is represented in figure 2.4 (Xu et al., 2017).

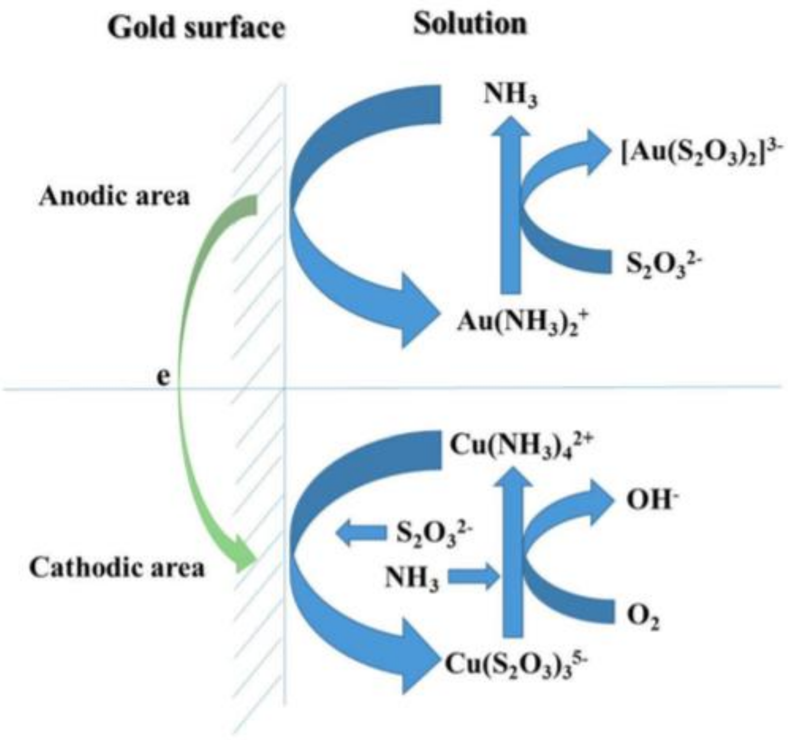


Figure 2-12: Sketch map of the electrochemical-catalytic mechanism of thiosulfate leaching (Xu et al., 2017)

According to Navarro et al. (2004), it is generally accepted that the thiosulphate species is the more stable gold(I) species at pH values around 10. Recently published data indicate that the formation of the gold(I)–ammoniacal species is not favored (Molleman & Dreisinger, 2002).

To recover the precious metals from these different solutions, a variety of methods are found in the literature. These methods are explained in section 2.7.

2.7 Conventional techniques used to recover precious metals

According to Tuncuk et al. (2012), the selection of the metal(s) recovery process is based on several factors. These include the leaching reagent system, the concentration of metal(s) and impurities.

Gold can be recovered using cementation (precipitation), electrowinning, solvent extraction, carbon adsorption, and resin adsorption techniques (Grosse et al., 2003).

2.7.1 Carbon adsorption

McQuiston and Chapman patented the carbon adsorption technique for the recovery of gold (Au) and silver (Ag) cyanide complexes on activated carbon in 1946. Since that time, new technologies have been developed and introduced, like carbon-in-pulp (CIP) and carbon-in-leach (CIL) which are commercially used for gold recovery from cyanide solutions (Cui & Zhang, 2008).

CIP is often preferred because the technique tends to reduce capital costs and higher recoveries of gold can be achieved by the scavenging used in the techniques (Grosse et al., 2003).

Grosse et al. (2003) state that in other studies, many types of carbon adsorbents were contacted with ammoniacal thiosulphate leach liquor, and were all found to have a poor capacity for aurothiosulphate $[Au(S_2O_3)_2]^{3-}$. Aurothiosulphate complex has significantly less affinity for carbon than the $[Au(CN)_2]^-$ anion and it has not been established whether this effect is due to the larger size or charge of the thiosulphate complex.

Carbon has been proven ineffective (< 20%) for adsorbing the gold from thiosulphate leach solutions. The lack of adsorption was thought to be caused by the relatively high negative charge of the gold thiosulphate complex, steric limitations attribute to the molecular structure or the lack of specific interactions of the ligand group with carbon active sites. The amount of gold adsorption by activated carbon was dependent on the temperature and pH of the solution. It was concluded that activated carbon would never effectively adsorb all the gold thiosulphate from solution (O'Malley, 2002).

2.7.2 Electrowinning

Electrowinning is the recovery of metal ions from solution by the application of direct current. Aurothiosulphate ions in the solution will migrate to the cathode and form a metallic deposit. The problem with electrowinning is the contamination of the metallic product that occurs in the presence of a great excess of unwanted cations [i.e. Cu (I) and Cu (II)]. This results in a degraded product requiring further purification. Electrowinning does not appear to be a viable option due to side reactions involving the oxidation or reduction of thiosulphate that may interfere with the process hence increasing the energy input required to recover the desired metals from solution, therefore, lowering the efficiency (Grosse et al., 2003). According to two parasitic cathodic reactions involving the reduction of water and dissolved oxygen cause problems and consume electricity.

2.7.3 Solvent extraction

Solvent extraction technique has been studied to meet gold-extraction requirements and several systems have been investigated, including organophosphorus, guanidine derivations and a mixture of amines-organophosphorus derivatives (Cui & Zhang, 2008).

During solvent extraction, the leach liquor is contacted with a solution of extractant in a water-immiscible organic solvent. The gold complex is separated into the organic phase, whereas the other metals remain in the aqueous phase. The separated organic phase is stripped of gold and returned to the extraction circuit (Grosse et al., 2003).
According to Riveros, (1990) Solvent extraction could be used in those operations that produce clarified solutions, such as heap leaching.

Several studies in which gold has been extracted from ammoniacal thiosulphate liquors by solvent extraction have been reported (Grosse et al., 2003). The extractants employed in these solvents were primary, secondary and tertiary alkyl amines, tertiary amine oxides, phosphines, phosphine oxides, and phosphate esters. (Zhao et al., 1999; Grosse et al., 2003).
Solvent extraction has several constraints that limit the scope of possible industrial applications. The application of solvent extraction is limited to clarified liquors, free of particulate matter. Additional plant equipment and processing time would be required to produce clarified liquor from a mineral pulp, and these steps would result in significant increases in capital costs and operating costs (Grosse et al., 2003). According to Zhao *et al*. (1999) higher capacity, better selectivity, and faster kinetics were obtained using solvent extraction in gold recovery.

2.7.4 Cementation

According to Guerra & Dreisinger (1999), the cementation process is the electrochemical precipitation of one metal by using another metal, called the precipitant as the reducing agent. Precipitation of most of the gold from pregnant leach liquor can be achieved by adding a pulverized metal. The primary mechanism of this recovery technique is the redox reaction between the zero valent base metal grains and the target noble metals. The majority of cementation studies are carried out in batch reactors. Stirring speed and temperature are some of the variables commonly manipulated.

2.7.5 Resin adsorption

Resin adsorption for the recovery of precious metals it's a relatively underdeveloped process of hydro-metallurgy. The main reason is the abundance and effectiveness of cheap activated carbon adsorbents. Resins are mostly used in the Commonwealth of Independent States (CIS) for the recovery of gold from cyanide liquors. Resin adsorbents are more expensive than carbon, and their application requires the installation of specialized apparatus. There are two methods employed, Resin-in-Leach (RIL) and Resin-in-Pulp (RIP). In RIL, the adsorbent is added at the same time as the leaching reagents, if the adsorbent is introduced after an initial leaching (i.e. induction) period the method is known as RIP (Grosse et al., 2003).

Ramesh et al. (2008) suggest adsorption as the most suitable method for the recovery of precious metals in the case of low concentration due to low cost and high efficiency.

The difficulties with ion-exchange resins, is that they are less selective than activated carbon for gold cyanide over the base metal cyanides and the resin particles are smaller, which gives engineering problems associated with the separation, transportation, and mixing of the RIP mixture (Van Den Berg, 2000).

2.7.6 Reductive precipitation

At room temperature, sodium borohydride can be used as an efficient agent for reducing gold in thiosulphate solutions. Sodium borohydride to the gold molar ratio of 0.625 at a pH of 6 over a one hour time period can cause a complete reduction of gold in thiosulphate solutions to occur. However, the presence of ferrous ions, cobalt, nickel or copper in solution decrease the efficiency of borohydride to reduce gold because of extensive co-precipitation of other metals (Aylmore et al., 2001; Aylmore, 2005).

Pressurizing thiosulphate solutions containing gold with hydrogen has also been used to recover gold, but a catalyst of nickel or platinum is required and the pressurized equipment used is more expensive than other recovery methods (Aylmore, 2005).

Grosse et al. (2003) also confirmed that this method is not highly favored, as it is less selective and tends to precipitate.

Reduction with sodium borohydride did not appear to be effective in gold and silver recovery from isothiourea solution since it precipitated the base metals along with gold and silver. Boron is toxic to the environment and hence the use of boron compounds is not recommended (Gurung et al., 2013).

2.7.7 Sulfide reduction

Addition of a sulfide, bisulfide, or hydrogen sulfide solution with regeneration of thiosulphate can also be used to recover gold. 97% of the gold is recovered during the precipitation stage and 99.9% during the sludge upgrade stage. In this recovery method, sulfide addition has to be suitably controlled because if more is added, excess sulfide has to be removed before recycling to the process water. Furthermore, the final product may require further processing to remove transitional metals and mercury (Aylmore, 2005).

2.8 Cementation

2.8.1 History

It is one of the oldest and most effective hydrometallurgical processes which allow recovering metals from solutions. This process was known since the ancient times of human culture, but in Europe, the knowledge of cementation was only spread at the beginning of the Middle Ages (Jaskula, 2009). The cementation process was used by alchemist when the transmutation of base metals into gold was their occupation (Habashi, 2009; Jaskula, 2009). According to Habashi (2009), the cementation process became known in the 16th century when the extraction of copper by wet methods received some attention.

2.8.2 Introduction

The term cementation comes from a Spanish word meaning “precipitation”. Cementation is an essential chemical process in hydrometallurgy (Arima et al., 2004). It is used to precipitate and recover an ionized metal from solution by spontaneous electrochemical reduction to its elemental state, with consequent oxidation of a sacrificial metal (Fouad & Abdel Basir, 2005).

The sacrificial metal must be more electropositive, more expensive and nobler than the ionized metal in solution (Hiskey & Lee, 2003; El-Saharty et al., 2015).
Cementation is a heterogeneous reaction and is limited by diffusion through the mass boundary layer. Cementation rate depends on the nature of the deposited metal as well as hydrodynamic conditions. The cementation rate may be increased by powdery non-coherent deposits while smooth coherent deposits may prohibit the cementation process (El-Saharty et al., 2015).

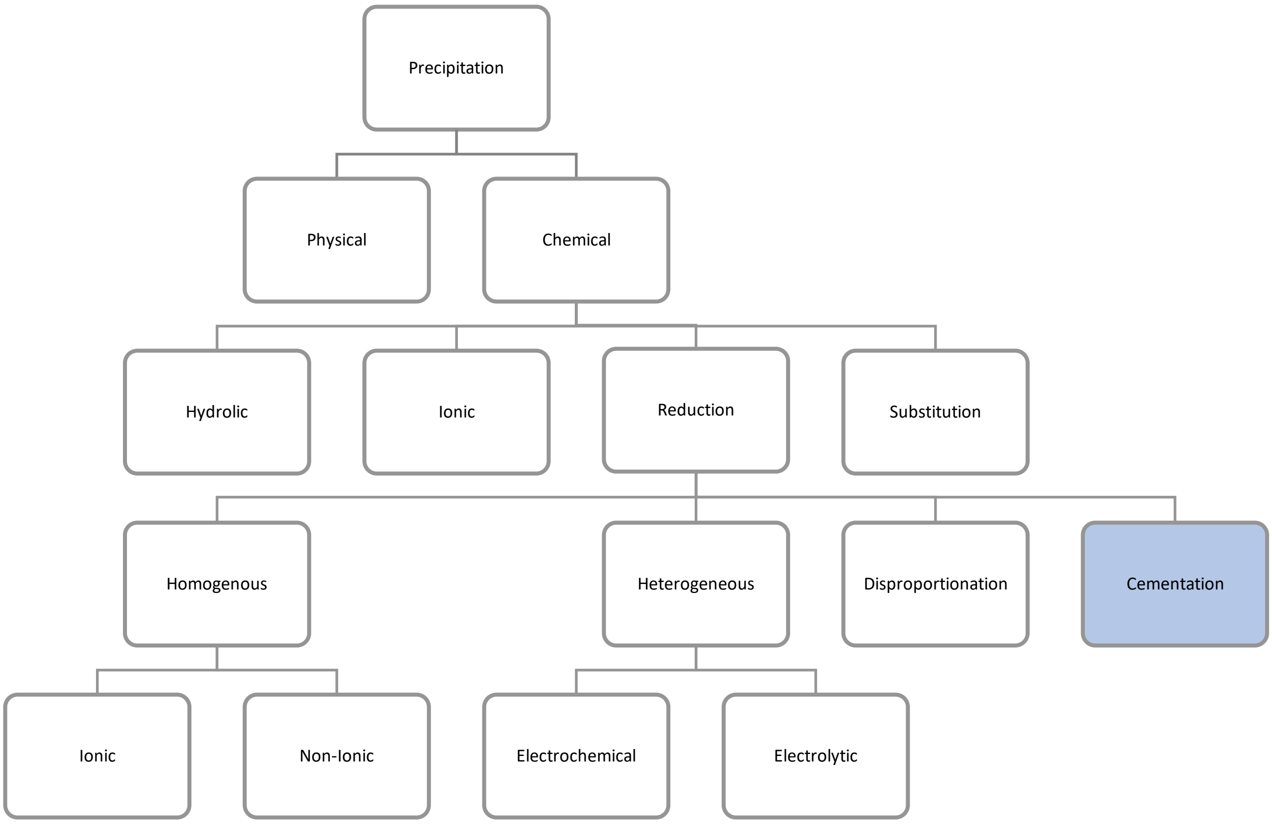


Figure 2-13: Different types of precipitation employed in hydrometallurgical operations. Adapted from (Bello, 2014)

Figure 2-13 above, shows the different types of precipitation employed in hydrometallurgical processes. Cementation reactions are considered chemical precipitation reactions. Chemical precipitation method is divided into ionic precipitation, hydrolysis, substitution, and reduction precipitation. Cementation reactions undergo chemical precipitation because there's a need for a suitable reagent to effect precipitation. Cementation reaction is a type of reduction reaction because it involves the reduction of ions by a different metal on the interface of that metal (Bello, 2014).

Cementation is considered as a surface reaction. The sacrificial metal is etched from the anodic sites after losing electrons to cemented metal reduced at the cathodic sites. The processing of cementation may induce two possible effects on the effects on the surface area of sacrificed metal namely (Ku & Lee, 1997):

1. The mass transfer barrier caused by the covering of cemented metal deposits on the surface of the sacrificed metal to inhibit the metal ions passes through the "etching channel" to and from the bulk solution
2. The surface roughness dug by etching may create more active sites on the surface area

Birloaga & Vegliò (2016) state that the cementation process is the preferred technique amongst all the others techniques of metals extraction from the solution because the process offers ultrahigh purity metals and has less consumption of materials and energy.

According to Farahmand et al. (2009), the advantages of the cementation process include:

(i) high process efficiency, permitting practically complete removal or detoxification of heavy metals;
(ii) high process rate;
(iii) the simplicity of treatment facilities;
(iv) recovery of most metals in pure metallic form; and
(v) a relative absence of sludge.

According to El-Saharty et al. (2015), the general reaction for a cementation process is given by equation (8)

$$mN^{n+}+nM \rightarrow nM^{m+}+mN \quad (8)$$

where N = noble metal
M = reductant metal

Using the redox potential, the precipitant is carefully chosen. Equation (9) represents the precious metal(s) in the solution being displaced stoichiometrically by the precipitant (Grosse et al., 2003).

$$2Au^{+} + M^{o}_{(soild)} \rightarrow 2Au^{o}_{(ppt)} + M^{2+} \quad (9)$$

Arima et al. (2004) suggest that one of the best methods of gold recovery is cementation by metal powders. Zinc, copper, iron or aluminum can be used as precipitants for gold cementation because of their lower reduction potentials than gold as shown in equations (10)-(15):

$$Au^{+} + e^{-} \rightarrow Au \qquad E_0 = 1.68\ V \quad (10)$$

$$4H_2O + O_2 + 4e^{-} \rightarrow 4OH \qquad E_0 = 1.23\ V \quad (11)$$

$$Cu^{2+} + 2e^{-} \rightarrow Cu \qquad E_0 = 0.34\ V \quad (12)$$

$$2H^{+} + 2e^{-} \rightarrow H_2 \qquad E_0 = 0\ V \quad (13)$$

$$Zn^{2+} + 2e^{-} \rightarrow Zn \qquad E_0 = -0.76\ V \quad (14)$$

$$Al^{3+} + 3e^{-} \rightarrow Al \qquad E_0 = -0.166\ V \quad (15)$$

2.8.3 The following precipitants are commonly used for the recovery of precious metals in the cementation process (Grosse et al., 2003):

Zinc, copper, iron, and aluminum;

2.8.3.1 Zinc cementation

According to Arima et al. (2004) the reaction of gold precipitation by zinc cementation in the presence of ammonia can be represented in the following reaction given by equation 16:

$$2\ Au(S_2O_3)^{2}_{3-} + 2Zn^0 + 2H_2O + 4NH_3 \longrightarrow 2\ Au^0 + 2\ S_2O^{3-}_{2} + Zn(S_2O_3)^{2-}_{2} + 2OH^- + H_2 + Zn(NH_3)^{2+}_{4} \quad (16)$$

Zinc cementation from thiosulphate solution is not practical because of the method suffers from high zinc consumption (Zhang & Dreisinger, 2004).

Navarro et al. (2004) add that it is very likely that zinc side reactions might have a negative effect on the rate of precipitation of gold. Zinc forms zinc–ammoniacal complexes, $Zn(NH_3)^{2+}_{m}$ (m ranging from 1 to 4) at alkaline pH, thereby causing a robbing effect on the complexing agent and decreasing its presence in the solution, with a negative effect on gold precipitation.

Impurities such as lead, copper, nickel, arsenic, antimony, and sulfur have the deleterious effect of reducing thiosulphate ions while producing unwanted cations, hence making recycling of the lixiviant complicated (Cui & Zhang, 2008).

Another disadvantage of this method includes the requirement for a separation stage prior to cementation. The solution must be clarified and degassed to remove the remaining solids and oxygen. The solution must be de-aerated to reduce the dissolved oxygen to <1 ppm, and if possible to <0.5 ppm (Mpinga et al., 2014).

2.8.3.2 Iron Cementation

According (Wang et al., 2007), since the iron (III), is the oxidant in thiocyanate gold leaching systems, iron may a great choice for gold cementation from thiocyanate solutions.

Karavasteva (2010) found that although iron can be used in gold cementation from ammonium thiosulphate ammonia solutions practice the cementation rate is tremendously slow.

2.8.3.3 Aluminum cementation

The earliest reference to the utilization of aluminum in the cementation process was in 1952 by Kamecki and Sedzimir. The utilization of aluminum scrap cans in the cementation process would help to solve the ecological problem of can-littering to a certain extent, in addition to the economical usage of the waste-cans as compared with the cost of energy required in reclaiming the aluminum metal (Dönmez et al., 1999).

According to Wang et al. (2007), aluminum powder is feasible as a method for gold recovery from acidic thiocyanate solution but the presence of the ferric ion in solution inhibits the cementation reaction significantly.

2.8.3.4 Copper cementation

The Cu/Au+ cementation reaction would occur according to the stoichiometry in equation (17). According to stoichiometry, one mole of gold needs three moles of copper in copper precipitation (Arima et al., 2004):

$$3Cu + [Au(S_2O_3)_2]^{3-} + 8NH_3 + H_2O + O_2 \rightarrow [Cu(S_2O_3)_2]^{3-} + 2[Cu(NH_3)_4]^{2+} + 4OH^- + Au \qquad (17)$$

Copper departs from the surface and a gold (I) ion is reduced and incorporated into the surface layer. Due to the difference in atomic mass between gold and copper the mass material on the surface increases (Choo & Jeffrey, 2004).

2.9 Copper cementation

Copper is the reasonable precipitant because during cementation copper in solution can be oxidized to Cu(II), which is the oxidant during the leaching process and can, therefore, be recycled (Choo & Jeffrey, 2004; Guerra & Dreisinger, 1999). In addition, copper is relatively cheap (Choo & Jeffrey, 2004).

According to Grosse et al. (2003), the solutions of copper ions in thiosulphate liquors can be recycled as leach liquor. Some contamination of the solid product often occurs, through either undissolved precipitant or by co-precipitation with other metal ions in solution, necessitating further purification.

Guerra & Dreisinger (1999) report that there have been several proposed methods for recovering gold but cementation using copper was selected as most worthy of examination since it is the most amenable for use with a leach solution in re-circulation.

Copper emerged as more desirable because it is relatively inexpensive and has lower reduction potential than those of gold but higher reduction potential than that of other base metals (Gurung et al., 2013).

Due to all the advantage factors mentioned regarding copper as the sacrificial metal used in the cementation process, this project will use copper to recover the gold in solution.

2.9.1 Pre-treatment of the cementation agent

Almost every metal that has been exposed to air at room temperature is covered with a surface oxide film (Verwey and De Broer, 1936). In most cases, the air-formed oxide grows to a thickness of about 3 nm. Cementation reactions take place at the surface of a metal in a solution (Hope, Ritchie and Wajon, 1977)

The oxide film can affect the rate of displacement during cementation because it alters chemical steps at the metal/ solution interface. The oxide can act as a barrier separating the reactants. Unless the oxide film is ruptured or dissolved in the reactant solution, the cementation process can only be sustained provided ions and electrons pass freely through the oxide. During cementation the ions move through the oxide go into solution; the electrons are required for the reduction of the less electropositive species (Hope, Ritchie and Wajon, 1977)

According to Karavasteva (2010), the copper powder can be treated with dilute sulphuric acid to remove any surface oxide layer.

2.9.2 Cementation reaction

It is reported that cementation reaction follows first order kinetics with respect to the noble metal ion. Cementation is a diffusion process (Demirkiran et al., 2007; Martinez et al., 2012).

According to (Martinez et al., 2012) cementation reaction rate is expected to be a function of the copper substrate area, the volume of the solution and gold concentration according to the following first-order rate expression:

$$-\frac{d[Au]}{dt} = k' \frac{A_o}{V_s}[Au] \tag{18}$$

where,

[Au] = the gold concentration,

t = time,

V_s = solution volume,

A_o = initial exposed substrate area and

k' =the apparent rate constant.

This kinetic relationship can be integrated to yield equation (19) below:

$$ln\frac{[Au]}{[Au]_o} = -k' \frac{A_o}{V_s}t = -k^*t \tag{19}$$

where

[Au] = gold concentrations at time t

$[Au]_o$ = initial gold concentration at time t = 0

The cementation rate is a function of the reaction area A and that in almost all cementation systems the initial exposed geometric area of the precipitant metal can be used in the analysis of initial rate data. However, in a more general sense, the area term is not always that simple to evaluate due to the changing nature of the noble metal deposit which grows on the active metal during the reaction (Martinez et al., 2012).

According to Wang et al. (2007) in a gold cementation system, the gold concentration is diminished continuously with time.

Lee, (2003) states that cementation is a heterogeneous reaction consisting of mass transport and electrochemical reaction. The reaction occurs through the following 4 steps:

(i) mass transfer of metallic ions from the bulk solution to boundary layer;
(ii) adsorption of ions to reaction surface;
(iii) chemical reaction on the surface and reduction of ions; and
(iv) mass transfer of product to bulk solution

The above steps are schematically represented in figure 2-14. If either step (i) or (iv) is the slowest, the reaction is said to be under mass transfer control but if step (ii) or (iii) or (iv) is the slowest then the reaction is under chemical control.

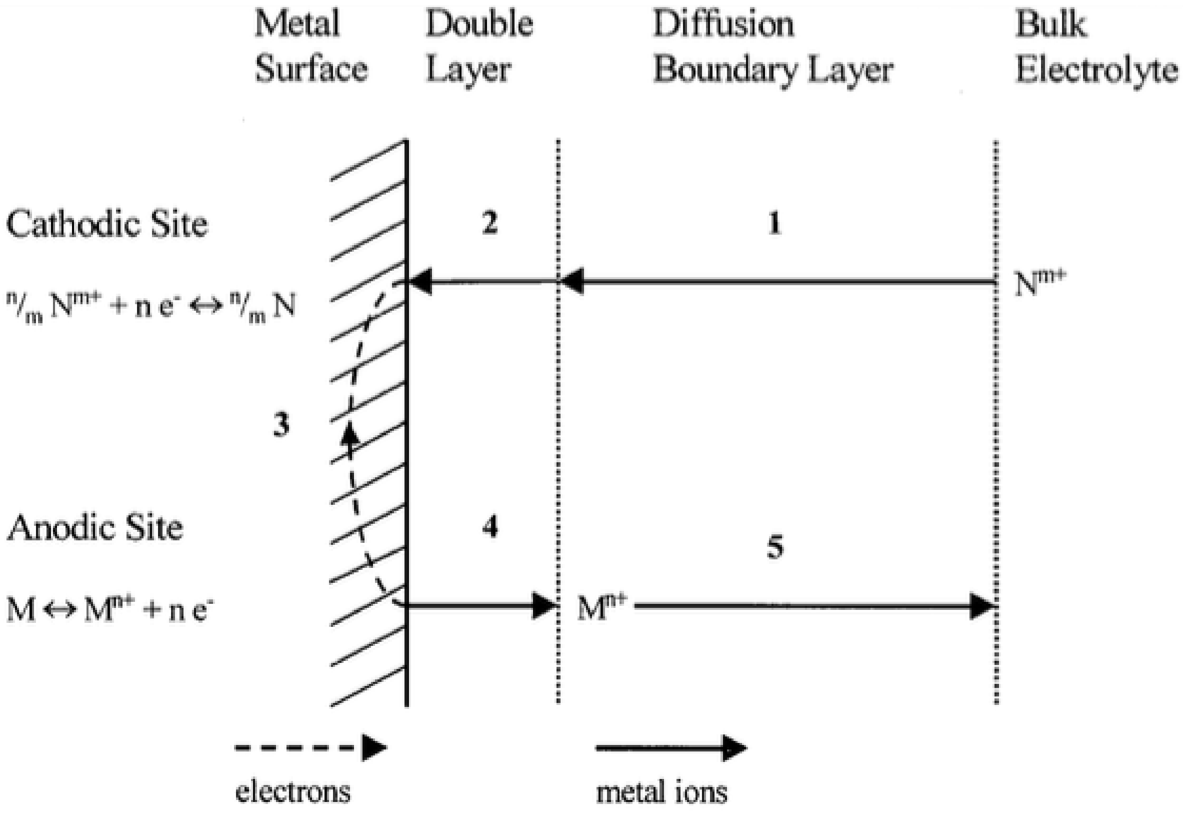


Figure 2-14: Physical steps of s simple cementation reaction (Guerra & Dreisinger, 1999)

According to Arima et al. (2002), the main cathodic reaction may be expressed in equation (19)

$$[Au(S_2O_3)_2]^{3-} + e^- \rightarrow 2S_2O_3^{2-} + Au \downarrow \qquad (19)$$

During cementation the cathodic reaction (19) will occur along with the following anodic reaction():

$$Cu + 2S_2O_3^{2-} \rightarrow [Cu(S_2O_3)_2]^{3-} + e^- \tag{20}$$

Furthermore, the copper powder will be oxidized to cupric amine complex by ammonia as expressed in equation (21)

$$2Cu + 8NH_3 + 2H_2O + O_2 \rightarrow 2[Cu(NH_3)_4]^{2+} + 4OH^- \tag{21}$$

Equations (19), (20) and (21) is the overall reaction of gold cementation with copper and is given by equation (22)

$$3Cu + [Au(S_2O_3)_2]^{3-} + 8NH_3 + 2H_2O + O_2 \rightarrow [Cu(S_2O_3)_2]^{3-} + 2[Cu(NH_3)_4]^{2+} + 4OH^- + Au \downarrow \tag{22}$$

2.9.3 Mass transfer

Mass transfer is the term used to denote the transference of a component in a mixture from a region where its concentration is high to a region where the concentration is lower. Mass transfer processes in cementation begin with Fick's first law of diffusion, represented by equation (23) (Coulson et al., 1999).

$$J = -D_c\left(\frac{\partial C}{\partial x}\right) \tag{23}$$

According to Free (2013) mass-transport-limited flux can be expressed mathematically as:

$$J = -k_1C_b \tag{24}$$

Equation 23 can be arranged to

$$\frac{dn}{dt}\frac{1}{A} = -k_1C_b \tag{25}$$

Assuming a constant volume basis allows for the transition from moles to concentration:

$$\frac{dC_b}{C_b} = -A_{perliter}k_1dt \tag{26}$$

After integration, equation (26) becomes:

$$\ln\left(\frac{C_b}{C_0}\right) = -A_{perliter}k_1t \tag{27}$$

Consequently, by plotting $\ln\left(\frac{C_b}{C_0}\right)$ versus time, the relationship should be linear. The mass transfer coefficient can be determined by assuming a constant are during the reaction.

Where:

C_b = the bulk concentration at time t,

C_0 = the bulk concentration at time 0.

In the particular case where the reducing agent is a powder, the variable A is replaced by a_eW. where (Anacleto & Carvalho, 1996):

a_e = Specific surface area; and

W = mass of the reducing agent.

Equation 25 then becomes:

$$\ln\left(\frac{C_b}{C_0}\right) = -ka_e\frac{W}{V}t \qquad (28)$$

However, the relationship is often not linear. Nonlinearity can be due to a mass transfer limitation of metal ions to the reaction interface. Nonlinearity can also be due to area enhancement through tree-like, dendritic product structures (Free, 2013).

2.9.4 Deviations from 1st order kinetics and side reactions

According to Lee (2003), cementation reactions are sometimes hindered and the cause is reflected in two cases:

1. When the transport of the depositing metal ions into the bulk of the solution is hindered by deposited metal to such an extent that, the rate of their removal (by diffusion) becomes smaller than the rate of their formation. Therefore, the concentration of these ions rises near the reaction surface and finally forms a passivating salt layer.
2. When the depositing metal is isolated from the electrolyte because the layer of the precipitated metal is so compact

Guerra & Dreisinger (1999) reported that there’s a negative deviation from first order kinetics, as shown in equation (26) and believed it was due to the progressive formation of a passivating substance on the copper surface. The passivating substances were speculated to be Cu_2O and CU_2S by X-ray powder diffraction (XRD) and energy-dispersive X-ray spectroscopy (EDS) analysis

$$ln\frac{[Au]}{[Au]_o} = -k_1\frac{A_o}{V_s}t \tag{29}$$

$$ln\frac{[Au]}{[Au]_o} = -k_1\frac{A_o}{V_s}t + \left(\frac{k_1k_2}{2V_s}\right)t^2 \tag{30}$$

The first term in Equation (29) contains the first order rate constant, k_1, which can be either a chemical rate constant or diffusion rate constant depending on the mechanism of rate control. According to Guerra & Dreisinger (1999) that is the term that dominates the overall rate of cementation. The second term in the 'passivation' model $k_1k_2/2V_s$, which also contains the first order rate constant, simply corrects for non-linear behavior.

According to Hiskey & Lee (2003), a possible degradation reaction involving the Cu(I)-thiosulphate complex is given by equation 28.

$$2Cu(S_2O_3)_3^{5-} + 2OH^- \longrightarrow Cu_2S + SO_3^{2-} + 5S_2O_3^{2-} + H_2O \tag{31}$$

In addition, thiosulphate undergoes disproportionation according to the following reactions:

$$S_2O_3^{2-} \longrightarrow SO_3^{2-} + S \tag{32}$$

$$3S_2O_3^{2-} + H_2O \longrightarrow 2SO_4^{2-} + 4S + 2OH^- \tag{33}$$

Reactions (31)– (33) illustrate the complex solution chemistry and redox equilibria associated with the thiosulphate system. Furthermore, the formation of solid products like Cu_2S in reaction (31) can result in altering the surface layer of the cementation agent and can inhibit the cementation reaction.

Hsu & Tran, (1996) indicate that in most cementation studies, depending on the deposit morphology, after the first period in which the first order rate law is followed, the cementation process could stop if a smooth deposit is formed. Conversely, the cementation would accelerate if a dendritic deposit is formed.

According to Guerra & Dreisinger (1999), cupric tetrammine may react with metallic copper to form a cuprous–thiosulphate complex, $Cu(S_2O_3)_3^{5-}$ as shown in reaction (34) below. Hence the blue color of cupric tetrammine was observed to gradually fade after the addition of copper powder.

$$Cu(NH_3)_4^{2+} + 3S_2O_3{}^{2-} \rightarrow [Cu(S_2O_3)_2]^{3-} + \frac{1}{2}S_4O_6^{2-} + 4NH_3 \tag{34}$$

2.9.5 Rate-limiting step of cementation

Jeffrey, (2001) states that to identify the rate-limiting step of a hydrometallurgical reaction kinetic rate studies must be conducted. Non-diffusion-controlled reactions usually have a high activation energy, and thus, changes in temperature considerably influence the reaction rate.

A diffusion-controlled process is characterized by being slightly dependent on temperature and usually have an activation energy of ≤25 kJ/mol, whereas the chemically controlled process is highly dependent on temperature and usually have an activation energy > 25 kJ/mol (Mpinga et al., 2014). According to Wang et al. (2007) cementation reactions whose constituent half-reactions have redox potentials which differ ($E_{cathode}^{o} - E_{anode}^{o}$) by greater than 0.36 V are likely to be diffusion-controlled.

2.9.6 Alloy formation

According to Karavasteva (2010), cementation deposits are Au-Cu alloys instead of pure gold. Alloy composition ranges from AuCu to $AuCu_3$ for the substrate side of the deposit, whereas the solution side ranges from Au_3Cu to AuCu depending on the mole ratio of Cu/Au in solution.
The possible reactions accounting for alloy formation are shown in Equations. (35) – (37) (Hiskey & Lee, 2003).

$$Au(S_2O_3)_2^{3-} + 2Cu + S_2O_2^{3-} \longrightarrow AuCu + Cu(S_2O_3)_3^{5-} \qquad (35)$$

$$3Au(S_2O_3)_2^{3-} + 4Cu + 3S_2O_2^{3-} \longrightarrow Au_3Cu + 3Cu(S_2O_3)_3^{5-} \qquad (36)$$

$$Au(S_2O_3)_2^{3-} + 4Cu + S_2O_2^{3-} \longrightarrow AuCu_3 + Cu(S_2O_3)_3^{5-} \qquad (37)$$

2.10 Gold concentration measurements

The following techniques were used to analyze gold concentration in the bulk solution as well as on the deposits recovered after cementation process.

SEM-EDS

According to Kriedemann (2014), Energy-dispersive X-ray spectrometry is a standard technique for the local identification of elements within a sample while using SEM or TEM.

The technique allows for the determination of the chemical composition of particles (Brodowski et al., 2005).

AAS

Atomic Absorption Spectrometry (AAS) is a technique used for measuring quantities of chemical elements present in samples by measuring the absorbed radiation by the chemical element of interest. This is done by reading the spectra produced when the sample is excited by radiation. Absorbance is directly proportional to the concentration of the analyte absorbed for the existing set of conditions. The concentration is usually determined from a calibration curve, obtained using standards of known concentration (Groessl et al., 2014).

2.11 Factors influencing the rate of copper cementation

The following factors influence the rate of copper cementation: Temperature, pH and initial copper concentration (Guerra & Dreisinger, 1999; Hiskey & Lee, 2003)

2.11.1 The effect of temperature

Copper cementation is improved by increasing the temperature to between 20 °C and 60 °C, resulting in a drop in solvent viscosity and allowing gold complexes to move more freely through the solution (Guerra & Dreisinger, 1999).

Hiskey & Lee (2003) observed that the reaction rate increased at temperature values ranging from 10 °C to 15 °C. However, there was a noticeable decrease in the cementation rate at temperature values ranging from 25 °C to 50 °C.

2.11.2 The effect of pH

High pH of 9.6 ± 0.3/high ammonia concentration has a positive effect on the cementation process because the gold-amine complex is lighter than the gold–thiosulphate complex hence it is more mobile leading to faster cementation (Guerra & Dreisinger, 1999).
The rate of gold cementation observed by Nguyen et al. (1997) in their study, increased slightly with a decrease in solution pH from 12 to 9.5 during cementation of gold onto copper evaluated using a copper rotating disc and copper powder systems.

2.11.3 Effect of stirring speed

Wang et al. (2007) studied the effect of stirring speed on gold cementation from thiocyanate solutions by iron powder and it was found that increasing the stirring speed increases the rate of gold cementation. Increasing the rate of stirring will decrease the diffusion layer thickness, hence increasing the cementation rate because the gold cementation from thiocyanate solutions was found to be a diffusion-controlled process.
Demirkiran et al. (2007) studied copper cementation with zinc in aqueous solutions and it was also found out that stirring speed increases the rate of cementation.

2.11.4 Effect of aeration

According to Guerra & Dreisinger (1999), dissolved oxygen can both directly attack the surface of copper particles or indirectly, by oxidizing cuprous ions to cupric ions which may subsequently be reduced on the surface of copper particles. However, O'Malley (2002) claimed that de-aeration is not critical for cementation if there is sufficient sacrificial metal added within a thiosulphate system. Wang et al. (2007) state that recovery of gold is generally performed under deoxygenated condition because oxygen has a deleterious effect on gold precipitation. Nguyen et al. (1997) state that high purity nitrogen is purged to deoxygenate system. Navarro et al. (2004) purged Nitrogen into the system until oxygen content in the solution was 1 ppm.

2.11.5 Effect of initial copper concentration

Guerra & Dreisinger (1999) confirm that the initial copper introduced into solution as copper sulfate has a negative effect on the rate of cementation. Cu (II) cupric ions in ammoniacal solutions which exist as cupric tetramine, (Cu$(\mathrm{NH_3})_4^{2+}$) decreases the concentration of the gold-amine complex, (Au$(\mathrm{NH_3})_2^{+}$), Competition between the copper reduction reaction and the gold cementation reaction on the surface of copper particles decreases the current efficiency and hence has a negative effect on the rate of cementation.

2.11.6 Effect of initial gold concentration

A study conducted by Hiskey & Lee (2003) showed that the effect of the initial gold concentration exhibited two kinetic regimes; an initially slow rate followed by an enhanced rate. A plot of the effect of the initial gold concentration on the cementation reaction exhibited two kinetic regimes. The plot showed a decrease in the initial stage period with increasing gold concentration. The initial rate is approximately first order with respect to gold concentration. The enhanced first order rate displayed a marked concentration effect.

2.12 The following literature demonstrates the different operating conditions on copper cementation of gold

pH	Temp. (℃)	Amount of Cu powder	Volume (mL)	Time (min)	Aeration	Rotating speed (rpm)	Source	Gold concentration	References
9.5 – 9.7	30	0.005 mol	250	10	Oxygen free	300	Synthetic solution	24 ppm	(Karavasteva, 2010)
9.5	22 -50	0.25 g	500	120	Dissolved oxygen of 7.8 ppm	500 – 2000 (Copper discs)	Synthetic solution	10 – 100 ppm	(Hiskey & Lee, 2003)
7.4 - 9.6	18 - 60	5 g	3750	90	Oxygen-free	1250	Synthetic solution	13.33 ppm	(Guerra & Dreisinger, 1999)
9.5 – 10.5	ambient	30-450 metal/Gold mass	100	60	without de-aeration	-	Gold Ore	8 ppm	(Arima et al., 2002)
-	30 - 50	REQCM	25		Oxygen-free	300	Synthetic solution	50 ppm 0.25 mM	(Choo & Jeffrey, 2004)

2.13 Calculation procedure of activation energy

The activation energy E is the minimum energy that must be possessed by reacting molecules before the reaction will occur (Fogler, 2006). According to Lee (2003), the effect of temperature on the magnitude of a reaction rate constant is described by the Arrhenius equation.

$$\ln(k_1) \propto \frac{1}{T}\left(-\frac{\Delta G^*}{R}\right) \tag{38}$$

For elementary reactions, theory predicts that the rate constant should be temperature-dependent in the following manner:
From Arrhenius' law,

$$k = A.exp\left(-\frac{E}{RT}\right) \tag{39}$$

Where: k = specific rate constant (1/s)
E = Activation energy (J/mol)
A = Frequency factor
R = Molar gas constant = 8.314 J/mol
T = Absolute temperature (K)

Equation 39 can be used to determine the activation energy and frequency factor for a reaction by taking natural logarithm to obtain equation 40 and plotting Ln (k) as a function of (1/T) (Fogler, 2006):

$$\ln k = -\frac{E}{RT} + \ln A \tag{40}$$

CHAPTER 3

3 Methodology

3.1 Introduction

This chapter provides details on experimental runs conducted, equipment and materials used. Descriptions of instruments used are also included. A quantitative approach was used during this research.

The equipment was available at the Cape Peninsula University of Technology (CPUT). Experimental consisted of the following two sections:

- Ammonia thiosulphate leaching of PCBs
- Precipitation of gold using a copper cementation process from a pregnant leach solution.

Figure 3-1 shows a graphical illustration of the process used in this study to recover gold from WEEE.

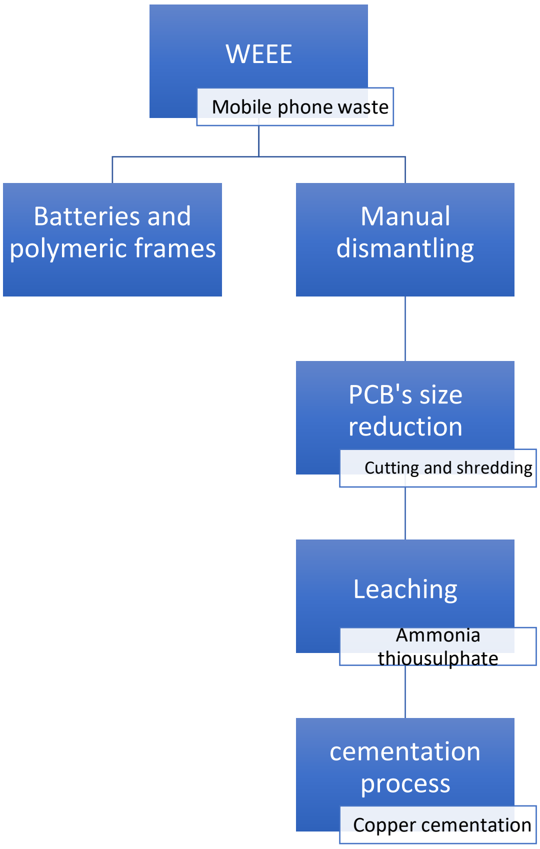


Figure 3-1: A schematic flow sheet showing the processes for recovery of gold from WEEE

3.1.1 List equipment used for experiments

- Reactor
- Water bath
- pH meter
- pipette
- Metal-cutter
- Shredder
- Sieve shaker
- Fume cupboard
- Stirrer
- pH meter
- Atomic Absorption Spectroscopy (AAS)

3.1.2 List of Material used for experiments

- 32% NH_3 solution
- Sulphuric acid
- Nitric acid
- Copper powder
- Nitrogen gas
- Gold stock
- Sodium tetrachloroaurate(iii) dihydrate
- Ammonia thiosulphate
- Cupric sulfate
- Waste mobile phones PCBs

3.1.3 Personal Protective Equipment (PPE)

PPE is essential to ensure personal safety. These are the protective equipment used:

- Respiratory masks
- Latex gloves
- Eye protective goggles
- Closed safety shoes

3.1.4 Description of reagents

Deionized water

Used to prepare solutions.

Crushed waste mobile phones PCBs

The PCBs have been crushed to allow a better surface contact and screened to different sizes using a shaker.

Ammonium Thiosulphate

Used as a source of thiosulphate ions. Ammonium thiosulphate is used as a leachant which is non-toxic as well as economical. It works to stabilize gold as anionic complex which is mainly accountable for the gold recovery.

Copper Sulphate

Used as a source of copper ions. Copper sulfate is used as a catalyst and oxidizing agent in the solution which forms a stable cupric tetra amine complex.

Ammonia Solution

32% ammonia solution was used to adjust the pH of the leach solution. Ammonia also stabilizes the oxidant, copper(II) in the leach solution.

Sulphuric acid

Used to adjust the pH of the solution

Nitrogen gas

99.99% nitrogen gas supplied by Afrox in a cylinder

3.1.5 Description of apparatus and equipment

Cementation reactor

500 mL glass reaction vessel with a jacket connected to a circulating heating water bath with temperature control. The lid has openings for nitrogen gas, an overhead stirrer, pH and temperature probes as well as for the addition of copper powder in the reaction vessel.

Ammonia thiosulphate Leaching reactor

The reactor has four baffles and a capacity of about 1L and is fitted with a perforated lid. The perforated lid allows for the different probes to be immersed into the solution and give readings for different parameters during the experiments

Hanna pH meter

The pH meter was used to read the instantaneous potential hydrogen of the solution

Jenway 3 in one pH meter, Redox potential and temperature instrument

Used to measure the redox potential as well as the temperature of the solution in the reactor at any given time during the reactions

Overhead stirrer

This mixer was used to mix the solution during the experiment to have an even mixing

Pipette, Syringes

Used to collect samples from the solution during experiments

Water bath

Used to supply heat needed for the reaction

Copper powder

99% assay copper powder with <75 μm particle size obtained from Sigma-Aldrich

3.2 Ammonia thiosulphate leaching experiment

Batch leaching experimental setup is shown in figure 3-2. The ammonia thiosulphate leaching experiments were carried out to determine the initial concentration of gold needed for the cementation experimental runs. Experiments were performed in a baffled cylindrical plastic reaction vessel immersed in a controlled temperature water bath. The setup consisted of a 1000ml beaker with an overhead stirrer; pH and temperature probes. The experiment took place in a fume hood. The vessel was open to the atmosphere.

3.2.1 Pre-treatment of PCBs

MPPCBs: Disassembly, size reduction, and particle size classification

Mobile phones from different companies, models, and year of manufacture were used in this study. The mobile phones were manually disassembled and batteries and polymeric frames were separated from PCBs. Electronic components (e.g. resistors and capacitors) were also manually removed from the circuit boards using pliers and screwdrivers. PCBs were cut into pieces of about 2 x 2 m using a metal-cutter once the various mountings on the PCBs were removed. A shredder was then used to further reduce the size of the pieces. The shredder uses a combination of compression and ripping or smashing and cutting (Menad, 2016). As previously mentioned, PCBs have a complex composition that includes polymers, ceramics, and metals. It is, therefore, necessary for the metals to be freed from the non-metallic fraction and made available for leaching (Kasper et al., 2011).

The shredded PCBs were milled in a ball mill. Different sizes of sieves were used to classify the sizes of particles using a sieve shaker. After screening, the samples from different sieves were weighed and labeled.

According to Menad (2016), screening is needed to classify WEEE materials by size in order to eliminate the nonvaluable materials they contain. A shaker was therefore used to classify the pieces separated by shredding.

The feed material is sorted into at least two size fractions known as:

1. Undersize material that passes through the screen at a determined cut size
2. Oversize material that remains on the screen surface

Table 3-1: particle sizes and subsequent mass fractions of pre-treated PCBs used for leaching experiment

Size (µm)	mass fraction	mass per 20g sample
0 - 125	0.19	3.8 g
125 – 300	0.28	5.6 g
300 - 600	0.23	4.6 g
600 - 1180	0.16	3.2 g
1180 -1350	0.14	2.8 g

3.2.2 Leaching procedure

The comminuted fractions of PCBs were leached by a thiosulphate leaching process. A solution of ammonia thiosulphate and the copper solution was prepared. Dropwise addition of 32% ammonia solution was added to the solution to pH adjust the solution to 9.5. A sample of 40 g of PCBs was added to the solution. Leaching experiments were performed in a 1 L baffled open-top reactor submerged in a water bath. A leaching solution of 500 ml with 5 g/L ammonium thiosulphate and 3 g/L copper sulfate was used for all experimental runs. 20 g sample with the desired mass fractions of waste mobile phones PCBs was consumed in each experiment, as shown in table 3-1. All experiments were performed at 30^{o}C and the speed of the stirrer was 350 RPM. The pH of the solution was maintained at 9.5 with 32% ammonia solution. The leaching experiments were allowed to run for 240 minutes. All experiments were carried out using solutions prepared by dissolving analytical grade reagents in deionized water. Duplicate runs were performed for each experiment to check for repeatability and reliability.

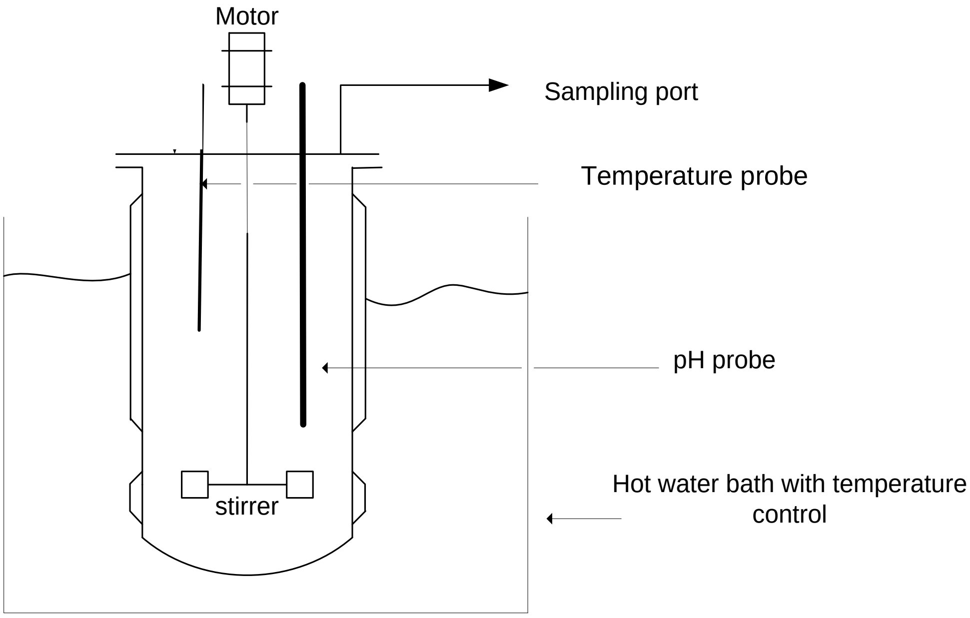


Figure 3-2: leaching reactor adapted from Guerra & Dreisinger (1999)

The samples were analysed using an atomic adsorption spectrophotometer to measure Au concentration in the leaching solution.

Table 3-2: Standard conditions used for leaching experiment

$[(NH_4)_2S_2O_3]$	5 g/L
$[CuSO_4.5H_2O]$	3 g/L
Temperature	30 ℃
pH	9.5
Time	3 h
Stirring speed	350 RPM

3.3 Copper cementation experiment

3.3.1 Preparation of synthetic solution

Cementation experimental runs were conducted using a synthetic gold leach solution in order to use a constant initial gold concentration during cementation experimental runs and therefore allow a rational comparison of experimental conditions.

Synthetic solution emulating the PCBs leach solution was prepared with deionized water as shown in table 3-3. Ammonia thiosulphate obtained from Merck was 98%+ pure. All other chemicals were analytical grade. 5 g/L ammonia thiosulphate and 3 g/L copper sulfate solution was prepared first with deionized water. 0.015 g of sodium tetrachloroaurate(iii) dihydrate was introduced to the solution to make an initial concentration of 15 mg/L gold solution. Gold was introduced to the thiosulphate solution as sodium tetrachloroaurate (iii) dihydrate obtained from Sigma-Aldrich. Gold introduced to thiosulphate solution formed the trivalent gold, $AuCl_4^-$ as previously reported by Zhang & Dreisinger (2004) and Navarro et al. (2004). Copper was added as $CuSO_4.5H_2O$, which immediately reduced the $AuCl_4^-$ to monovalent gold, $Au(S_2O_3)_2^{3-}$ as suggested by Guerra & Dreisinger (1999). The pH of the solution was adjusted with 32% ammonia solution and deionized was added to top up the volume of the solution to 500 ml.

The solution was thoroughly and uniformly stir mixed in the reaction vessel, and then conditioned by bubbling nitrogen gas through the solution for 30 minutes prior to cementation experiments could be initiated.

Table 3-3: Synthetic leach solution composition and characteristics

Chemical composition	**Concentration**
$[(NH_4)_2S_2O_3]$	5 g/L
$[CuSO_4.5H_2O]$	3 g/L
NH_3	1 – 5 mL
[NaAu$Cl_4.2H_2O$]	15 mg/L
pH 9.5	

The batch cementation experimental setup is shown in figure 3-3. Experimental runs were performed in a 500 mL glass reaction vessel with a heating jacket connected to a circulating water bath with temperature control. The setup consisted of an overhead stirrer, pH and temperature probes. Nitrogen gas was bubbled in the vessel to minimize oxygen concentration in the vessel. All experiments were carried out using synthetic feed.

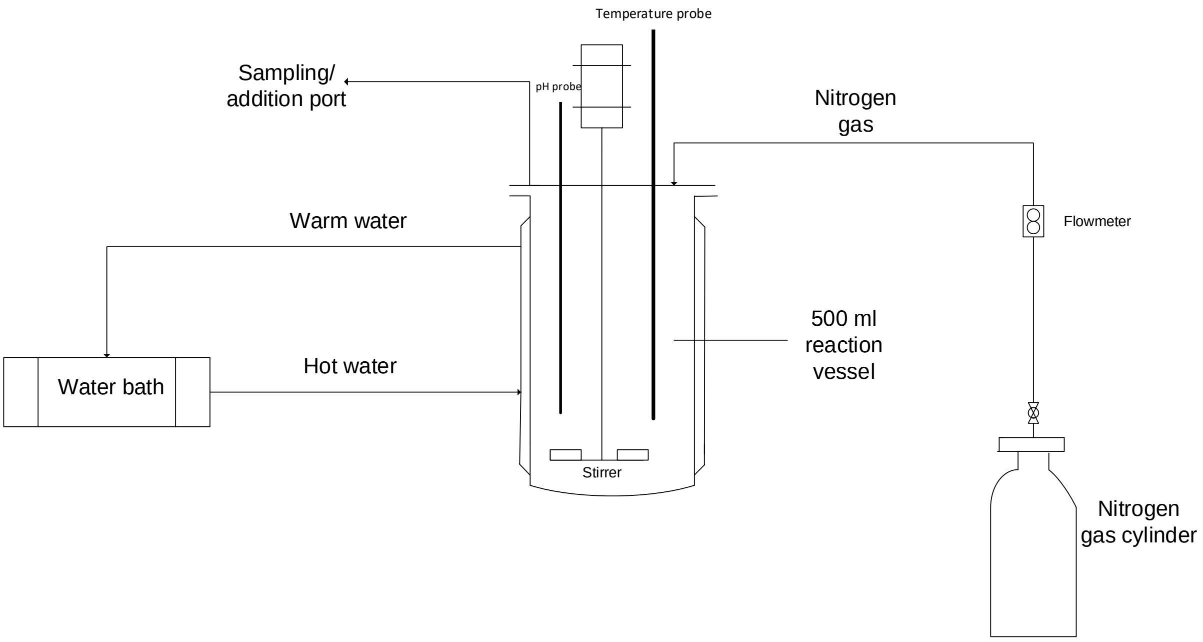


Figure 3-3: Experimental setup for cementation of gold by copper powder

3.3.2 Pre-treatment of the cementation agent

Copper powder was pre-treated using sulphuric acid as suggested by Karavasteva (2010). 2 mL of dilute sulphuric acid solution was sprinkled on the copper powder using a micropipette for 1 min. The cementing metal was rinsed twice with deionized water for the 30s. Water remaining in the treated material was absorbed by pressing with filter paper as previously done by Silthampitag et al. (2016).

3.3.3 Cementation procedure

Cementation experimental runs were carried out by introducing the synthetic solution into the vessel. The pH of the solution was adjusted to 9.5 ±0.5 with 32 % ammonia solution or dilute sulphuric acid. Experimental runs were performed using different amounts of copper powder added to the vessel. The system was mechanically stirred at required stirring speeds.

Each 500 mL solution underwent 30 minutes of conditioning using nitrogen gas, to remove dissolved oxygen. The solution was then slowly stirred and heated to the set temperature. Nitrogen gas was continuously bubbled into the solution during experimental runs. The rotation speed of the impeller was raised to required rpm and a predetermined amount of copper powder was then added to the vessel.

Experiments were allowed to run for 240 minutes. After the cementation experiment, the solution was filtered using a vacuum filter immediately. During the reaction, aliquots of 2 ml of samples were taken from the proceeding reaction solution at different time intervals and diluted to 10 ml using deionized water.

3.3.4 Experimental strategy

A full factorial experimental procedure was performed for the cementation of gold by copper powder while varying temperature, stirring speed and copper powder additions. The experimental design is shown in table 3-3 where 3 variables at different levels were tested, resulting in 27 experimental runs with duplications. For reproducibility results, all runs were repeated.

Table 3-4: Cementation of gold by copper powder tests parameters

A **Temperature**	**B** **[Cu]**	**C** **Rotation speed**
30 ℃	0.5 g/L	300 RPM
40 ℃	1 g/L	900 RPM
50 ℃	1.5 g/L	

One of the objectives of this study was to determine the significance of interactions that exist between the temperature, the amount of copper used and the stirring speed. Design expert software was further used to assess the effects and significance of abovementioned variables interactions.

Literature also suggests that cementation reaction is diffusion controlled, which means the agitation speed should have a noticeable effect on the gold recovery.

The following were kept constant during the experiments:

- Residence time
- Initial gold concentration
- pH
- Initial thiosulphate concentration

3.4 Sampling and Analytical methods

3.4.1 Leaching experiment

1ml samples were taken out using a pipette after 180 minutes. Immediately after sampling, the samples were ejected into a 10 ml volumetric flask and were diluted with 5ml deionized water. The diluted samples were ejected in 10 ml syringes fitted with 0.45 μm syringe filters to filter out the PCBs, thus stopping the reaction. The filtered samples were stored in a fridge until completion of the experiment.

3.4.2 Cementation experiment

2 ml samples were withdrawn and diluted to 10 ml using deionized water. The diluted samples were ejected in 10 ml syringes fitted with 0.45 μm syringe filters to filter out the cementing agent, thus stopping the reaction. After 240 minutes, the solution was filtered out using a vacuum filter and the residues were collected. The precipitates were rinsed with distilled water followed by ethanol and they were air dried (Hung et al., 2005).

Atomic adsorption spectrophotometer (AAS) was used to measure gold concentration firstly every 15 min for the first hour, then hourly for 3 hours. The analysis was conducted with an oxidizing air-acetylene flame at 242.8 nm wavelength. 10 ppm, 20 ppm, 30 ppm, and 40 ppm gold standards were prepared measurements of gold concentration.

The gold concentration on the precipitate after cementation was analyzed using FEI NovaSEM230 Scanning electron microscope (SEM) equipped with an Oxford X-Max Energy-dispersive x-ray spectrography (EDS) detector.

3.5 Proposed flow sheet for the recovery of gold from waste mobile PCBs

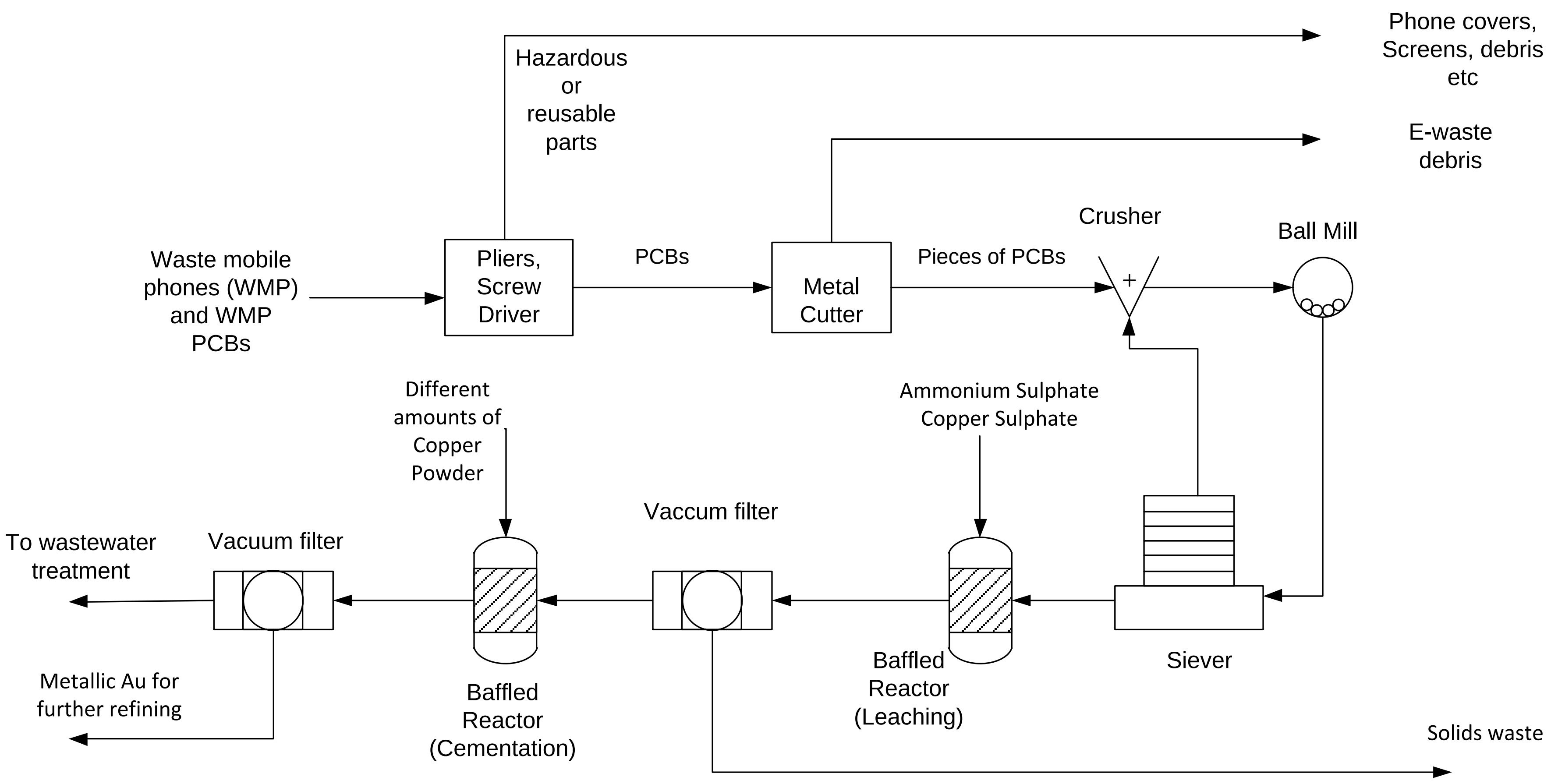


Figure 3-4: The proposed flow sheet for the recovery of gold from waste *mobile phones PCBs*

CHAPTER 4

4 Results and discussion

The results presented in this chapter are divided into 3 categories:

- Effects of operations conditions on gold recovery
- Analysis of gold concentration
- Calculation of Activation Energy

Statistical analysis on experimental data obtained using design expert 10 software, is included under this section.

4.1 Leaching of gold from the PCBs

Determination of the initial concentration of gold

Waste mobile phones PCBs after comminution underwent an ammonia thiosulphate leaching process in order to determine the initial concentration of gold needed for the cementation process. The experiment was conducted at 30 ℃ with the solution maintained at a pH of 9.5. These parameters were set based on optimum conditions of previous studies (Ha et al., 2010).

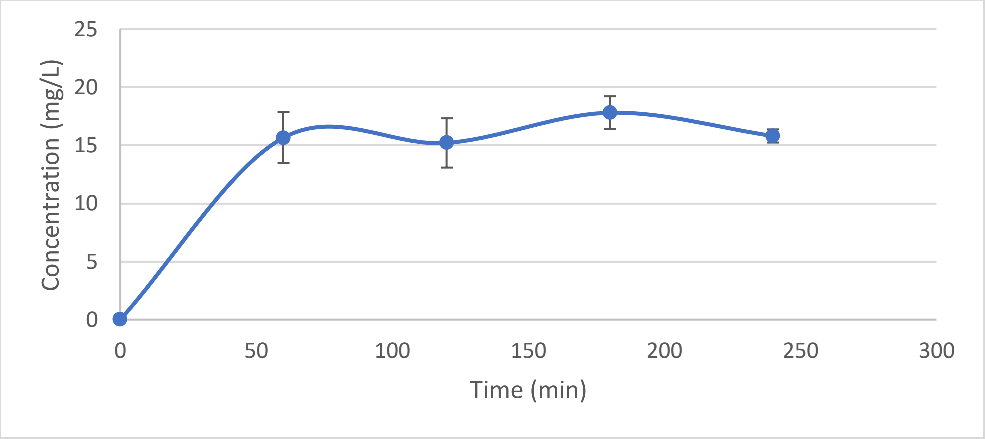


Figure 4-1: Gold concentrations observed during ammonia thiosulphate leaching of mobile phones PCBs

The average Au concentrations attained during the leaching process are shown in figure 4-1 above. It can be observed that the concentration of Au increased with an increase in time. Au concentrations obtained after 4 h were 15.80 and 16.20 mg/L respectively, after the first and second experimental runs. However, the change in gold concentration after 4 h was not significant due to an effective dissolution rate of the gold caused by the initial amount of thiosulphate in the first few hours. Thereafter dissolution rate decreased when all the thiosulphate was consumed (Mohammadi et al., 2017). Navarro et al., (2002) and Mohammadi et al., (2017) have also observed that the gold leaching rate becomes slower after a given period of the reaction, which they attributed to the change in the mechanism of leaching. On the other hand, it is important to reduce leaching time in order to minimize the use of the reagents and avoid possible precipitation reaction (Aylmore et al., 2001). It has been reported that the leaching time of gold using cyanide is more than 24 h (Zhang et al., 2014). It can, therefore, be said that leaching of gold using thiosulphate is way faster than cyanide leaching.

4.2 Cementation of gold from the leach solution

Gold cementation using copper powder was conducted with a synthetic solution simulating mobile phones PCBs leach solutions. An initial gold concentration of 15 mg/L was used for all experimental runs. The process parameters; agitation speed, temperature, and copper powder, were investigated at different levels.

4.2.1 Effects of process variables

The following process variables were investigated as shown table 3-3 and table 4-1 below.

Table 4-1: Cementation of gold by copper powder tests parameters

A **Temperature**	**B** **[Cu]**	**C** **Rotation speed**
30 ℃	0.5 g/L	300 RPM
40 ℃	1 g/L	900 RPM
50 ℃	1.5 g/L	

Effect of agitation (rotation speed)

The effect of agitation on the recovery of gold was tested at two levels, namely 300 and 900 rpm. Figure 4-2 below shows the effect of agitation on gold recovery for experimental runs performed using 0.25, 0.50 or 0.75 g Cu powder as a cementing agent. As shown in figure 4-2 (a) and (b), at 30℃, gold recovery increases significantly as the stirring speed was increased from 300 to 900 rpm. After 4 hours, 48% of gold were recovered at a stirring speed of 300 RPM and 0.75 g Cu powder addition. The percentage recovery almost doubled with an increase in stirring speed of 900 rpm at the same copper powder concentration. This was caused by the intense mixing pattern of the suspended particles which positively affected the kinetics of the cementation process (Nguyen et al., 1997). According to Alturi (2003) and Wang (2007), this possibly points to film diffusion being the rate controlling step. Wang *et al.* (2007) also studied the effect of stirring speed on gold cementation with thiocyanate solutions using iron powder as a cementation agent. The escalation of stirring speed increases the rate of gold cementation due to the decrease of the diffusion layer thickness, thus, increasing the cementation rate. Similar observations were made for experimental runs performed with lower copper powder and temperatures. However, the effect of stirring speed on gold recovery was less significant at temperatures of 40 and 50℃ and copper powder of 0.5 and 0.75 g, respectively, as observed in figure 4-2 (e) –(f).

Effect of temperature

Figure 4 shows the effect of temperature on gold recovery was studied at 30, 40 and 50 °C, respectively**.** It can be observed that there is no significant change in the recovery when the temperature was increased at the start of experimental runs for the first 60 minutes. Navarro et al. (2004) investigated zinc cementation and discovered an increase in the precipitation rate for the first 10 minutes when using temperatures of 20 and 50 °C respectively. After 60 minutes the gold recovery increased gradually as the temperature increases from 30 to 40 °C. This was caused by the free movement of the gold thiosulphate complex through the liquid phase, which can be attributed to the decrease in the solution viscosity (Wang et al., 2007). However, a slight decrease in the recovery was observed at the 50 °C temperature experimental run. This is understandable because in the presence of a measurably higher copper concentration and with increasing temperature, the instability of thiosulphate intensifies; Chalcocite, Cu_2S can be formed from degradation of cuprous–thiosulphate complex, $2Cu(S_2O_3)_3^{5-}$ and deposited as a passive film on the surface of the copper powder (Guerra & Dreisinger 1999; Hiskey & Lee, 2003).

Effect of the amount of copper powder used

Gold recovery was investigated at the following copper concentrations; 0.25 g, 0.50 g, and 0.75 g. In Figures 4-2(a)-(f) the percentage of gold precipitated increased slightly from 0.25 g to 0.5 g at a temperature of 30, 40 and 50 ℃ respectively. This observation could be due to the fact that an increase in copper concentration, expands the surface area and enhance the presence of active sites for gold precipitation (Navarro et al., 2004). However, the recovery slightly decreases when the copper concentration is increased from 0.5 g to 0.75 g at temperatures of 40 and 50 ℃.

In some cases, especially when a lower amount of copper powder is used (0.25 g or 0.5 g), the deposited gold was observed to re-dissolve in the solution as the experimental time increases. This could be due to the fact that the oxidation potential of the thiosulphate solution is increased to its initial state as the cementation proceeds (Ku & Lee, 1997). According to Anacleto & Carvalho (1996), this re-dissolution phenomenon can be avoided by choosing shorter residence times.

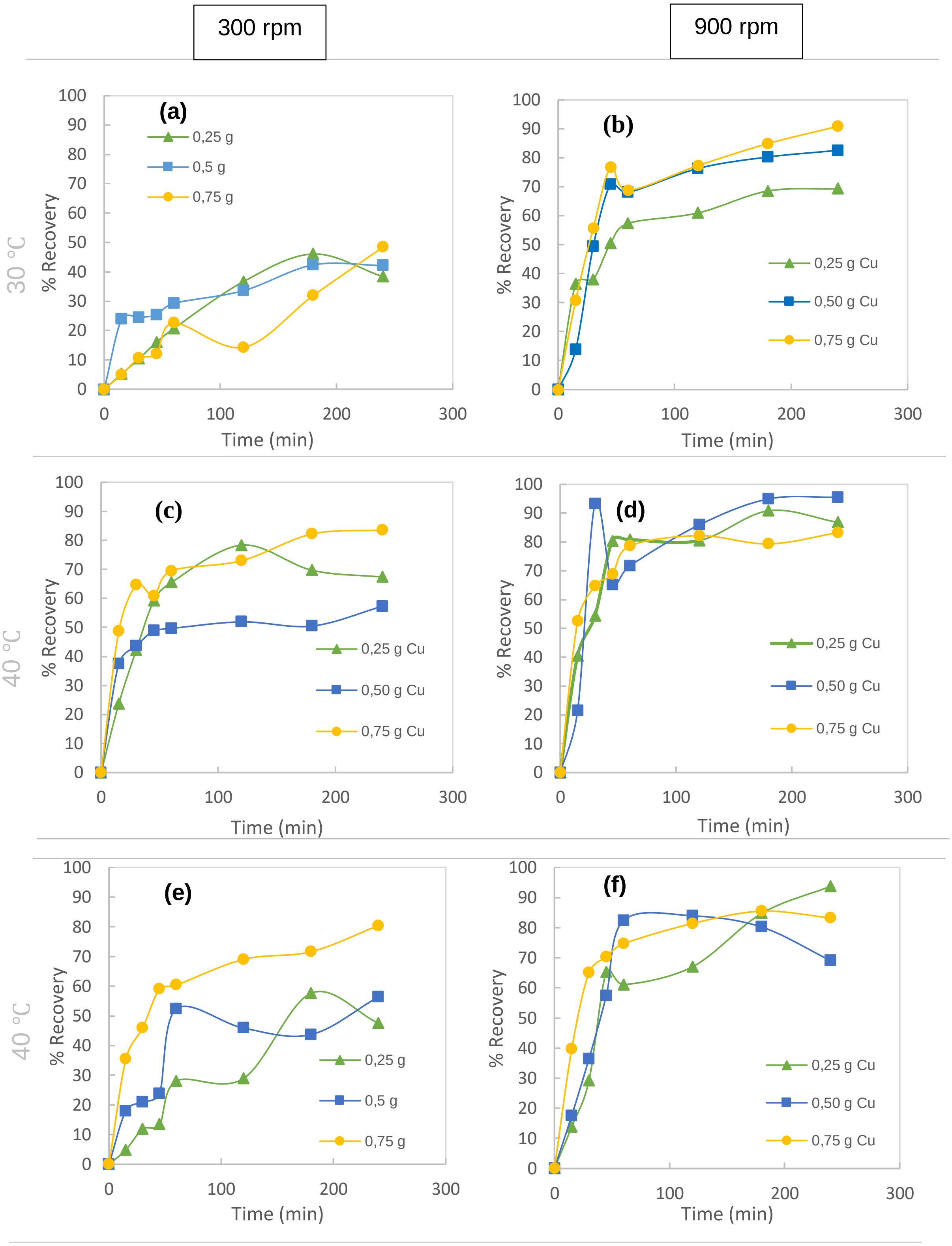


Figure 4-2: Effect of agitation and amount of copper powder used on gold recovery (a) Temperature: 30 ℃; agitation speed; 300 rpm (b) Temperature: 30 ℃; agitation speed; 900 rpm (c) Temperature: 40 ℃; agitation speed; 300 rpm (d) Temperature: 40 ℃; agitation speed

Figure 4-3 graphically illustrates the maximum Au % recovery achieved after 4h of copper cementation process. The highest % recovery was obtained at 40℃ with a stirring speed of 900 rpm and 0.5 g of Cu powder; while operating conditions of 30℃, 300 rpm, and 0.5 g Cu gave the lowest Au % recovery. As previously explained, a lower stirring speed entails a weak mixing pattern, hence a negative effect to the cementation process (Nguyen et al., 1997). At lower temperature, the viscosity of the solution does not allow a free movement through the liquid phase (Wang et al., 2007).

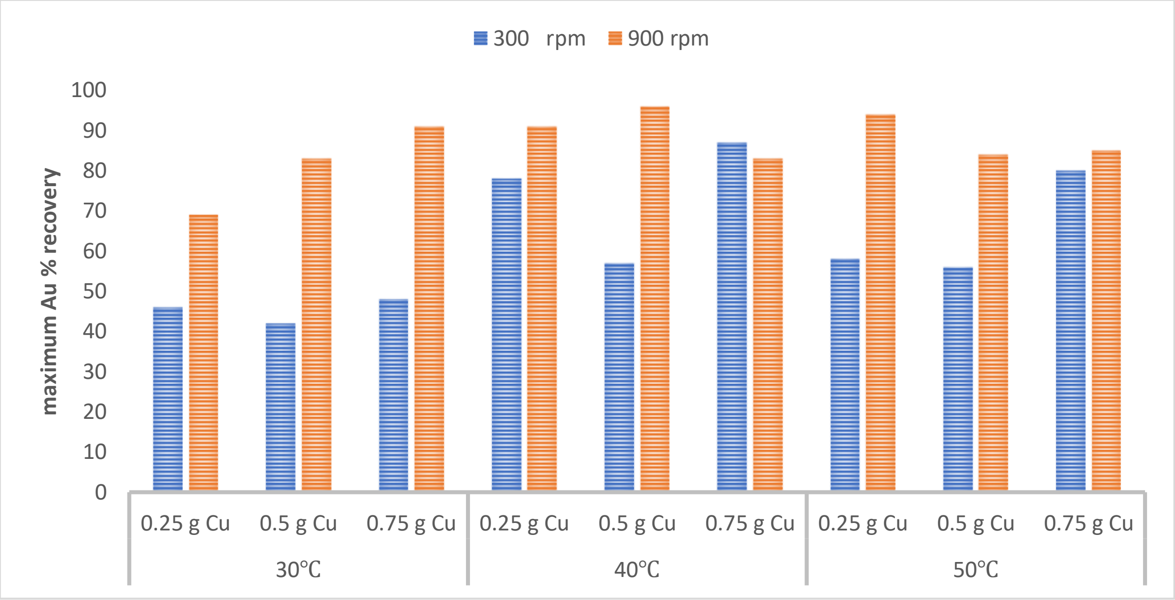


Figure 4-3: Observed maximum gold precipitation at various process variables

4.2.2 The effect of temperature on cementation rate

The effect of temperature on the kinetics of gold onto copper powder was investigated at temperatures of 30, 40 and 50 ℃ while other variables were kept constant. It is reported that cementation reaction follows first order kinetics with respect to the noble metal ion (Nguyen et al., 1997; Demirkiran et al., 2007; Leobardo Valenzuela et al., 2012). The first order kinetic plots of $\ln\left(\frac{C_b}{C_0}\right)$ versus time are shown in Figure 4-4. Where:

C_b = the bulk Au concentration at time t,

C_0 = the bulk Au concentration at time 0.

The rate constants, k, of the cementation reaction obtained at various experimental conditions are shown in table 4-2. The pH was kept constant at 9,5. Thiosulphate and copper sulphate concentrations were also kept constant at 5 g/l and 3 g/l respectively.

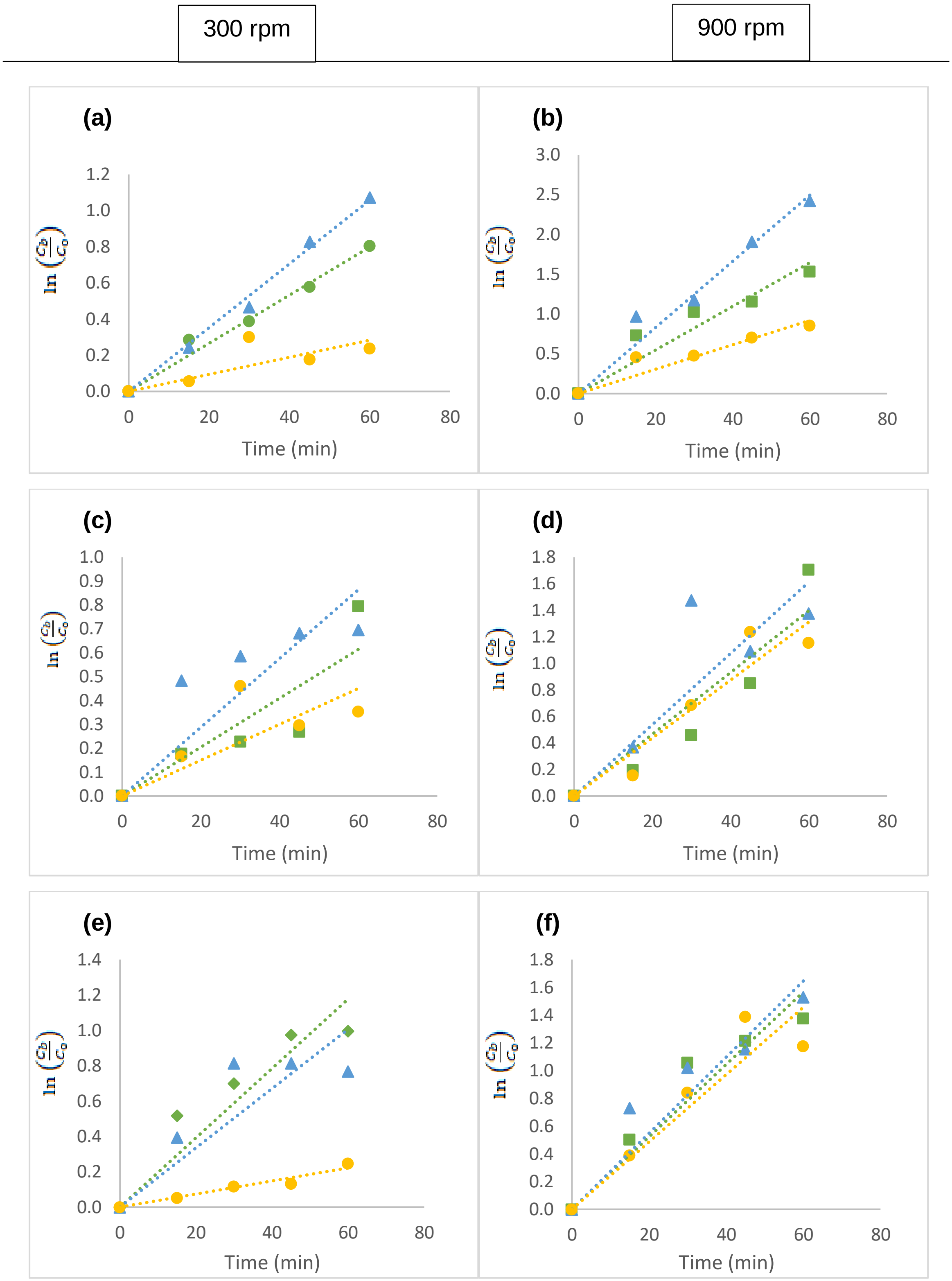


Figure 4-4: Effect of temperature on gold cementation. (a) 0,25 g Cu powder; agitation speed; 300 rpm (b) 0,25 g Cu powder; agitation speed; 900 rpm (c) 0,50 g Cu powder; agitation speed; 300 rpm (d) 0,50 g Cu powder; agitation speed; 900 rpm (e) 0,75 g Cu powder

Table 4-2: Equations and R-squared values of plots shown in figure 4-4 at various process variables

	30 ℃ ●	40 ℃ ▲	50 ℃ 🟩
(a) **0,25 g Cu; 300 rpm**	y = 0,0047x R² = 0,5342	y = 0,0176x R² = 0,992	y = 0,0133x R² = 0,9787
(b) **0,25 g Cu; 900 rpm**	y = 0,0153x R² = 0,8686	y = 0,0416x R² = 0,9626	y = 0,0274x R² = 0,877
(c) **0,50 g Cu; 300 rpm**	y = 0,0075x R² = 0,4528	y = 0,0144x R² = 0,6206	y = 0,0102x R² = 0,7853
(d) **0,50 g Cu; 900 rpm**	y = 0,0233x R² = 0,8806	y = 0,0269x R² = 0,6901	y = 0,0218x R² = 0,905
(e) **0,75 g Cu; 300 rpm**	y = 0,0037x R² = 0,9455	y = 0,0196x R² = 0,8444	y = 0,0168x R² = 0,6544
(f) **0,75 g Cu; 900 rpm**	y = 0,0243x R² = 0,8601	y = 0,0274x R² = 0,877	y = 0,0261x R² = 0,903

The cementation rate constants obtained from the slopes of these first-order kinetic plots increased with an increase of temperature from 30 to 40 ℃, however, there is a noticeable decrease in the rate of cementation with an increase of temperature from 40 to 50 ℃.
The high R-squared values indicate that the cementation process follows first order kinetics.

Table 4-3:First order rate constants k *(*$\times 10^{-6}$ *m/min) at various experimental conditions*

Experimental conditions		**Temperature (℃)**		
Copper powder (g)	**Agitation speed (rpm)**	**30**	**40**	**50**
0,25	**300**	9,40	35,2	17,7
	900	29,5	80,2	52,8
0,5	**300**	7,50	14,4	9,83
	900	21,0	25,9	22,4
0,75	**300**	2,38	12,8	12,6
	900	1,56	17,5	1,67

From the slopes of the plots of $Ln\ k$ versus I/T, the activation energies of the reaction, E, can be calculated according to the Arrhenius relationship.

4.2.3 Arrhenius plot and activation energies

In the temperature range from 30 to 40 ℃ the cementation rate was found to increase in with the increase in temperature. However, there is a noticeable decrease in the rate of cementation with increasing temperature from 40 to 50℃. According to Guerra and Dreisinger (1999), it is understandable because in the presence of a measurably higher copper concentration and with increasing temperature, Cu_2S can be formed from degradation of $2Cu(S_2O_3)_3^{5-}$and deposited as a passive film on the surface of the copper powder in this case. This is in accordance with reaction 41.

$$2Cu(S_2O_3)_3^{5-} + 2OH^- \quad \rightarrow \quad Cu_2S + SO_3^{2-} + 5S_2O_3^{2-} + H_2O \qquad (41)$$

According to Lee (2003), the decrease of the cementation rate at high temperatures could be due to the instability of thiosulphate and its decomposition. The formation of solid products like Cu_2S in reaction 41 can result in passivating surface films that inhibit the cementation reaction (Hiskey and Lee, 2003).

Cementation reaction exhibited two different kinetic regions as shown in figure 4-5, similarly to Hiskey and Lee (2003). Two distinct activation energies were therefore obtained, namely 104 kJ/mol, between 30 to 40 ℃ regions and 54.58 kJ/mol between 40 to 50 ℃ region**.** The high activation energy at low temperature indicates that the rate was probably controlled by surface reaction. The low activation energy at high temperature indicates that the rate was probably controlled by a boundary layer ionic diffusion mechanism (Lamya & Lorenzen, 2005)**.** The shift in the activation energy probably could also be a result of the change in the reaction mechanism, hence, it may be assumed that two consecutive two processes controlled the reaction rate (Demirkiran et al., 2007).

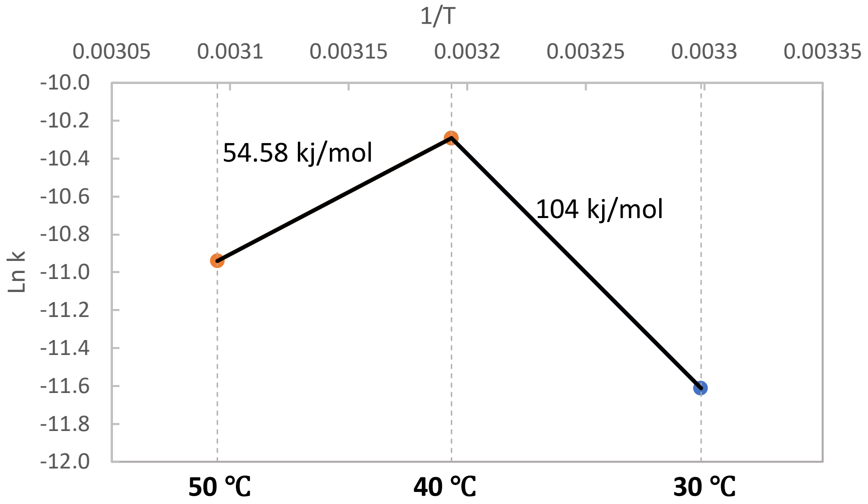


Figure 4-5:Arrhenius plot for the reaction between 30 to 50 °C with 15 ppm Au, agitation speed of 900 RPM and 0, 25 g of copper powder was used

Moreover, the decrease of cementation rate of gold at high temperature could be explained by the passivation phenomenon causing a blockage of the electrode surface (Nguyen et al., 1997).

Similar trend was observed at various experimental conditions as shown in figure 4-6. Two distinct activation energies were obtained at high temperatures (50-40°C) and lower temperatures (30-40°C); Lower energies between 50-40°C and higher energies at 50-40°C regions.

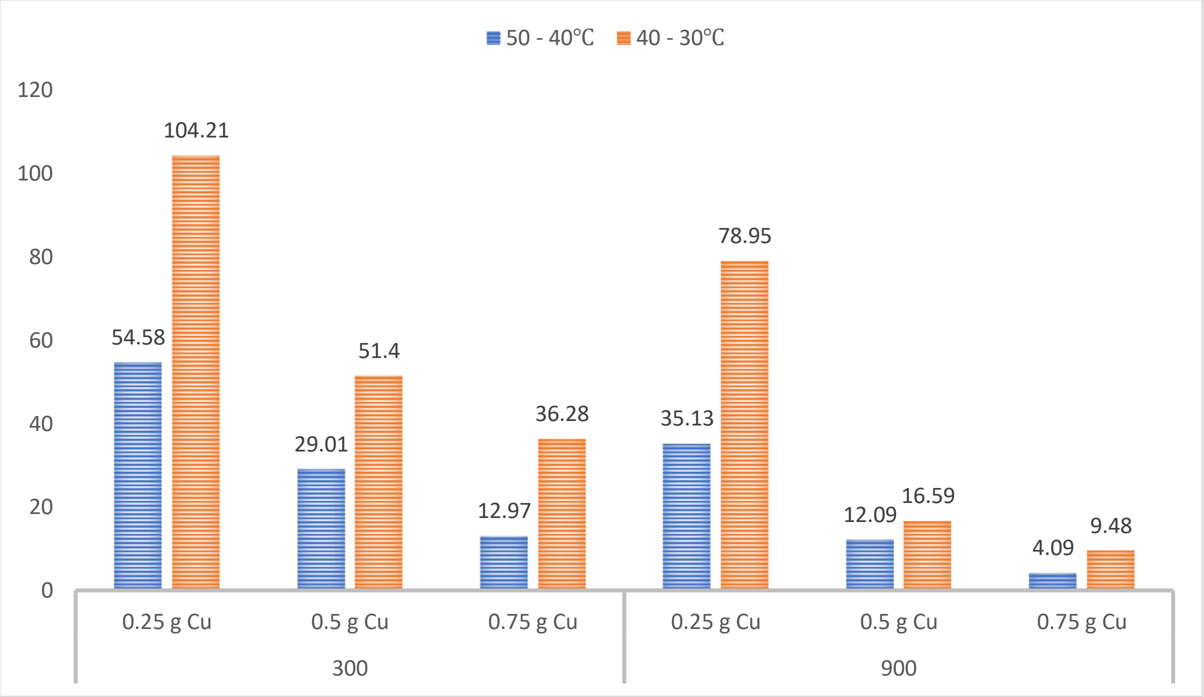


Figure 4-6: Activation energies (KJ/mol) at different experimental conditions

4.3 SEM-EDS analysis

The copper powder before and deposits recovered after cementation, were analyzed by scanning electron microscopy (SEM-EDX), in order to evaluate the chemical composition and the morphology of the solids. EDS analysis was performed at several spots on the deposits recovered. The gold concentration was at a constant at 15 ppm. The analysis revealed that the precipitates were made up of different compositions of sulfhur, gold, carbon, copper, and oxygen. The transient copper–sulphur-oxygen precipitate and some other sulphur-bearing species were formed in the surface, and these species contributed to passivation (Guerra & Dreisinger, 1999).

Quantitative analysis of the copper powder before cementation is presented in table 4-4.

Table 4-4: Quantitative EDS analyses of copper powder weight % before and after pre-treatment with H_2SO_4

	C	O	Mg	Cu	Total
Before	20,24	8,50	1,03	70,23	100
After	22,89	4,65	-	72,47	100

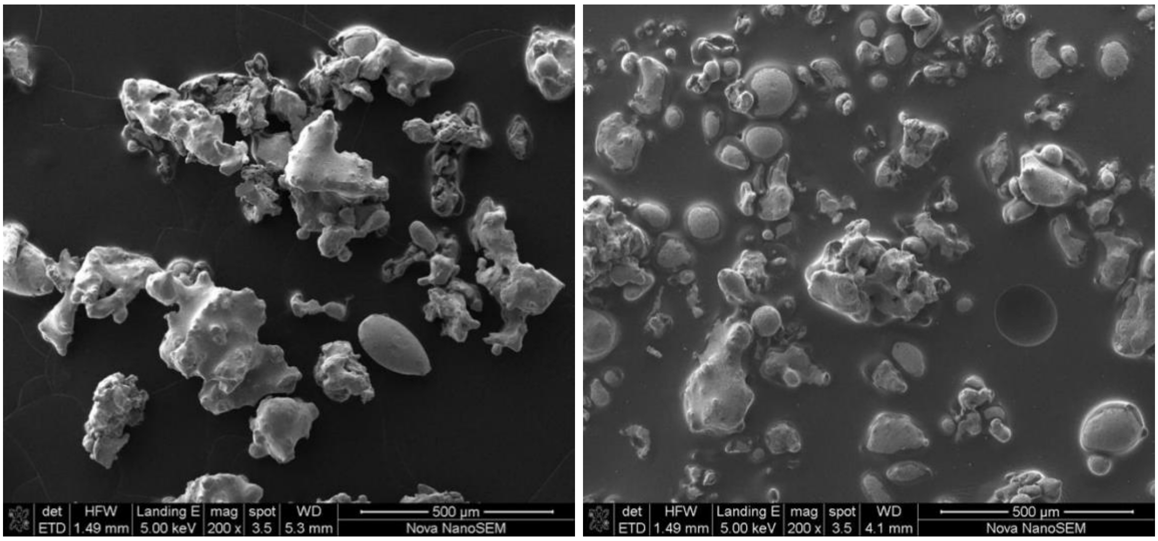


Figure 4-7: SEM images of copper powder prior to pre-treatment with sulphuric acid (Left) and after pre-treatment (Right)

EDS analysis was further used after cementation to study the composition of the precipitate formed. The analysis revealed that the precipitates were made up of different compositions of sulfur, gold, carbon, copper, and oxygen. Carbon and oxygen are common environmental

contaminants hence their presence on the deposit could be expected (Lee, 2003). Figure 4-7 above shows SEM images of copper powder prior to pre-treatment with sulphuric acid and after pre-treatment.

4.3.1 The effect of process variables on the concentration of gold on precipitates

Table 4-5 shows the quantitative analyses of the precipitates formed during tests performed at various experimental conditions. A decrease in the concentration of gold on the precipitate was observed when the amount of copper powder used was increased from 0.5 to 0.75 g. However, the concentration of gold increases as the amount of powder used increased from 0,25 to 0,5 g. Increasing the temperature slightly increased the concentration of gold on the precipitates. At an agitation speed of 900 rpm, 40 °C and 0.5 g of copper powder, the concentration of gold on the precipitates was 24%.

Table 4-5: Quantitative analyses of the precipitates formed during tests performed at various experimental conditions

Experimental conditions		**Mean concentration (%)**				
		C	**O**	**S**	**Cu**	**Au**
0,25 g copper powder	300 RPM / 40 ℃	18,52	4,53	8,59	45,6	22,77
	900 RPM / 40 ℃	22,36	4,65	7,32	41,81	23,88
	300 RPM / 50 ℃	17,33	13,34	6,15	46,89	16,3
0,5 g copper powder	900 RPM / 40 ℃	22,5	16,48	4,42	46,31	10,28
	900 RPM / 30℃	25,88	15,06	4,95	4,95	14,59
	300 RPM / 40 ℃	27,31	4,35	4,32	48,05	15,98
,75 g copper powder	900 RPM / 40 ℃	22,07	4,33	4,94	50,62	18,03
	300 RPM / 30 ℃	41,77	6,91	3,57	34,71	13,05
	900 RPM / 30 ℃	20,48	4,58	5,41	50,39	19,15
	900 RPM / 40 ℃	21,11	2,61	5,9	48,85	21,54
	900 RPM / 40 ℃	16,79	10,91	5,03	52,09	15,18
	900 RPM / 50 ℃	23,95	6,03	5,52	48,35	16,16

4.4 Statistical analysis tools

A statistical analysis was conducted using design expert 10 software, to assess the interactions and significance of process variables on gold recovery. The percentage Au recovery was considered as the response for the analysis. The experiments were conducted in duplicate for reproducibility and to minimize experimental error.

A custom design, user-defined was adopted. The selected factors were A: Temperature, B: Copper powder concentration and C: Stirring speed. A and B were performed in three different levels whereas C in two different levels.

The significance of the effects and their interactions over responses were evaluated using analysis of variance (ANOVA) where *p*-values were generated to prove the null hypothesis (If the p-value is sufficiently small. The null hypothesis is rejected) with a confidence level of 95% ($\alpha = 0.05$). The results of ANOVA consisting of probability (p-value), sum of square, mean square, model significance (F-value) and degree of freedom are shown in Table 4-6. Speed has the most significant effect on the gold recovery ($p = 0.0003$), temperature ($p = 0.1190$) has some significant effect whereas the amount of copper powder ($p = 0.4070$) has no significant effect on the Au recovery.

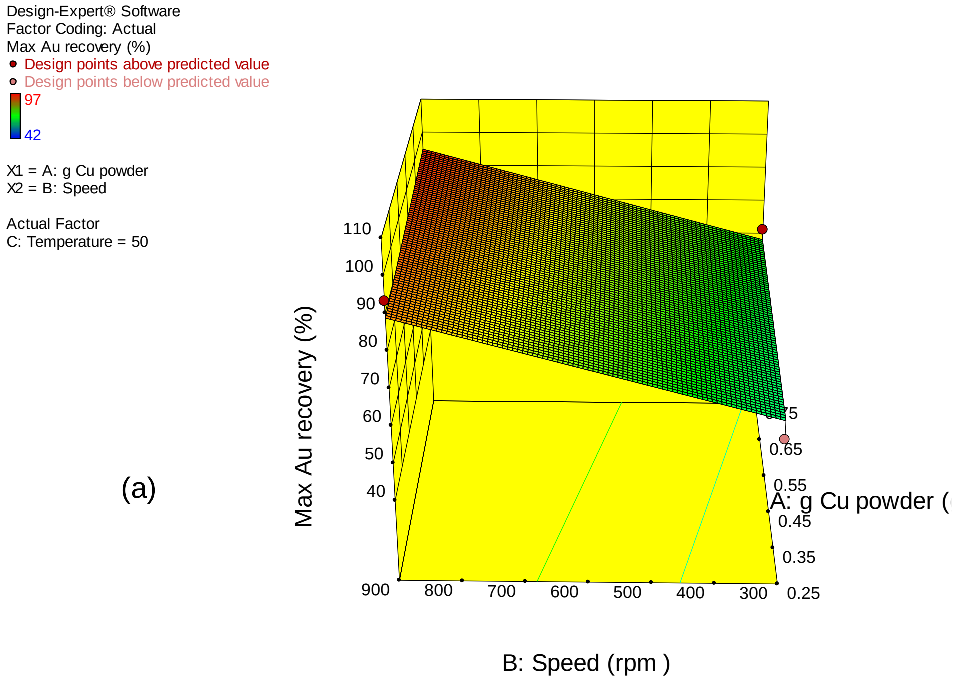
Table 4-6: ANOVA for response surface linear model

Source	Sum of Squares	df	Mean Square	F-value	P-value
Model	3634.31	3	1211.44	8.67	0.0017
A-g Cu powder	102.08	1	102.08	0.73	0.4070
B-Speed	3146.89	1	3146.89	22.53	0.0003
C-Temperature	385.33	1	385.33	2.76	0.1190
Residual	1955.69	14	139.69		
Cor Total	5590.00	17			

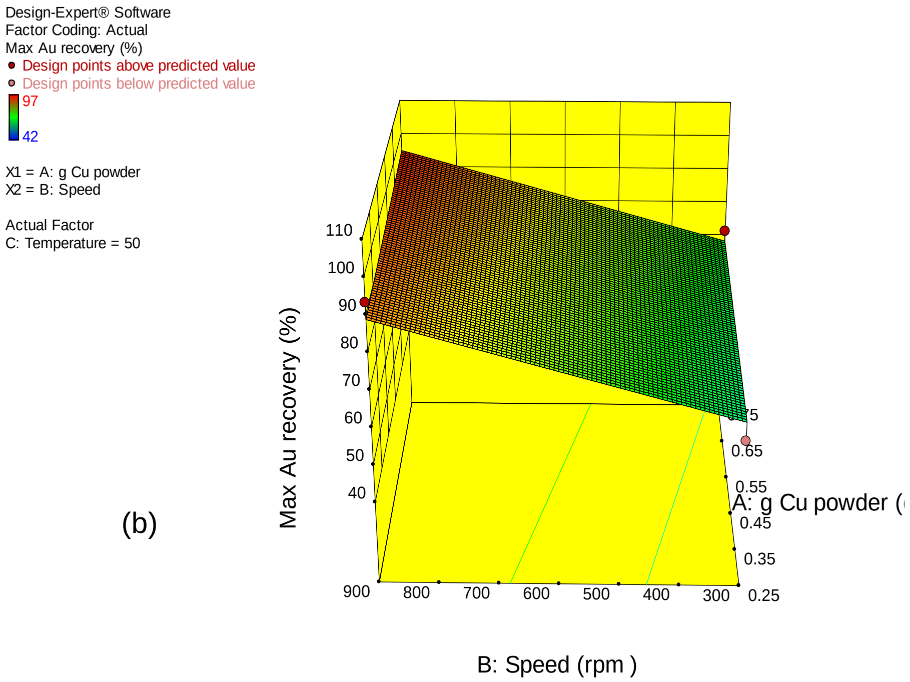
The Model F-value of 8.67 implies the model is significant. An equation considering the linear model with the fixed factors was generated to predict the behavior of gold recovery as a response:

$$\text{Maximum Au recovery} = 73{,}67 + 2{,}92\text{A} + 13{,}22\text{B} + 5{,}67\text{C} \qquad (42)$$

Surface plots were generated for the combination of three factors with actual values where the third factor, the temperature was fixed. Figure 4-8 (a) –(c) shows a red region on the left of the surface operation where the recoveries of gold were greater than 80%. Figure 4-9 also shows high recoveries were obtained at agitation speed of 900 rpm and Cu powder of between 0.25 and 0.5 g.



(a)



(b)

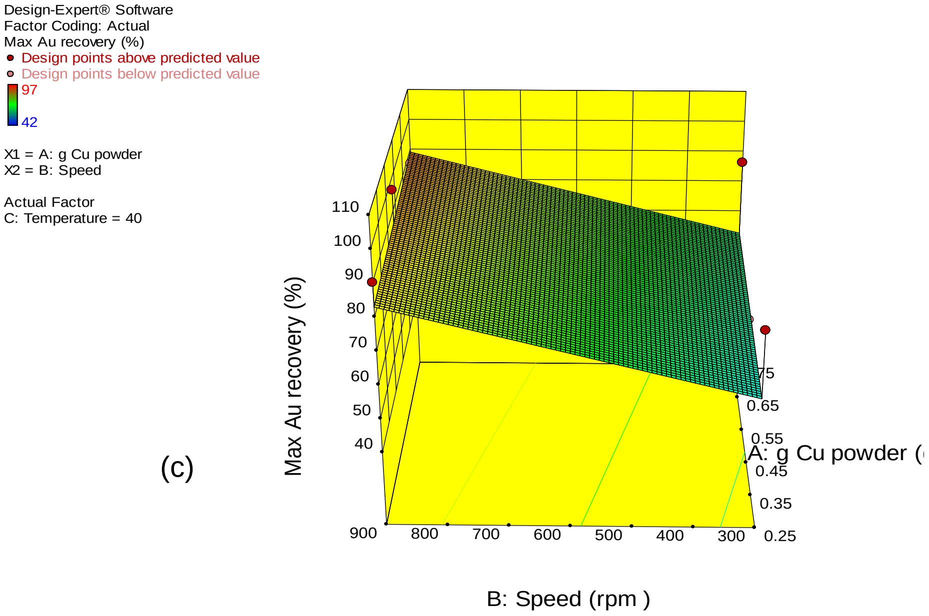


Figure 4-8: Surface plots of Au recovery (a) A: g Cu powder and B: Speed with C = 50 °C; (b) A: g Cu powder and B: Speed with C = 40 °C; (c) A: g Cu powder and B: Speed with C = 30°C

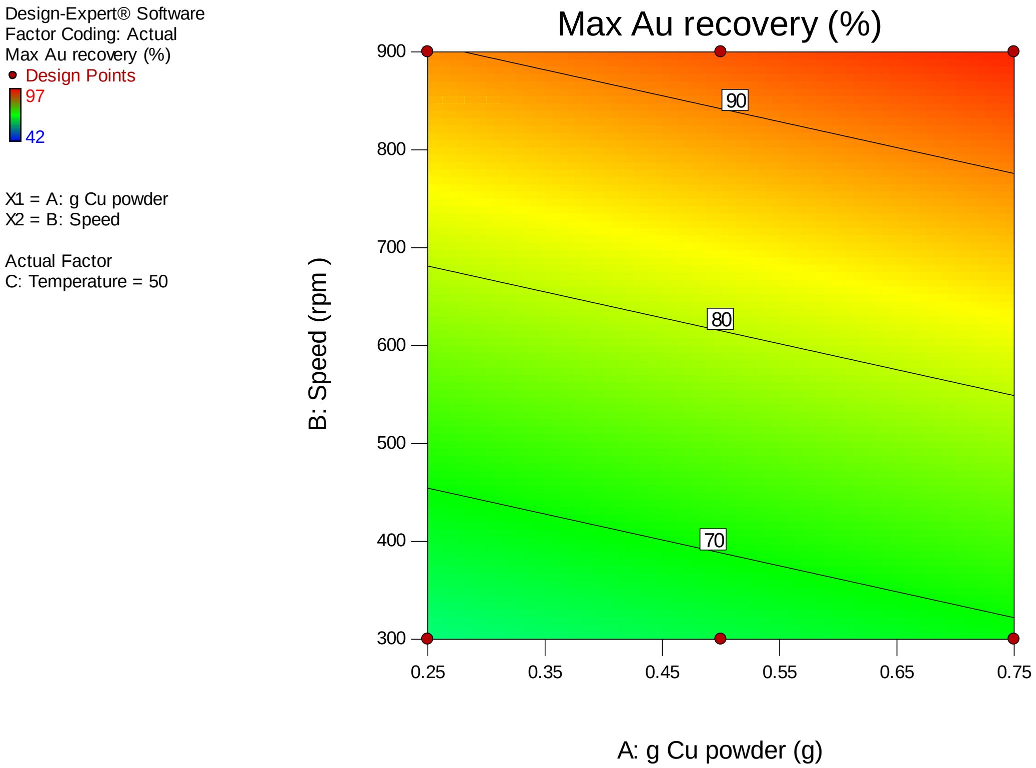


Figure 4-9: Contour plot of Au recovery

Figure 4-10 shows how the model predicts over the range of data. The plot shows the line going through the middle of the data which is good.

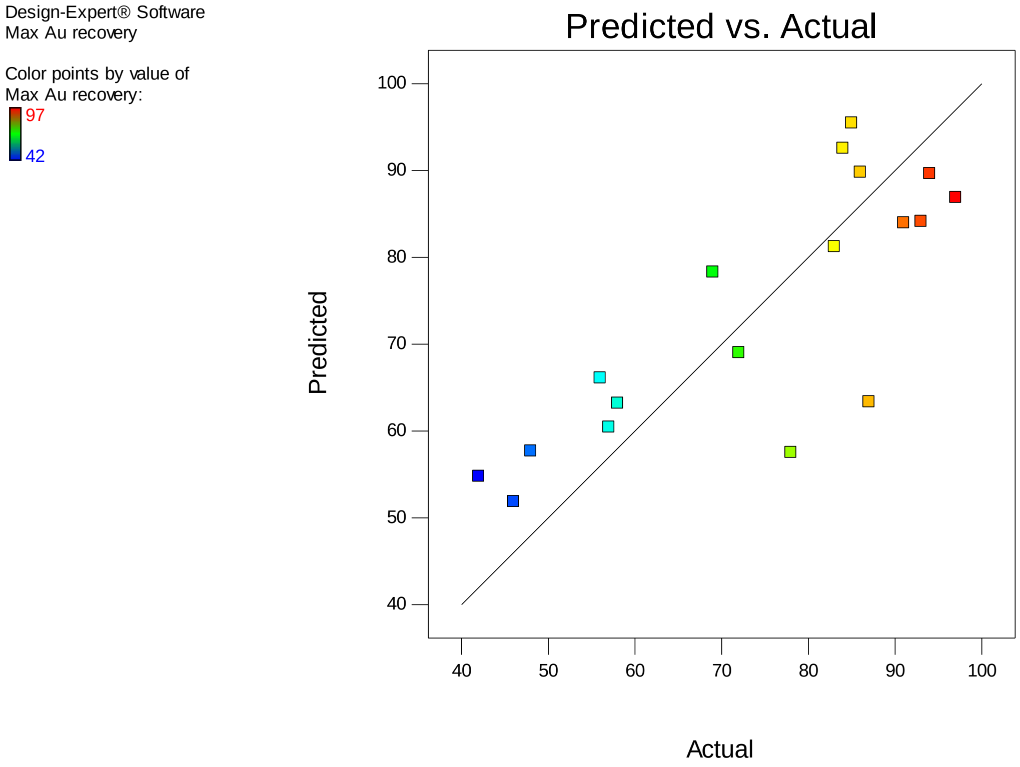


Figure 4-10: Predicted values of the recovery against actual values of recoveries obtained

CHAPTER 5

5 Conclusions and Recommendations

Gold cementation onto copper was carried out from a 15 mg/L Au ammonia thiosulphate leach solution simulating leach solution from mobile PCBs, by using <75 µm particle size copper powder. The pH, thiosulphate, and copper sulfate concentrations in the pregnant leach solution were kept constant at 9.5, 0.034 M and 0.012 M respectively. Cementation of gold onto copper is dependent on various factors such as agitation speed and temperature. The temperature effect was more complex. The cementation rate increased as temperature was increased from 30 to 40 °C. However, when the temperature was increased from 40 to 50 °C there was a noticeable decrease in the rate of cementation. It was found that the recovery of gold from ammonia thiosulphate leach solution was greatly affected by agitation speed. Copper powder recovered up to 96% of gold from the leach solution after 4 hours. The effects of the agitation speed were more significant than those of temperature and the amount of copper powder used. It was established that the rate of the reaction was first-order with respect to the gold concentration. The change in experimental conditions greatly affected the gold concentration on the precipitate recovered after tests.

Recycling of WEEE is an important part of waste management. Traditional methods of managing WEEE including disposing of in landfills, burning in incinerators or exporting to underdeveloped countries are not permitted anymore. EEE contain various fractions of valuable material most of which are found in printed. Increasing demand for highly developed versions of mobile phones combined with the relatively short life cycle of the existing mobile phones floating in the market has increased waste tonnage. In developing and developed countries this alarming increase in e-waste can have a detrimental effect on the environment if suitable recycling technologies are not adopted. The presence of precious metals in E-waste makes recycling an attractive and viable option both in terms of environment and economics (Akci et al., 2015).

CHAPTER 6

6 References

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APPENDICES

APPENDIX A

EXPERIMENTAL DATA

Appendix A: Experimental data

Table A 1: AAS results for experimental run 1

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,21	2,93	3,07
2	15	2,95	2,86	2,91
3	30	2,86	1,69	2,28
4	45	2,64	2,51	2,58
5	60	2,35	2,50	2,43
6	120	1,97	1,91	1,94
7	180	1,49	1,80	1,65
8	240	1,81	1,96	1,89

Table A 2: AAS results for experimental run 2

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	4,59	4,32	4,46
2	15	3,22	2,45	2,84
3	30	3,10	2,44	2,77
4	45	2,54	1,88	2,21
5	60	2,12	1,69	1,91
6	120	1,48	1,98	1,73
7	180	1,05	1,73	1,39
8	240	1,32	1,41	1,37

Table A 3: AAS results for experimental run 3

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,19	3,79	3,49
2	15	2,30	3,62	2,96
3	30	2,33	2,08	2,21
4	45	2,48	2,71	2,60
5	60	2,40	2,51	2,46
6	120	1,98	2,68	2,33
7	180	2,17	1,79	1,98
8	240	1,84	2,20	2,02

Table A 4: AAS results for experimental run 4

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	2,67	2,52	2,60
2	15	2,11	2,35	2,23
3	30	1,20	1,42	1,31
4	45	0,71	0,80	0,76
5	60	0,57	1,07	0,82
6	120	0,48	0,74	0,61
7	180	0,28	0,73	0,51
8	240	0,55	0,36	0,46

Table A 5: AAS results for experimental run 5

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,15	2,71	2,93
2	15	2,94	2,62	2,78
3	30	2,69	2,53	2,61
4	45	2,70	2,44	2,57
5	60	2,75	1,83	2,29
6	120	2,89	2,16	2,53
7	180	2,16	1,83	2,00
8	240	1,82	1,23	1,53

Table A 6: AAS results for experimental run 6

		Run A	Run B	Average
Sample no.	**Time (min)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**
1	0	2,53	3,03	2,78
2	15	2,12	1,65	1,89
3	30	1,46	0,94	1,20
4	45	0,11	1,28	0,70
5	60	0,86	0,86	0,86
6	120	0,33	0,98	0,66
7	180	0,33	0,52	0,43
8	240	0,28	0,22	0,25

Table A 7: AAS results for experimental run 7

		Run A	Run B	Average
Sample no.	**Time (min)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**
1	0	2,14	4,03	3,09
2	15	1,49	3,35	2,42
3	30	0,88	3,00	1,94
4	45	0,67	2,03	1,35
5	60	0,76	1,35	1,06
6	120	0,56	0,69	0,63
7	180	0,49	1,52	1,01
8	240	0,41	1,86	1,14

Table A 8: AAS results for experimental run 8

		Run A	Run B	Average
Sample no.	**Time (min)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**
1	0	3,90	3,19	3,55
2	15	3,15	2,36	2,76
3	30	2,35	1,92	2,14
4	45	0,95	0,92	0,94
5	60	1,15	0,55	0,85
6	120	1,15	0,59	0,87
7	180	0,65	0,10	0,38
8	240	0,60	0,68	0,64

Table A 9: AAS results for experimental run 9

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,78	2,67	3,23
2	15	1,86	1,51	1,69
3	30	1,74	1,53	1,64
4	45	1,60	1,20	1,40
5	60	1,64	0,99	1,32
6	120	1,72	0,50	1,11
7	180	1,88	0,95	1,42
8	240	1,87	0,89	1,38

Table A 10: AAS results for experimental run 10

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,87	3,40	3,64
2	15	2,18	2,00	2,09
3	30	1,73	1,78	1,76
4	45	1,23	0,70	0,97
5	60	0,82	0,50	0,66
6	120	0,48	0,30	0,39
7	180	0,34	0,15	0,25
8	240	0,21	0,25	0,23

Table A 11: AAS results for experimental run 11

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,40	4,81	4,11
2	15	1,20	3,24	2,22
3	30	0,90	2,13	1,52
4	45	1,15	2,13	1,64
5	60	0,50	2,23	1,37
6	120	0,45	1,96	1,21
7	180	0,25	1,36	0,81
8	240	0,25	1,23	0,74

Table A 12: AAS results for experimental run 12

		Run A	Run B	Average
Sample no.	**Time (min)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**
1	0	5,31	4,96	5,14
2	15	3,57	1,38	2,48
3	30	3,03	0,67	1,85
4	45	2,26	0,98	1,62
5	60	1,66	0,57	1,12
6	120	1,46	0,40	0,93
7	180	1,53	0,62	1,08
8	240	1,35	0,40	0,88

Table A 13: AAS results for experimental run 13

		Run A	Run B	Average
Sample no.	**Time (min)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**
1	0	3,28	2,18	2,73
2	15	3,12	1,82	2,47
3	30	2,89	1,57	2,23
4	45	2,84	0,85	1,85
5	60	2,36	0,58	1,47
6	120	2,33	0,47	1,40
7	180	1,39	0,46	0,93
8	240	1,72	0,38	1,05

Table A 14: AAS results for experimental run 14

Sample no.	Time (min)	Conc (mg/L)
1	0	2,88
2	15	2,48
3	30	2,04
4	45	1,00
5	60	1,12
6	120	0,95
7	180	0,44
8	240	0,18

Table A 15: AAS results for experimental run 15

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,23	3,17	3,20
2	15	2,87	2,39	2,63
3	30	2,64	2,42	2,53
4	45	2,50	2,37	2,44
5	60	1,22	1,82	1,52
6	120	1,61	1,85	1,73
7	180	2,30	1,31	1,81
8	240	1,33	1,46	1,39

Table A 16: AAS results for experimental run 16

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,36	3,85	3,61
2	15	2,79	3,15	2,97
3	30	2,28	2,28	2,28
4	45	1,34	1,75	1,55
5	60	0,32	0,99	0,66
6	120	0,39	0,79	0,59
7	180	0,71	0,71	0,71
8	240	0,57	1,73	1,15

Table A 17: AAS results for experimental run 17

		Run A	Run B	Average
Sample no.	Time (min)	Au Conc (mg/L)	Au Conc (mg/L)	Au Conc (mg/L)
1	0	3,65	3,43	3,54
2	15	3,19	1,43	2,31
3	30	2,71	1,16	1,94
4	45	2,01	0,92	1,46
5	60	1,89	0,94	1,42
6	120	1,80	0,43	1,12
7	180	1,65	0,40	1,02
8	240	1,06	0,35	0,70

Table A 18: AAS results for experimental run 18

		Run A	**Run B**	**Average**
Sample no.	**Time (min)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**	**Au Conc (mg/L)**
1	0	4,99	4,69	4,84
2	15	3,15	2,70	2,93
3	30	1,54	1,83	1,69
4	45	1,48	1,40	1,44
5	60	1,16	1,29	1,23
6	120	0,90	0,90	0,90
7	180	0,63	0,77	0,70
8	240	0,79	0,83	0,81

APPENDIX B

SAMPLE CALCULATIONS

Appendix B: Sample Calculations

1. Calculation of initial gold concentration in synthetic leach solution

$NaAuCl_4.\ 2H_2O$, Sample mass = 0.015 g; Molar mass $NaAuCl_4.\ 2H_2O$ = 397.80 g/mol; Volume solution = 0.5 L; Purity = 99%,

$$\text{Purity (\%)} \ = \frac{\text{Pure mass}}{Sample\ mass} \qquad (43)$$

$$\text{Pure mass} = 0.99 \times 0.015 = 0.01485 \text{ g}$$

1 mol $NaAuCl_4.\ 2H_2O$ ⟶ 1 mol Au

397.80 g $NaAuCl_4.\ 2H_2O$ ⟶ 197 g Au

0.01485 g $NaAuCl_4.\ 2H_2O$ in 0.5 L solution

$$[Au] \ \longrightarrow \ \frac{197 \times 0.01485}{397.80 \times 0.5} = \mathbf{15\ ppm}$$

2. Determining initial gold concentration and mass present in PCBs using ammonia thiosulphate leaching

I. After ammonia thiosulphate leaching of the sample, the concentration of the gold was found to be

15.80 mg/l

II. The volume used for leaching was 500ml.

III. Determine the mass of gold:

$$\text{Mass of gold} = [Au] \text{ x Volume} \qquad (44)$$

$$= 15.80 \text{ x } 0.5$$

$$= \mathbf{7.9\ mg}$$

IV. Determining the mass fraction of gold. The sample mass used for leaching was 20 g. The mass fraction of gold can then be determined as follows:

Mass fraction of gold = $\frac{Mass\ of\ gold}{Sample\ mass} = \frac{0.0079}{20} = \mathbf{0.000395}$

3. Calculation of initial thiosulphate concentration in leach solution

$(NH_4)_2S_2O_3$, Sample mass = 2.5 g; Molar mass $(NH_4)_2S_2O_3$= 148.195 g/mol; Volume solution = 0.5 L; Purity = 99%,

1 mol $(NH_4)_2S_2O_3 \longrightarrow$ 1 mol $S_2O_3^{2-}$
148.195 g $(NH_4)_2S_2O_3 \longrightarrow$ 112.128 g $S_2O_3^{2-}$
For 2.5 g $(NH_4)_2S_2O_3$ in 0.5 L solution

$[S_2O_3^{2-}] \longrightarrow \frac{112.128\times2.5}{148.195\times0.5} =$ **0.04 M**

4. Calculation of initial copper sulphate concentration in leach solution

$CuSO_4\,.5H_2O$, Sample mass = 1.5 g; Molar mass $CuSO_4\,.5H_2O$ = 245.68 g/mol; Volume solution = 0.5 L; Purity = 99%,

1 mol $CuSO_4\,.5H_2O \longrightarrow$ 1 mol Cu^{2+}
245.68 g $CuSO_4\,.5H_2O \longrightarrow$ 63.54 g Cu^{2+}
For 1.5 g $CuSO_4\,.5H_2O$ in 0.5 L solution
$[Cu^{2+}] \longrightarrow \frac{63.54\times1.5}{245.68\times0.5} =$ **0.01 M**

5. Preparation of 1 L 2M H_2SO_4

Proper PPE was used and the solution was prepared under at a fume cupboard

Molar mass H_2SO_4= 98,08 g/mol
Density H_2SO_4= 1.84 g/cm^3

$$2\text{M}\ \ H_2SO_4 = \frac{1.84\ \text{g}/cm^3}{98{,}08\ \text{g/mol}}\ x$$

106.6 ml of H_2SO_4 was mixed with distilled water to up to 1 L.

6. Cementation percentage (Yield)

According to Aktas (2012) cementation percentage during the process is given by equation 20.

Cementation (%) = $\frac{(C_o - C_t)}{C_o} \times 100$ (45)

where

C_o = initial concentration and

C_t = concentration in solution at the end of the experiment

7. Calculation of cementation rate, K

First order reaction equation:

$$\ln\left(\frac{C_b}{C_0}\right) = -ka_e\frac{W}{V}t \tag{46}$$

Table B 1: Calculation of the cementation rate, k from experimental run using 0.75g Cu Powder

Sample no.	Time (min)	Avg Conc. (mg/L)			$\ln\left(\frac{C_b}{C_0}\right)$		
		50 ℃	**40** ℃	**30** ℃	**50** ℃	**40** ℃	**30** ℃
1	0	23,43	24,05	14,65	0,0	0,0	0,0
2	15	13,95	16,20	13,90	0,5	0,4	0,1
3	30	11,63	10,65	13,05	0,7	0,8	0,1
4	45	8,85	10,65	12,85	1,0	0,8	0,1
5	60	8,65	11,15	11,45	1,0	0,8	0,2
6	120	6,30	9,80	12,63	1,3	0,9	0,1
7	180	5,78	6,80	9,98	1,4	1,3	0,4
8	240	4,10	6,15	7,63	1,7	1,4	0,7

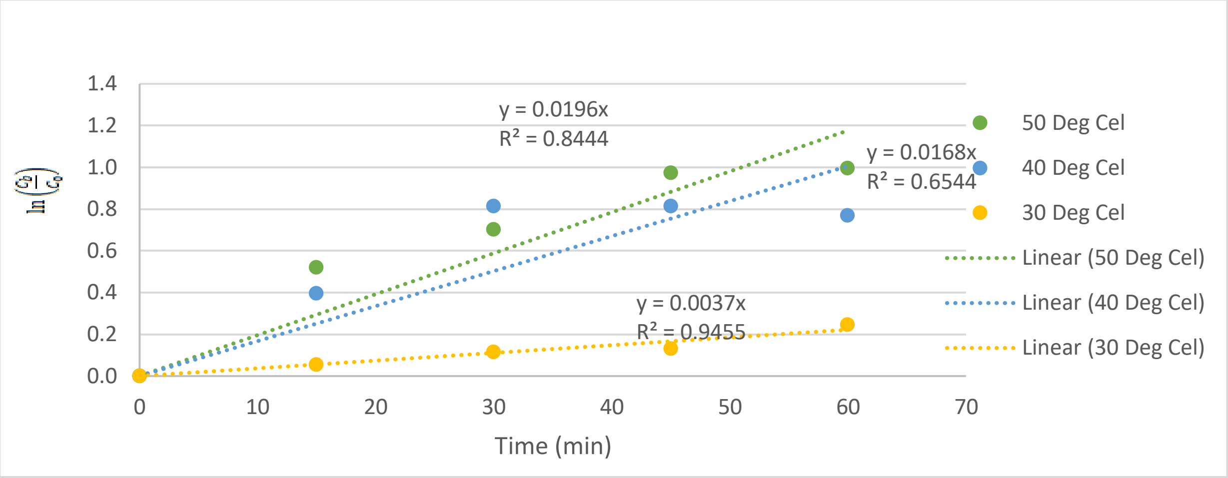


Figure B 1: Calculation of the cementation rate, k from experimental run using 0.75g Cu Powder

Gradient = $ka_e\frac{W}{V}$

a_e =1,038 m^2/g

W = 0,75 g

V = 0,0005 m^3

$$0{,}0037 = ka_e\frac{W}{V}$$

$$\frac{1}{k} = 1{,}038 \times \frac{0{,}75}{0{,}0005} \times \frac{1}{0{,}0037}$$

$\therefore k = \mathbf{2.38 \times 10^{-6}}$ m/min

8. Calculation of activation energy, E

Table B 2: Cementation rates, k from experimental run using 0.75g Cu Powder

Temp (℃)	Temp (K)	K (m/min)
30	303,15	2,38E-06
40	313,15	1,08E-05
50	323,15	1,26E-05

Equation 46 below can be used to determine the activation energy and frequency factor for a reaction by plotting Ln (k) as a function of (1/T) (Fogler, 2006):

$$\ln k = -\frac{E}{RT} + \ln A \qquad (46)$$

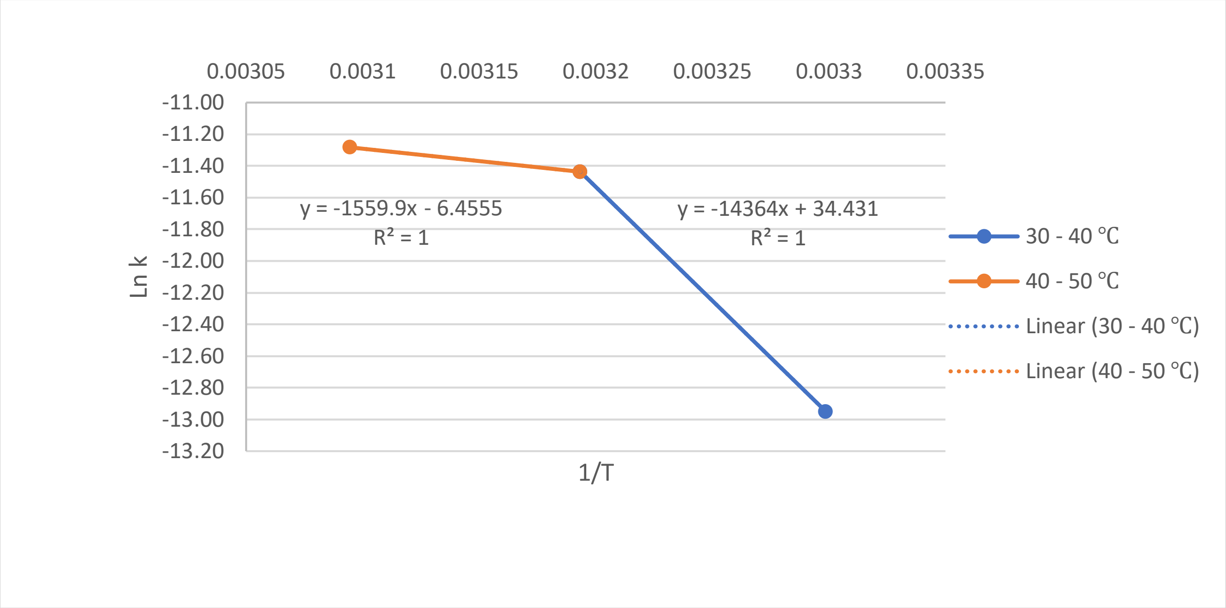


Figure B 2: Arrhenius plot for the reaction between 30 to 50 °C with 15 ppm Au, agitation speed of 900 RPM and 0,25 g of copper powder was used.

From figure B 2 above;

$$Gradient = -\frac{E}{R}$$

R = 8, 314 J/mol

For the 40 – 50 °C region:

$$-1559{,}9 = -\frac{E}{8{,}314}$$

$\therefore E$ = 12969,00 J/mol

= 12,97 kJ/mol

APPENDIX C

OPERATING PROCEDURES

Appendix C: Operating procedures

Preparing ammonia thiosulphate leach solution

1. Weigh 20g Pre-treated PCB's according to prescribed mass fractions and particle sizes
2. Weigh 5 g/L ammonium thiosulphate and 3 g/L copper sulphate and prepare a solution of 500ml using de-ionized water.
3. Place into the water bath and initial experimental conditions started:
   - Temperature adjusted to 32ºC
   - pH of the solution was adjusted to 9.5 and kept constant by adding 32% ammonia solution
   - The redox was adjusted between 0 - 50 mV whilst adding addition $CuSO_4$ powder, The PCB samples were added to the solution and the pH and redox were kept constant.
4. Draw samples for chemical analysis every 30 minutes during the 2.5 hour experimental run.

Preparing synthetic leach solution

1. Weigh 5 g/L ammonium thiosulphate and 3 g/L copper sulphate and prepare a solution in a beaker using 250 ml de-ionized water.
2. Weigh required amount of Sodium tetrachloroaurate (III) aihydrate ($NaAuCl_4$. $2H_2O$).
3. pH adjust the solution to 9.5 using 32% ammonia solution
4. Top up the solution to 500 ml with de-ionized water
5. Add the required amount of $NaAuCl_4$. $2H_2O$
6. Introduce the solution into the reaction vessel. Stir mix the solution thoroughly.
7. Adjust the temperature to heat up the contents in the vessel
8. Bubble nitrogen gas for 30 minutes (flowrate of between 0.5 and 1 L/min)

Aqua regia

The metal solvent, aqua regia solution was prepared from a 3:1 mixture of hydrochloric acid (HCl, 35%): nitric acid (HNO_3, 60~61%). Hydrochloric acid was added to the Nitric acid. The reaction was exothermic and released chlorine gas. The solution needed to be prepared in a fume cupboard to prevent any chlorine inhalation. Experiments were undertaken in a 200 mL Pyrex beaker which was initially charged with 20 ml of aqua regia. A total of 5 g with desired mass fractions, as shown in table 3.4 of crushed mobile phones PCBs was added to the solution in small increments to control the reaction rate and minimize temperature change due to the exothermic reaction.

The overall weight was selected to provide a solid/liquid ratio of 1 g solid to 4 mL aqua regia (Sheng and Etsell, 2007).

5 ml samples were taken out using a pipette after every 30 minutes and diluted 2x using deionized water. The diluted samples were ejected in 10 ml syringes fitted with 0.45 μm syringe filters to filter out the solids. The leached metal concentration in aqua regia was analysed via atomic absorption spectrometry (AAS).

Batch Cementation procedure

1. Introduce pregnant ammonia thiosulphate leach solution (PCBs or synthetic leach solution) into the reactor.
2. Nitrogen gas must be bubbled throughout the experiment(s) to create an oxygen free environment.
3. Initiate operating conditions (Temperature, pH, stirring speed) for specific experiment
4. Once desired operating conditions are reached, Add premeasured copper powder (pre-treated with dilute sulphuric acid) into reaction vessel.
5. Draw samples for chemical analysis at 0, 15, 30, 45, 60, 120, 180, 240 and 300 minutes
6. Once the reaction was complete, filter solution with a vacuum pump.

APPENDIX D

SEM-EDS DATA

Appendix D: SEM-EDS data

Copper powder before cementation as well as the deposits recovered after cementation was analyzed by scanning electron microscopy (SEM-EDX) in order to evaluate the chemical composition and the morphology of the solids. EDS analysis was performed at several spots on the copper powder sample as well as on the deposits recovered.

Copper powder before cementation

Table D 1: Quantitative EDS analyses (weight %) of copper powder before cementation

Spectrum	C	O	Mg	Cu	Total
Spectrum 1	21,16	7,49	1,46	69,89	100
Spectrum 2	17,67	6,78	1,18	74,36	100
Spectrum 3	22,31	8,76	0,54	68,39	100
Spectrum 4	21,68	11,47	0,95	65,9	100
Spectrum 5	18,35	8,01	1,01	72,62	100
Mean	**20,24**	**8,5**	**1,03**	**70,23**	**100**
Std. deviation	2,08	1,81	0,34	3,36	

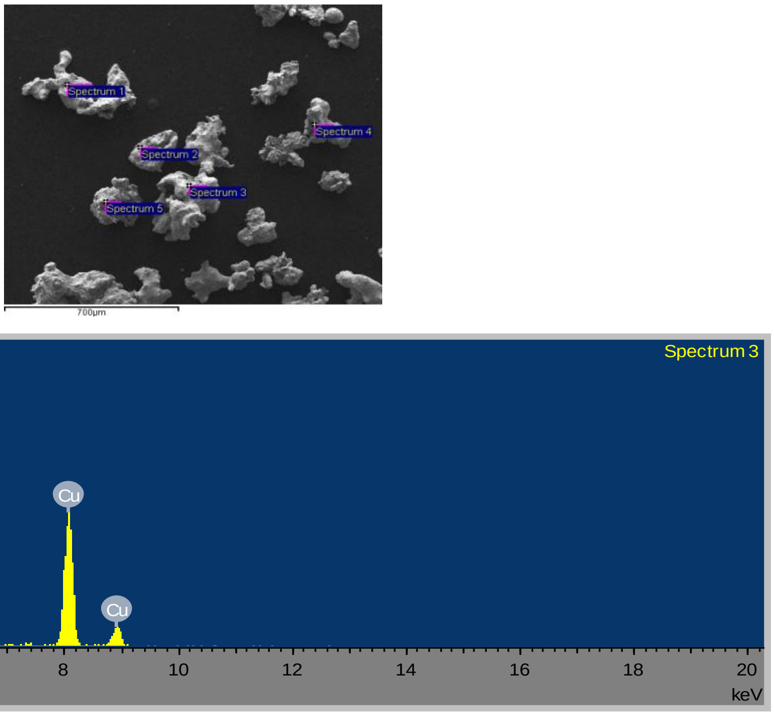


Figure D 1: (a) SEM image of copper powder (b) EDS analysis spectra of copper powder before cementation

Table D 2: Quantitative EDS analyses (wt%) of copper powder after pre-treatment with dilute sulphuric acid

Spectrum	C	O	Cu	Total
Spectrum 1	17,72	3,83	78,45	100
Spectrum 2	22,79	4,05	73,16	100
Spectrum 3	18,29	3,37	78,34	100
Spectrum 4	34,27	6,36	59,37	100
Spectrum 5	21,36	5,61	73,03	100
Mean	**22,89**	**4,65**	**72,47**	**100**
Std. deviation	6,7	1,28	7,79	

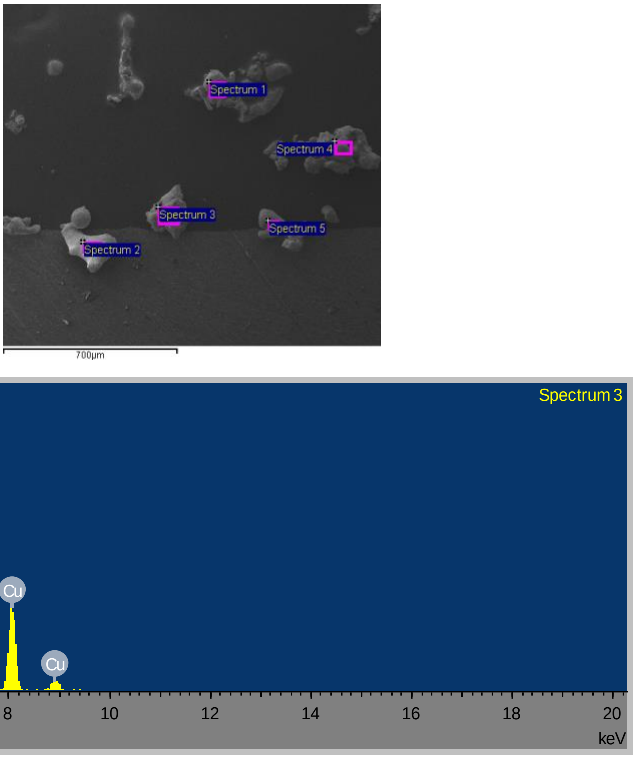


Figure D 2: (a) SEM image of copper powder (b) EDS analysis spectra of copper powder after pre-treatment

Precipitates recovered after cementation

Effect of the amount of copper powder added

Table D 3 and table D 4 show the quantitative analyses of the precipitates formed during tests performed at 40 and 300 RPM. By looking at the tables one can see that there is a decrease in the concentration of gold on the precipitate when the amount of copper powder used was increased from 0.25 to 0.5 g. At test performed at at 40 ℃ and 300 RPM the wt.% of Au decreased from 22,77 % to 15,98 %. One can also notice the concentration of sulphur on the precipitates also decreased as the amount copper powder used is increased. The same trend was observed for tests performed at 900 RPM and 30 ℃ as shown in table D 5 and table D 6.

Table D 3: Quantitative EDS analyses (wt.%) of solid sample obtained after the completion of test at 40 ℃ and 300 RPM with 0.25 g addition of copper powder

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	23,27	4,09	6,5	47,52	18,62	100
Spectrum 2	18,9	4,74	9,68	40,46	26,22	100
Spectrum 3	17,44	4,07	8,67	48,12	21,7	100
Spectrum 4	14,5	5,24	8,21	48,46	23,58	100
Spectrum 5	18,49	4,5	9,88	43,4	23,72	100
Mean	**18,52**	**4,53**	**8,59**	**45,6**	**22,77**	**100**
Std. deviation	3,16	0,49	1,36	3,52	2,82	

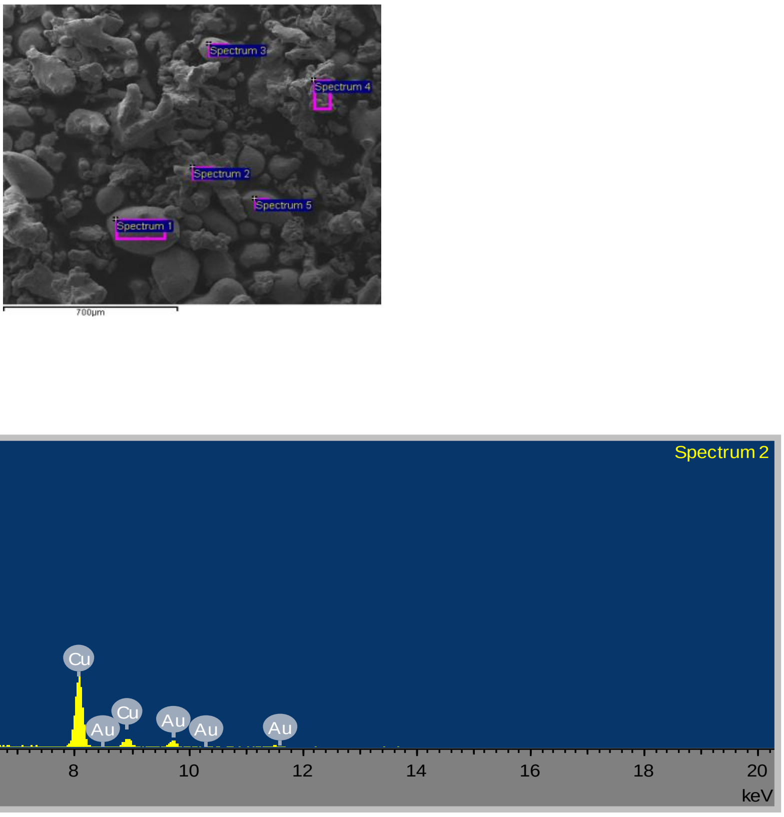


Figure D 3: SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the completion of test performed at 40 ℃ and 300 RPM with 0.25 g addition of copper powder

Table D 4:Quantitative EDS analyses (wt.%) of precipitate obtained after the completion of test at 40 ℃ and 300 RPM with 0.50 g addition of copper powder

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	21,36	4,72	6,2	45,1	22,62	100
Spectrum 2	17,72	2,79	5,19	55,09	19,2	100
Spectrum 3	14,07	3,59	4,48	60,36	17,49	100
Spectrum 4	49,25	5,81	2,74	32,59	9,61	100
Spectrum 5	34,13	4,81	3	47,1	10,96	100
Mean	**27,31**	**4,35**	**4,32**	**48,05**	**15,98**	**100**
Std. deviation	14,41	1,17	1,46	10,6	5,54	

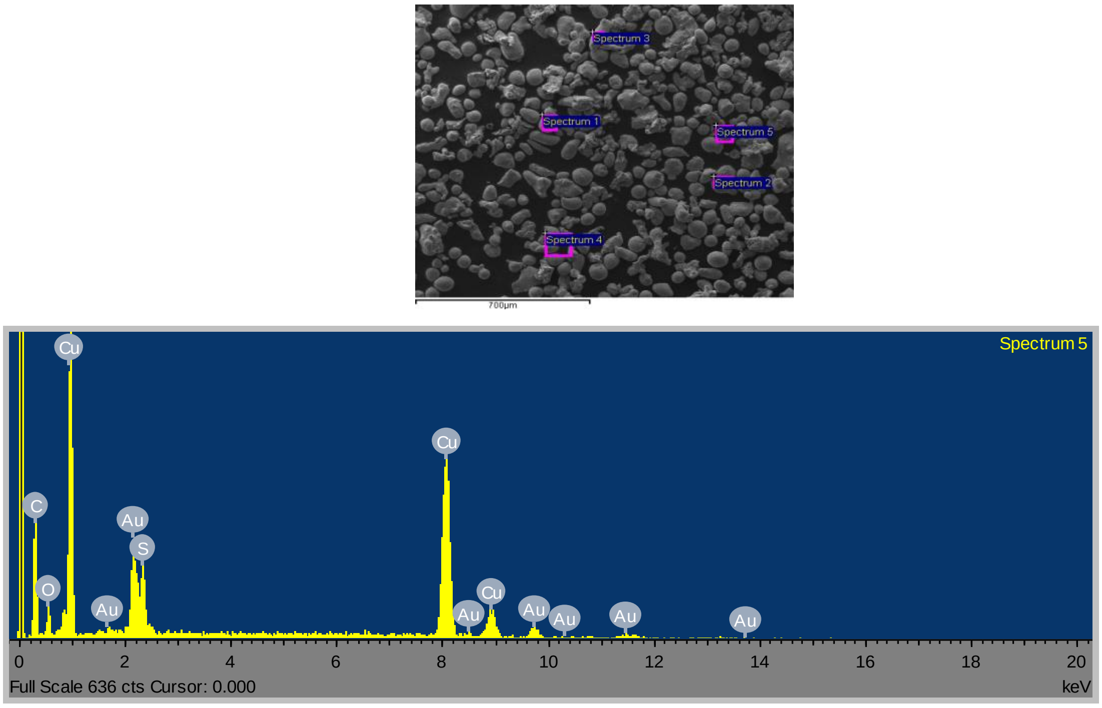


Figure D 4: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the completion of test performed at 40 ℃ and 300 RPM with 0.50 g addition of copper powder

However, at a high agitation speed of 900 RPM and with an increase of the amount of copper powder used from 0.5 to 0.75 g there is an increase in concentration of gold on the precipitate when the amount of copper powder used. Table D 5 and table D 6 shows tests performed at at 30 ℃ and 900 RPM. The wt.% of Au increased creased from 10,28 % to 13,05%.

Table D 5: Quantitative EDS analyses (wt.%) of precipitate obtained after the completion of test at 30 ℃ and 900 RPM with 0.50 g addition of copper powder

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	20,09	14,74	4,33	52,55	8,3	100
Spectrum 2	17,5	10,75	5,03	49,43	17,28	100
Spectrum 3	15,9	16,93	4,61	53,54	9,03	100
Spectrum 4	29,98	22,34	4,52	36,72	6,44	100
Spectrum 5	29,04	17,66	3,62	39,32	10,36	100
Mean	**22,5**	**16,48**	**4,42**	**46,31**	**10,28**	**100**
Std. deviation	6,58	4,24	0,52	7,77	4,16	

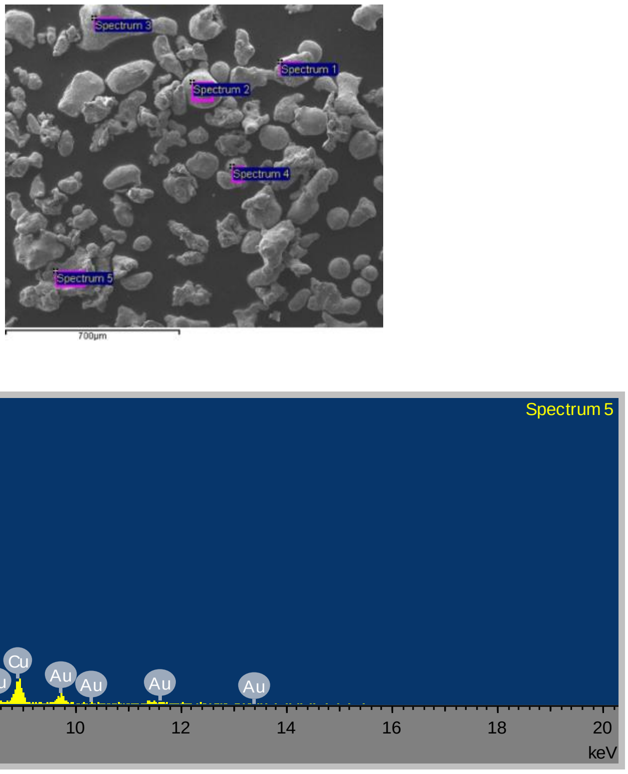


Figure D 5: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the completion of test performed at 30 ℃ and 900 RPM with 0.50 g addition of copper powder

Table D 6: Quantitative EDS analyses (wt.%) of precipitate obtained after the completion of test at 30 ℃ and 900 RPM with 0.75 g addition of copper powder

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	20,97	2,38	5,08	53,08	18,49	100
Spectrum 2	15,79	4,03	6,67	50,74	22,76	100
Spectrum 3	33,02	7,64	3,62	41,08	14,62	100
Spectrum 4	15,65	4,37	7,48	46,48	26,03	100
Spectrum 5	16,95	4,49	4,18	60,55	13,83	100
Mean	**20,48**	**4,58**	**5,41**	**50,39**	**19,15**	**100**
Std. deviation	7,34	1,91	1,64	7,29	5,23	

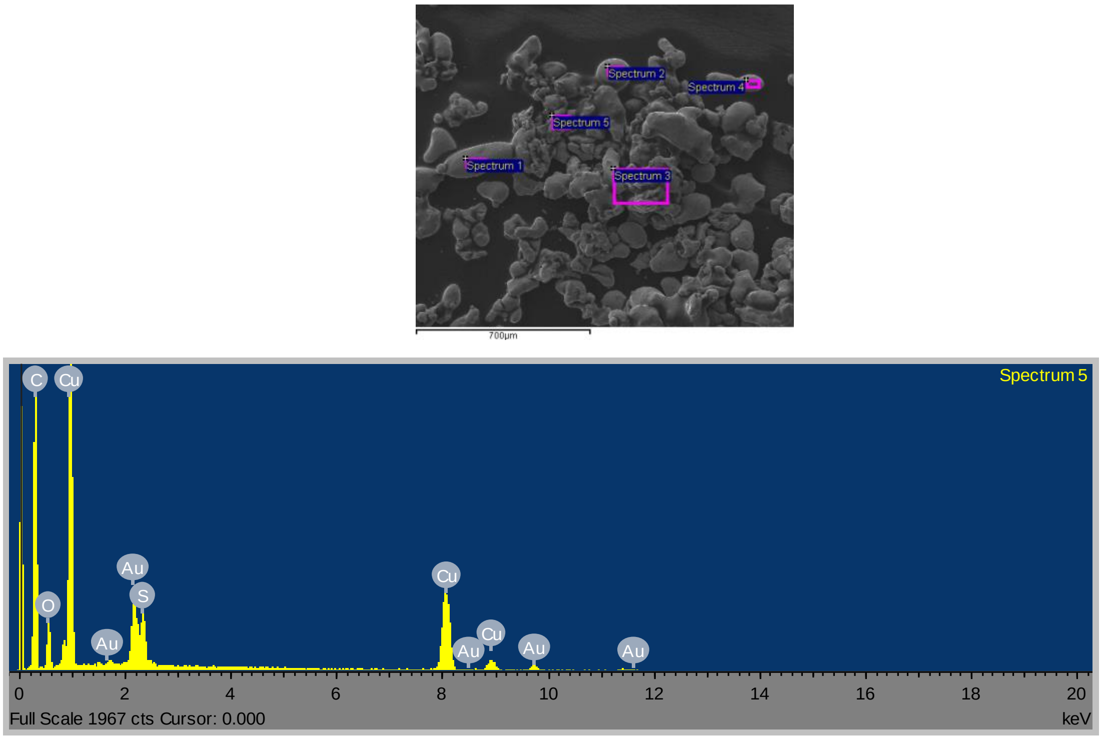


Figure D 6: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the completion of test performed at 30 ℃ and 900 RPM with 0.75 g addition of copper powder

Effect of temperature

Table D 7: Quantitative EDS analyses (wt.%) of precipitate obtained after the completion of test at 30 ℃ and 900 RPM with 0.75 g addition of copper powder

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	20,97	2,38	5,08	53,08	18,49	100
Spectrum 2	15,79	4,03	6,67	50,74	22,76	100
Spectrum 3	33,02	7,64	3,62	41,08	14,62	100
Spectrum 4	15,65	4,37	7,48	46,48	26,03	100
Spectrum 5	16,95	4,49	4,18	60,55	13,83	100
Mean	**20,48**	**4,58**	**5,41**	**50,39**	**19,15**	**100**
Std. deviation	7,34	1,91	1,64	7,29	5,23	

Table D 7 shows the outcome of the quantitative EDX analysis of the precipitate recovered after a test at 30 ℃. Figure D 7 shows the SEM image and EDS analysis spectra of precipitate recovered. By comparing table D 7 and table D 8 one can deduce that increasing the temperature for 30 to 40 ℃ decreased the concentration of gold on the precipitate from19,15% to 15,18%.

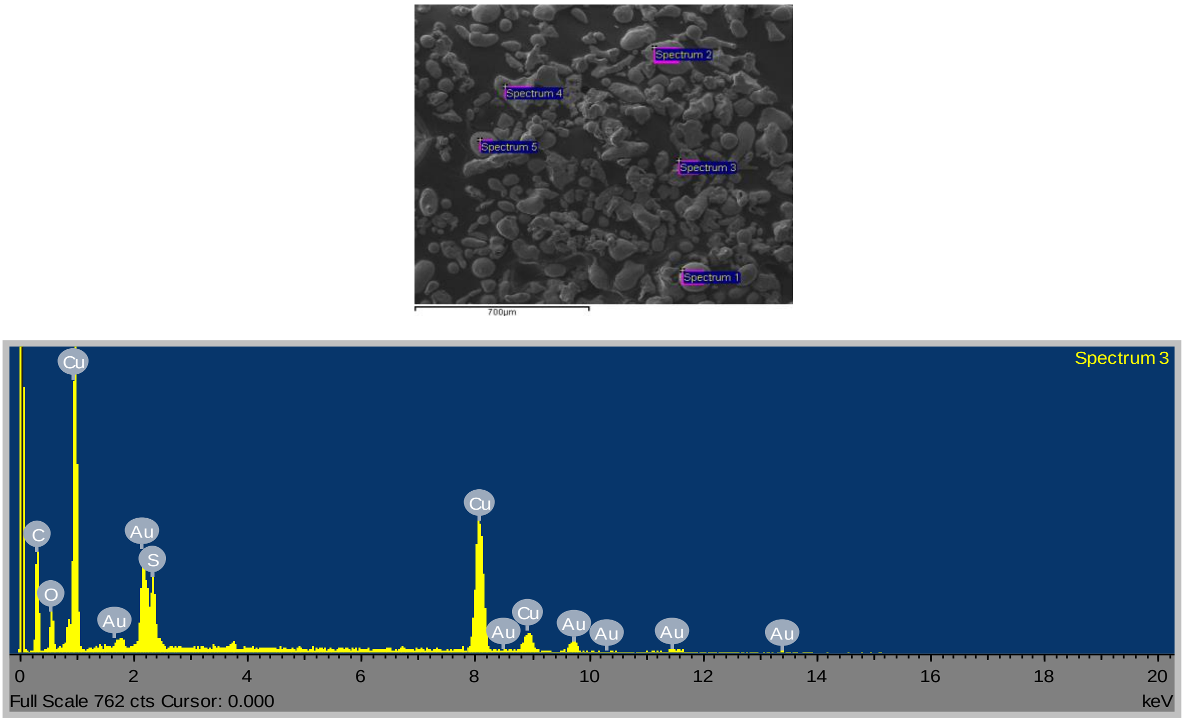


Figure D 7: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the completion of test performed at 30 ℃ and 900 RPM with 0.75 g addition of copper powder

Table D 8: Quantitative EDS analyses (wt.%) of precipitate obtained after the completion of test at 40 ℃ and 900 RPM with 0.75 g addition of copper powder

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	12,795	16,21	6,9	47,015	17,075	100
Spectrum 2	20,915	12,1	4,73	46,385	15,87	100
Spectrum 3	21,585	5,645	3,955	56,175	12,635	100
Spectrum 4	15,97	8,815	4,78	54,66	15,77	100
Spectrum 5	12,705	11,78	4,765	56,21	14,54	100
Mean	**16,794**	**10,91**	**5,026**	**52,089**	**15,178**	**100**
Std. deviation	2,68	8,89	0,45	5,1	4,42	

Table D 8 and Table D 9 show the outcome of the quantitative EDX analysis of the precipitate recovered after a test at 40 and 50℃ respectively. One can notice that increasing the temperature from 40 to 50℃ decreased the concentration of Au on the precipitate from 22,77% to 16,3%.

Table D 9: Quantitative EDS analyses (wt.%) of solid sample obtained after the completion of test at 40 ℃ and 300 RPM with 0.25 g addition of copper powder

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	23,27	4,09	6,5	47,52	18,62	100
Spectrum 2	18,9	4,74	9,68	40,46	26,22	100
Spectrum 3	17,44	4,07	8,67	48,12	21,7	100
Spectrum 4	14,5	5,24	8,21	48,46	23,58	100
Spectrum 5	18,49	4,5	9,88	43,4	23,72	100
Mean	**18,52**	**4,53**	**8,59**	**45,6**	**22,77**	**100**
Std. deviation	3,16	0,49	1,36	3,52	2,82	

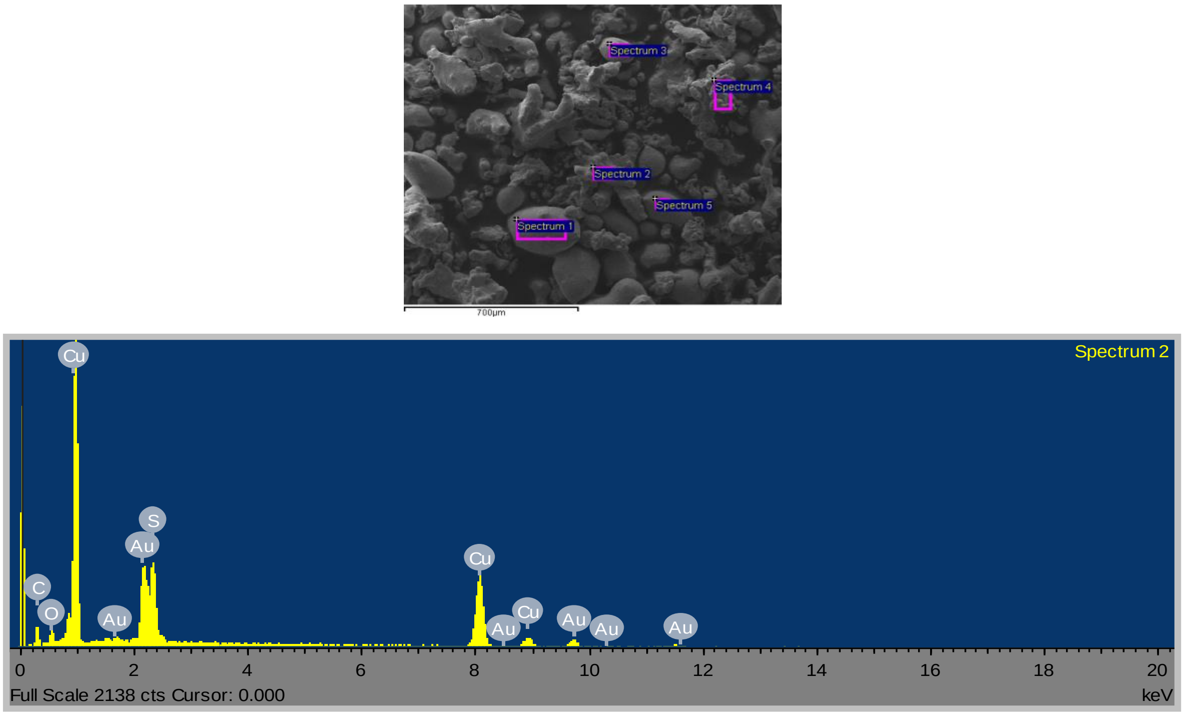


Figure D 8: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the completion of test performed at 40 ℃ and 300 RPM with 0.25 g addition of copper powder

Table D 10: Quantitative EDS analyses (wt.%) of solid sample obtained after the completion of test at 50 ℃ and 300 RPM with 0.25 g addition of copper powder

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	11,29	15,97	6,42	50,96	15,36	100
Spectrum 2	10,06	15,56	6,06	55,5	12,82	100
Spectrum 3	24,27	10	4,84	46,42	14,48	100
Spectrum 4	18,43	11,32	6,51	44,25	19,49	100
Spectrum 5	22,58	13,86	6,91	37,3	19,34	100
Mean	**17,33**	**13,34**	**6,15**	**46,89**	**16,3**	**100**
Std. deviation	6,45	2,61	0,79	6,89	2,99	

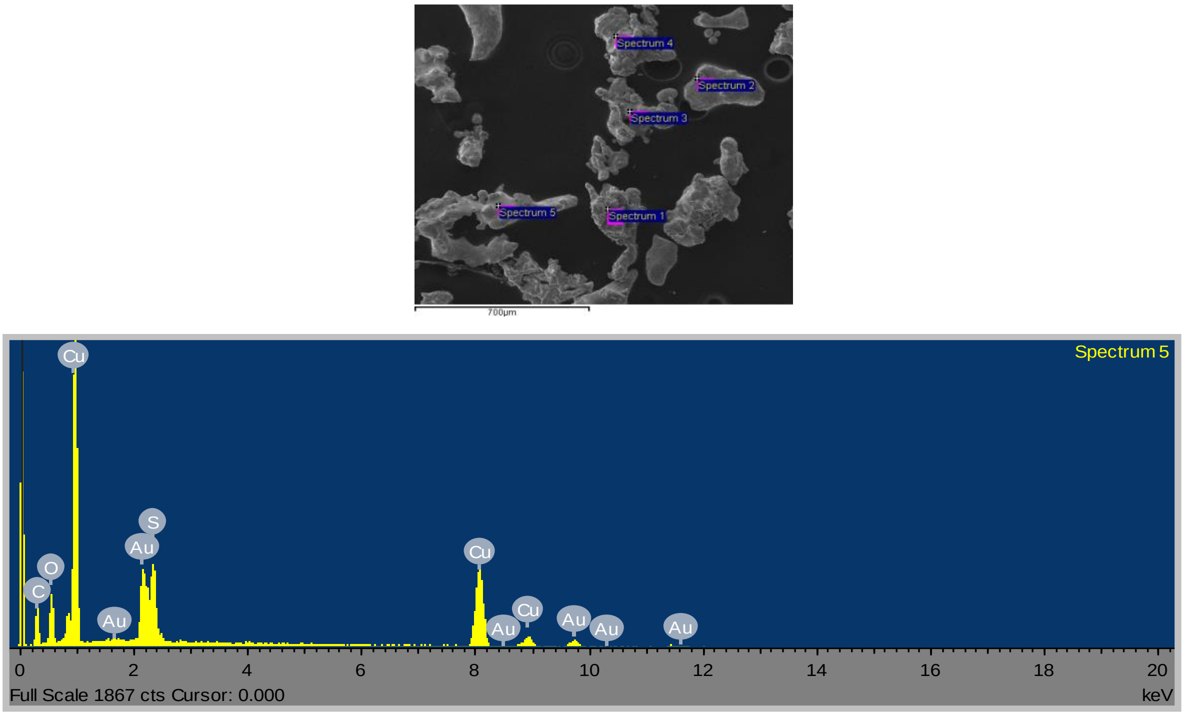


Figure D 9: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the completion of test performed at 50 ℃ and 300 RPM with 0.25 g addition of copper powder

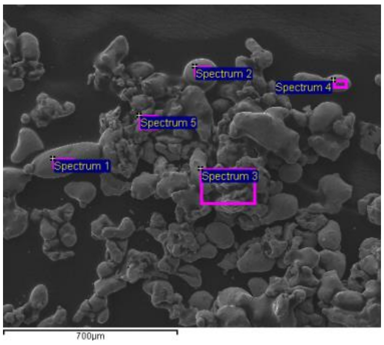
Effect of agitation speed

Table D 11 to table D 14 show the quantitative analyses of the precipitates recovered after tests performed at either 300 or 900 RPM. From the tables one can observe that agitation speed increases the amount of gold on the surface of the precipitate only when a higher (i.e. 0.5 or 0.75 g) amount of copper is used.

Table D 11 and table D 12 show a test performed at 30 ℃ and 0.75 g. One can observe that the concentration of Au on the precipitate increased from 13,05% to 19,15%. Increasing the agitation only positively affect the amount of Au on the deposits when a high amount of the cementation agent is used.

Table D 11: Quantitative EDS analyses (wt. %) of precipitate obtained after the completion of test at 30 ℃ and 0.75 g addition of copper powder at 300 RPM

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	27,48	4,02	4,32	48,97	15,21	100
Spectrum 2	29,62	5,04	6	37,66	21,68	100
Spectrum 3	59,98	10,92	1,8	20,4	6,9	100
Spectrum 4	36,1	4,63	3,37	43,02	12,88	100
Spectrum 5	55,66	9,95	2,34	23,49	8,56	100
Mean	**41,77**	**6,91**	**3,57**	**34,71**	**13,05**	**100**
Std. deviation	15,07	3,26	1,67	12,37	5,86	



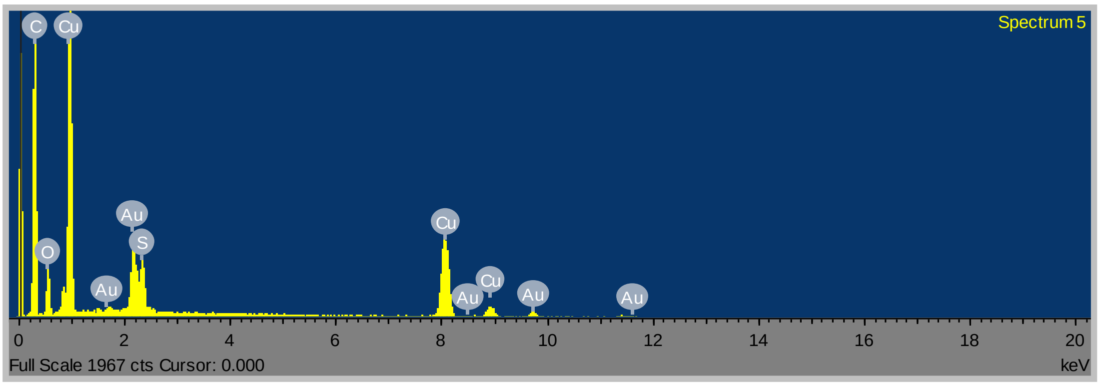


Figure D 10: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the after the completion of test at 30 ℃ and 0.75 g addition of copper powder at 300 RPM

Table D 12: Quantitative EDS analyses (wt. %) of precipitate obtained after the completion of test at 30 ℃ and 0.75 g addition of copper powder at 900 RPM

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	20,97	2,38	5,08	53,08	18,49	100
Spectrum 2	15,79	4,03	6,67	50,74	22,76	100
Spectrum 3	33,02	7,64	3,62	41,08	14,62	100
Spectrum 4	15,65	4,37	7,48	46,48	26,03	100
Spectrum 5	16,95	4,49	4,18	60,55	13,83	100
Mean	**20,48**	**4,58**	**5,41**	**50,39**	**19,15**	**100**
Std. deviation	7,34	1,91	1,64	7,29	5,23	

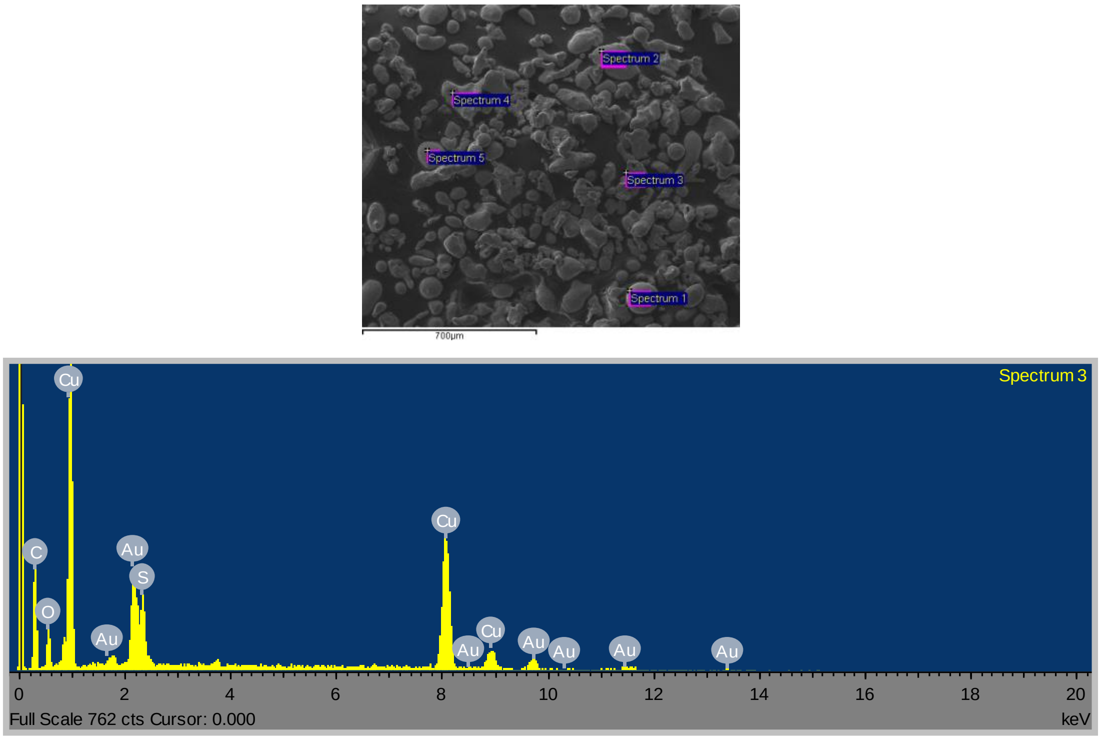


Figure D 11: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the after the completion of test at 30 ℃ and 0.75 g addition of copper powder at 900 RPM

Table D 13 and table D 14 show a test performed at 40 ℃ and 0.25 g copper powder was used. One can observe that increasing the agitation speed from 300 to 900 RPM slightly decreased the concentration of gold from 22.77 wt.% to 20.75 wt.%.

Table D 13: Quantitative EDS analyses (wt. %) of precipitate obtained after the completion of test at 40 ℃ and 0.25 g addition of copper powder at 300 RPM

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	23.27	4.09	6.5	47.52	18.62	100
Spectrum 2	18.9	4.74	9.68	40.46	26.22	100
Spectrum 3	17.44	4.07	8.67	48.12	21.7	100
Spectrum 4	14.5	5.24	8.21	48.46	23.58	100
Spectrum 5	18.49	4.5	9.88	43.4	23.72	100
Mean	**18.52**	**4.53**	**8.59**	**45.6**	**22.77**	**100**
Std. deviation	0.49	1.36	3.52	2.82		

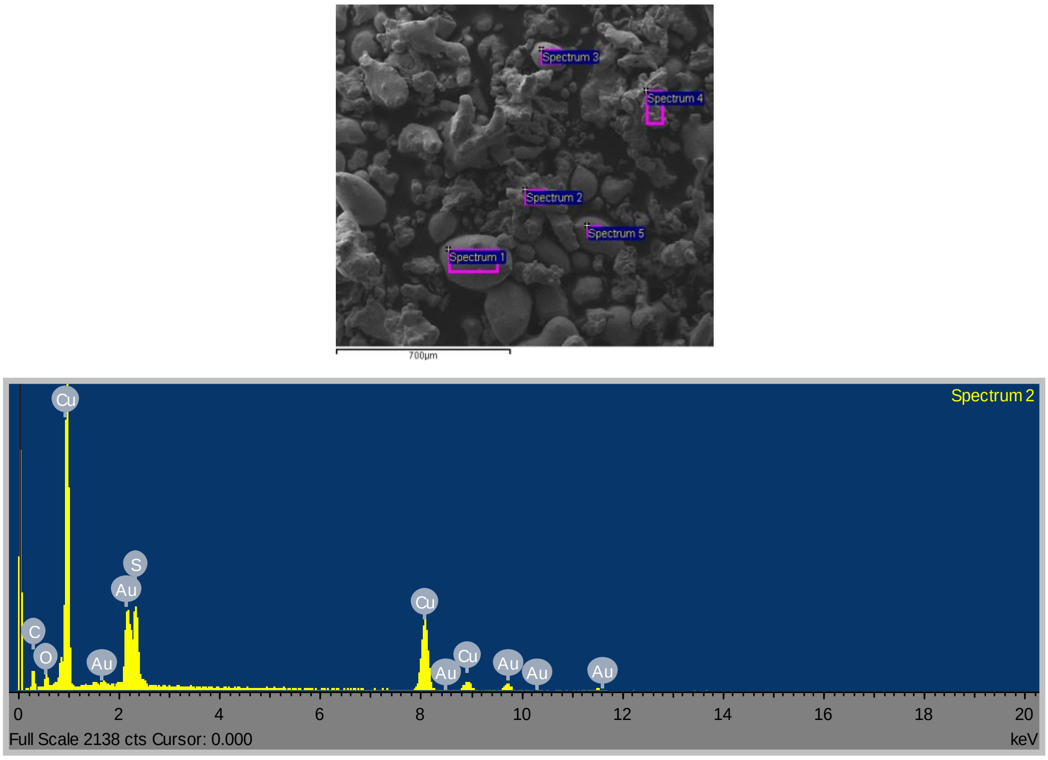


Figure D 12: (a) SEM image of precipitate (b) EDS analysis spectra of precipitate obtained after the completion of test performed at 40 ℃ and 300 RPM with 0.25 g addition of copper powder

Table D 14: Quantitative EDS analyses (wt. %) of precipitate obtained after the completion of test at 40 ℃ and 0.25 g addition of copper powder at 900 RPM

Spectrum	C	O	S	Cu	Au	Total
Spectrum 1	16.15	3.11	9.18	45.74	25.82	100
Spectrum 2	20.78	3.38	6.55	49.79	19.5	100
Spectrum 3	28.09	4.82	7.26	37.57	22.27	100
Spectrum 4	12.33	15.1	9.25	41.3	22.03	100
Spectrum 5	33.03	4.97	4.48	43.38	14.14	100
Mean	**22.07**	**6.27**	**7.35**	**43.56**	**20.75**	**100**
Std. deviation	5	1.99	4.6	4.33		

APPENDIX E

STATISTICAL DATA

Appendix E: Statistical data

Table E 1: Summary of the treatment of combinations and their observed responses

Run	Temperature	g Cu powder	Speed	Max % recovery
1	30	0,25	300	46
2	30	0,25	900	69
3	30	0,5	300	42
4	30	0,5	900	83
5	30	0,75	300	48
6	30	0,75	900	91
7	40	0,25	300	78
8	40	0,25	900	91
9	40	0,5	300	57
10	40	0,5	900	96
11	40	0,75	300	87
12	40	0,75	900	83
13	50	0,25	300	58
14	50	0,25	900	94
15	50	0,5	300	56
16	50	0,5	900	84
17	50	0,75	300	80
18	50	0,75	900	85