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# NICKEL AMMONIUM THIOSULPHATE LEACHING OF GOLD FROM WASTE MOBILE PHONE PRINTED CIRCUIT BOARDS

by

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# DECLARATION

I, Yhab Romy Mboko, 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.

December 2019

**Signed** **Date**

# ABSTRACT

Over the years, the quantity of e-waste, primarily waste mobile phone printed circuit boards (PCBs), has increased worldwide, as a result of technological advancements in the fields of electronics, telecommunications and computing. Therefore, to sustain the protection of the environment and human health, sustainable measures should be implemented. Electronic waste (e-waste) is known for its wider variety of base and precious metal content compared to naturally occurring ores. Waste mobile phone PCBs are the most attractive type of e-waste due to their higher and more structured precious metal content. Ammonium thiosulphate leaching is considered as one of the promising alternatives to cyanidation in hydrometallurgy. However, its industrial application is limited due to the high reagent consumption which has a direct impact on its cost-effectiveness.

This research aimed to investigate the ammonium thiosulphate leaching of gold from waste mobile phone PCBs, with an emphasis on the thiosulphate consumption and interference of the extractable copper in the leaching process. The objectives were to study the effect of acid pre-treatment and copper replacement with nickel as the metal oxidant on gold extraction and thiosulphate consumption.

The experiments in this study were all conducted in a batch setup. The PCBs were reduced to less than 3 mm particle size by cutting and crushing. In the acid pre-treatment, sulphuric acid and hydrogen peroxide concentrations were varied between two levels, namely 2 M and 3 M, to identify the optimum conditions that maximised copper extraction and minimised gold extraction. In the ammonium thiosulphate leaching, PCB pre-treatment and metal oxidant were investigated as categorical factors to establish the optimum conditions that maximised gold extraction and minimised thiosulphate consumption. The PCB pre-treatment was varied between two levels: acid-pretreated PCBs and untreated PCBs. The metal oxidant factor was varied between copper and nickel. The other leaching conditions were fixed, as prescribed in the existing literature.

The mobile phone PCBs used in this study were found to contain 524 g Au/ton-PCB and 461.8 kg Cu/ton-PCB, as determined by aqua regia leaching. Copper thus contributed to more than 40% of the total PCB mass.

In the acid pre-treatment, the optimum reagent combination was 2 M $H_2SO_4$ and 3 M $H_2O_2$ and resulted in 93.72% copper extraction and 8.83% gold loss in 150 minutes at a pulp density of 50 g/L, 25°C and stirring speed of 350 rpm. Furthermore, it was determined, through material balance, that the PCB mass reduction induced by the acid pre-treatment was mostly attributed to the copper extraction, evidence that the other base metals such as iron and aluminium that could have dissolved in the acid pre-treatment stage were in small quantities in the PCBs to impact the overall mass reduction significantly. The acid pre-treatment was a PCB beneficiation process with an increase in the extractable gold content from 524 to 842 g/ton-PCB and a decrease in the copper content from 461.8 to 51.1 kg/ton-PCB. The variation in $H_2SO_4$ concentration had more statistical impact on gold extraction, whereas varying $H_2O_2$ concentration had a more statistical influence on copper extraction. The analysis of the goodness of fit of the shrinking-core model to the experimental results indicated that the acid pre-treatment was chemically controlled, with moderate control due to the turbulence.

In ammonium thiosulphate leaching, the optimum conditions consisted in using nickel as the oxidant in the thiosulphate leaching of acid-pretreated PCBs at a pulp density of 50g/L, 0.1 M thiosulphate, 0.2 M $NH_3$, 0.03 M $Ni^{2+}$, pH 10.5, 25°C and stirring speed of 350 rpm. The gold extraction and thiosulphate consumption were found to be 65.41% and 61.03 kg/ton-PCB in 5 hours of leaching time, a significant improvement from the conventional copper-thiosulphate leaching of untreated PCBs which resulted in gold extraction and thiosulphate consumption of 18.61% and 90.9 kg/ton-PCB, respectively. The statistical analysis of experimental results indicated that the variation of the metal oxidant had a higher significance level than the PCB pre-treatment with respect to gold extraction. The assessment of the goodness of fit of the shrinking-core model to the experimental data indicated that the copper-thiosulphate and nickel-thiosulphate leaching processes were both chemically controlled.

To assess the degree of comparison between the copper-thiosulphate and nickel-thiosulphate leaching processes for gold extraction from waste PCBs, a preliminary economics assessment was performed, with emphasis on production costs. Considering a basis of 1 metric ton of processed PCB, replacing copper with nickel as the metal oxidant reduced the raw materials costs from 3,768 USD to 2,868 USD, approaching previously reported cyanidation costs closely. The revenue and gross margin were increased from 8,969 and 5,201 USD in copper-thiosulphate leaching to 16,287 and 13,419 USD in nickel-thiosulphate leaching, respectively. Therefore, the use of ammonium thiosulphate as an environment-friendly alternative lixiviant shows potential by virtue of the improved process economics.

# RESEARCH OUTPUTS

## Oral Presentations

- **Mboko, Y.R**. and Aziz, M. 2018. The ammonium thiosulphate leaching of gold from waste mobile phone printed circuit boards – emphasis on acid pre-treatment and nickel catalysis. 15th SAIMM Annual Student Colloquium [Mintek, Johannesburg, South Africa, 24 October 2018].

- **Mboko, Y.R.** and Aziz, M. 2018. The effect of nickel catalysis on the thiosulphate leaching of gold from waste mobile phones. CPUT Postgraduate Research Conference (SARETEC, CPUT, Bellville, South Africa, 07 November 2018].

## Journal Publication

- **Mboko, Y.R.** and Aziz, M. 2019. The Nickel-Oxidised Thiosulphate Leaching of Gold from Waste Mobile Phones. Waste Management. Submitted 19 December 2019 [Paper ID.: WM-19-3367]

- Aziz, M.; **Mboko, Y.R** and Morkel, F.D. 2020. The Ammonium Thiosulphate Leaching of Gold from waste mobile phone printed circuit boards: Effects of Particle Size Distribution and Pulp Density, Journal of Mining and Metallurgy. Submitted 22 January 2020 [Paper ID.: JMMAB-24909]

# DEDICATION

To the Almighty and All-knowing God, Creator of heaven and earth, I would like to express my deepest gratitude for the spiritual, moral and physical support that You granted me. For everything that You have done and continue to do for me, I am forever grateful. Your Name shall be glorified, praised and celebrated for eternity. In the Mighty Name of Jesus-Christ. Amen.

To my father **Maurice Mboko** and my mother **Marie-Jeanne Munze**, you have supported and raised me to the man I am today. I am forever grateful for your presence in my life.

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# TABLE OF CONTENTS

# LIST OF FIGURES

# LIST OF TABLES

# LIST OF ACRONYMS

| | |
|---|---|
| **AAS** | Atomic absorption spectroscopy |
| **ADC** | Ash diffusion control |
| **AP** | Acid pre-treatment |
| **ATS** | Ammonium thiosulphate |
| **EOL** | End-of-life |
| **E-waste** | Electronic waste |
| **FDC** | Fluid diffusion control |
| **FDC-SR** | Fluid diffusion control with Stokes regime |
| **FDC-TR** | Fluid diffusion control with turbulent regime |
| **PCB** | Printed circuit board |
| **PSD** | Particle size distribution |
| **RC** | Reaction control |
| **SCM** | Shrinking-core model |
| **USD** | United States Dollar |
| **ZAR** | South African Rand |

# LIST OF SYMBOLS

| **Symbol** | **Description** | **Unit** |
|---|---|---|
| $C_{Af}$ | Concentration of A in fluid phase | mol/$m^3$ |
| $\mathcal{D}$ | Molecular diffusion coefficient | $m^2$/s |
| $\mathcal{D}_e$ | Effective diffusion coefficient of fluid reactant in ash layer | $m^3$/m-solid/s |
| $df$ | Degrees of freedom | |
| $E°$ | Standard reduction potential | V |
| $k''$ | First-order rate constant | $s^{-1}$ |
| $k_f$ | Mass transfer coefficient between liquid and particle | $m^3$ liquid/$m^2$ surface/s |
| $n$ | Sample size | |
| $N$ | Number of moles | |
| $R$ | Pearson correlation | |
| $R$ | Particle size | µm |
| $R^2$ | Coefficient of determination | |
| $r_c$ | Unreacted core size | µm |
| $t/\tau$ | Fractional time for complete conversion | |
| $X$ | Conversion | |
| $\beta_i$ | Stability constant | |
| $\rho_B$ | Molar density of component B | mol/$m^3$ |
| $\tau$ | Time for complete conversion | s |

# GLOSSARY

| | |
|---|---|
| **Atomic Absorption Spectroscopy** | It is used to determine the concentration of elements. It is based on the absorption of electromagnetic radiation by atoms. The wavelengths of light absorbed by atoms are indicative of the energies required for these particles to increase their energy levels |
| **Electronic Waste** | A waste material comprising of any destroyed or undesired electronic devices |
| **Gross Margin** | The sum of product and raw materials revenues minus raw materials cost |
| **Leaching** | In extractive metallurgy, leaching is an extractive process which involves the dissolution of a specific mineral (or minerals) from ore or a concentrate |
| **Lixiviant** | The primary reagent used in metal dissolution |
| **PCB Pre-treatment** | Denotes the processing stage involving acid leaching |
| **Printed Circuit Board** | It is the principal constituent of any electronic device. It is a fixed flat insulating sheet to which integrated circuits and other electrical components are affixed |

# CHAPTER 1

## INTRODUCTION

# CHAPTER 1 : INTRODUCTION

## 1.1 Background to Research Problem

The rapid development and growth in the field of computing and telecommunications have resulted in the growing production of electronic products in the last 20 years. Furthermore, the rapid obsolescence of these products has caused a reduction in their lifespan. Hence the predominant quantities of electronic waste (e-waste) generated worldwide, requiring appropriate management in accordance with environmental regulations (Ghosh et al., 2015; Albertyn, 2017).
Among the various types of e-waste, mobile phone printed circuit boards (PCBs) have gained interest because of their high metallic content, inclusive of base and precious metals. A typical mobile phone PCB can contain up to 40% metals (Cu, Al, Fe, Sn, Ni, Zn, Pb, Au, Pd, Ag), the remainder consisting mostly of plastics (30%) and ceramic materials (30%) (Grosse et al., 2003; Hanafi et al., 2012; Chehade et al., 2012; Cui & Anderson, 2016). The metallic content of PCBs has been reported to be higher than that of naturally occurring ores (Grosse et al., 2003; Montero et al., 2012; Cui & Anderson, 2016). The recovery of the metallic fraction of PCBs, especially precious metals, is financially and environmentally driven.

According to Baldé et al. (2015), it was estimated that approximately 41.8 million tonnes of e-waste were generated worldwide in 2014, and this figure was expected to increase up to 49.8 million tonnes in 2018, with an estimated 5% increase per annum. An investigation conducted by the e-Waste Association of South Africa (eWASA) in 2008 estimated that the total quantity of e-waste generated in South Africa amounted to 875 687 tonnes and that this quantity was expected to increase significantly in the future, a clear indication of the proliferation of e-waste in developed and developing countries is an imminent issue that needs addressing (Finlay & Liechti, 2008).

Since e-waste has a high metal content, the provision for appropriate methods to extract these metals is not only economically attractive but, more importantly, will ensure the sustainment of the environment and human health. The recycling of e-waste is becoming extensively necessary as an alternative to landfilling or heat treatment processes (Cui & Anderson, 2016).

In recent years, hydrometallurgical treatment has gained preference over pyro-metallurgical techniques in the recycling of the metal content (more specifically precious metals such as gold and silver) of waste mobile phone PCBs because of its reduced capital cost, low impact on the environment, and relatively easy management (Cui & Anderson, 2016; Hanafi et al., 2012; Grosse et al., 2003). Hydrometallurgical processes mainly consist of the following steps: leaching, recovery and purification (Cui & Anderson, 2016; Gupta, 2003). Cyanide has been used for many years as a leaching agent, but due to environmental and human health concerns, alternative lixiviants are considered. As such, thiosulphate is among the promising non-cyanide lixiviants by virtue of its higher selectivity, significantly reduced toxicity and corrosiveness (Albertyn, 2017; Petter et al., 2014; Grosse et al., 2003; Nicol & O'Malley, 2002; O'Malley, 2001).

Although thiosulphate is praised as a promising replacement to cyanidation, the use of copper as an oxidant incurs an increase in the thiosulphate consumption which, in turn, leads to fluctuations in the gold extraction when similar leaching conditions are applied to various ores and e-waste types. The copper-ammonia-catalysed thiosulphate leaching of gold requires high amounts of cupric ions which are directly linked to the gold leaching kinetics and thiosulphate consumption (Xu et al., 2017; Syed, 2012; Cui & Zhang, 2008; Arima et al., 2004; Zipperian et al., 1988). Furthermore, if cementation and resin adsorption are used as recovery methods, the presence of copper would lead to the contamination of the precipitate in cementation and adsorbate in resin adsorption (Arima et al., 2004; Arima et al., 2003). Adding to these constraints is the fact that, during the leaching process, reagent consumptions are reported to be higher in the treatment of waste mobile phone PCBs compared to that of natural ores (Arima et al., 2004; Arima et al., 2003). Therefore, to counteract the high reagent consumption in the thiosulphate leaching of gold and enhance the efficiency of any subsequent recovery technique, the use of alternative oxidants and pre-treatment schemes should be considered.

## 1.2 Statement of Research Problem

The hydrometallurgical extraction of precious metals from e-waste has proven to be an attractive and economic recycling route. Hence, the increased interest in the leaching of gold from discarded mobile phone PCBs. The use of thiosulphate as the leaching reagent is more environmentally friendly than the conventional cyanidation. Ammonia and copper have been used as stabilizing agent and metal oxidant, respectively, for the leaching process. However, the use of copper is deemed to incur high reagent consumption and contamination of the leachate that could cause severe interference in downstream recovery processes such as resin adsorption. Therefore, for the industrial implementation of thiosulphate leaching to be envisaged, there is a need to address the high reagent consumption associated with the process.

## 1.3 Research Aim and Objectives

This research aimed to investigate the ammonium thiosulphate leaching of gold from waste mobile phone printed circuit boards, with an emphasis on the thiosulphate consumption and interference of extractable copper in the leaching process.

The following objectives were pursued:

- The effect of acid-pretreatment on gold extraction and thiosulphate consumption.
- The effect of nickel as the metal oxidant on gold extraction and thiosulphate consumption.

## 1.4 Research Hypotheses

- *Hypothesis 1*: the use of acid pre-treatment has a significant impact on gold extraction and thiosulphate consumption.
- *Hypothesis 2*: the replacement of copper(II) ion with nickel(II) ion has a pronounced impact on gold extraction thiosulphate consumption.

## 1.5 Significance of the Study

The accelerated increase in waste electrical and electronic equipment and the improper disposal of this waste is becoming a significant concern for human health and the ecosystem. With the rising concerns on e-waste management and disposal methods, there are attempts to delay e-waste generation by multiple regulatory techniques worldwide. However, in the South African context, there are still deficits on regulatory initiatives related to the unlawful trafficking and handling of e-waste. The imminent task at hand is to devise techniques for the collection, processing and disposal of e-waste. The hydrometallurgical treatment of e-waste is a promising route because of its advantages including job creation in the engineering sector, the profitability of the operation due to the high market value of the extractable metals and the reduction in size and amount of hazardous materials contained in this waste. This study focused on the mitigation of the operability issues related to the use of ammonium thiosulphate leaching to recycle gold from waste PCBs. The use of nickel to reduce reagent consumption in the leaching process, with specific application to waste PCBs, has been reported for the first time in this research, thus contributing to the body of knowledge in this field. Therefore, it is believed that this research will contribute to the advancement of e-waste handling techniques and procedures in South Africa and other developing countries.

## 1.6 Thesis Outline

This thesis is organized in five chapters. *Chapter 1* has discussed the background and rationale for undergoing this research, along with aim and objectives pursued. *Chapter 2* describes the hydrometallurgical techniques used in the gold extraction from e-waste with emphasis on the ammonium thiosulphate leaching process, the chemistry, thermodynamics and factors influencing the process. This chapter also includes references to recent applications of the thiosulphate leaching to extract gold from waste printed circuit boards. *Chapter 3* details the experimental setup and procedures used in this study. *Chapter 4* discusses the results obtained with reference to the existing literature and statistical analysis. Finally, *Chapter 5* concludes the thesis with recommendations for future research.

# CHAPTER 2

## LITERATURE REVIEW

# CHAPTER 2 : LITERATURE REVIEW

## 2.1 Characterisation and Classification of Electronic Waste

Although no standard definition can be attributed to this waste type, e-waste can be portrayed as a waste material comprising of any destroyed or undesired electronic devices. Electronic waste incorporates computers, entertainment gadgets, mobile phones and other electronics that have reached their end of life and have been disposed of by their users. Although they are regarded as waste, end-of-life (EOL) electronics can still find use through refurbishing and recycling (Ari, 2016).

E-waste is a complex blend of ferrous, non-ferrous, plastic and ceramic materials. Printed circuit boards (PCBs) are an essential part of all electronic devices. They are commonly known to contain approximately 40% metals, 30 % plastics and 30 % ceramics (Ari, 2016; Khaliq et al., 2014; Szałatkiewicz, 2014). In general, the metals present in e-waste can be categorised as precious metals (PMs), base metals (BMs), platinum group metals (PGMs), metals of concern (MCs) and scarce elements (SEs), such as the following (Khaliq et al., 2014):

| | |
|---|---|
| *PMs:* | Au, Ag |
| *PGMs:* | Pd, Pt, Rh, Ir and Ru |
| *BMs:* | Cu, Al, Ni, Sn, Zn and Fe |
| *MCs (hazardous):* | Hg, Be, In, Pb, Cd, As and Sb |
| *SEs:* | Te, Ga, Se, Ta and Ge. |

The recyclability of EOL devices is dependent on these constituents. A detailed classification of e-waste is provided by Cui & Zhang (2008). It has been shown that, out of all EOL devices, the most predominant sources of e-waste are computers and mobile phones. Furthermore, they contain the highest amount of base and precious metals (Cui & Zhang, 2008; Akcil et al., 2015). The elemental composition of waste PCBs is provided in Table 2-1.

**Table 2-1: Elemental composition of waste PCBs**

| Element Weight (%) | (Zhang et al., 2016) PC-PCB | (Akcil et al., 2015) MP-PCB | (Akcil et al., 2015) PC-PCB | (Szałatkiewicz, 2014) MP-PCB | (Szałatkiewicz, 2014) PC-PCB |
|---|---|---|---|---|---|
| Gold | 0.00385 | 0.00 | 0.13 | 0.0347 | 0.0076 |
| Palladium | 0.0435 | - | - | 0.0151 | <0.0027 |
| Silver | 0.0541 | 0.21 | 0.16 | 0.363 | 0.0241 |
| Copper | 30.8752 | 34.49 | 20.19 | 13 | 24.69 |
| Nickel | 0.3854 | 2.63 | 0.43 | 1.5 | 0.11 |
| Zinc | 0.3968 | 5.92 | 4.48 | - | - |
| Aluminium | - | 0.26 | 5.7 | - | - |
| Iron | 4.0756 | 10.57 | 7.33 | 7 | 0.22 |
| Lead | 2.0986 | 1.87 | 5.53 | 0.6 | 0.63 |
| Tin | - | 3.39 | 8.83 | 1 | 2.31 |

*MP-PCB: mobile phone printed circuit board*

*PC-PCB: computer printed circuit board*

## 2.2 Waste Mobile Phone Printed Circuit Boards

Gold recovery from waste mobile phone PCBs has gotten the most consideration because of the extensive amount of this metal in this waste as compared to metal-bearing ores. It was reported that the gold content of mobile phone PCBs is about 100 times greater than that of naturally-occurring rocks (Kim et al., 2011; Cui & Zhang, 2008). The size of cellular phones might be small, but when tons of these items become obsolete, the amount of extractable valuable metals in these items becomes much more significant (Baba et al., 2010).

PCBs from mobile phones can incorporate up to 40 different elements, some of which are shown in Table 2-1. A typical cellular phone weighs between 112 and 192 grams, and the metallic fraction is about 25% of its mass. The gold content of mobile phone PCBs has been reported to be twice as high as that of computer PCBs. Copper and iron are known to represent approximately 55% and 30% of the metallic fraction, respectively (Szałatkiewicz, 2014).

## 2.3 General Reasons for E-Waste Processing

The main reasons for treating e-waste include health and environmental concerns, energy and resource conservation, and economic benefits.

### 2.3.1 Health and Environmental Aspects of E-Waste

Many components of waste electrical and electronic equipment are considered intrinsically hazardous and significantly toxic. If not subjected to environmentally benign recycling techniques, this waste can harm living beings and the environment (Ari, 2016).

The primary hazardous materials contained in e-waste and their health and environmental implications have been outlined and discussed extensively in the existing literature (Ecroignard, 2006; Robinson, 2009; Khaliq et al., 2014). They include arsenic, barium, beryllium, brominated flame retardants (BFRs), cadmium, chlorofluorocarbons (CFCs), chromium, dioxins and furans, lead, mercury, polychlorinated biphenyls, polyvinyl chloride (PVC) and selenium.

Landfilling is the most common method in handling e-waste. It is inclined to unsafe consequences owing to the unwanted presence of heavy metals in the leachate, even in the best landfilling technologies employed (Al-Anzi et al., 2017; Mehta, 2018; Singh et al., 2018). Although lead has not been found to leach from modern municipal solid waste landfills above regulatory levels (Robinson, 2009), there are numerous reports on the leaching of lead from discarded lead-containing glasses, such as the cone glass of cathode ray tubes (CRTs) (Ari, 2016). Electronic devices and lead-acid batteries are significant sources of lead in municipal solid waste (USEPA, 1989). Lead-based solder, which is a mixture of tin and lead in a ratio of 60:40, is the dominant type of solder used in the manufacture of PCBs (Hedemalm, 1995; FWI, 2001). FWI (2001) identified about 50g of tin-lead solder/m$^2$ of PCBs, and Monchamp (2000) indicated roughly 0.7% lead in the total mass of PCBs. In CRTs, leaded glass finds use as a shield against X-rays originating from the picture projection process. The amount of lead in colour CRTs averages 1.6 - 2.2 kg (Pedersen, 1995).

E-waste incineration would pose a problem due to the release of mixtures of toxic gaseous compounds such as polychlorinated dibenzo-p-dioxins (PCDDs) and polychlorinated dibenzofurans (PCDFs). These compounds are produced when some of the components of e-waste, including lead, brominated flame retardants, polyvinyl chloride and polychlorinated biphenyls are subjected to combustion (Ecroignard, 2006; Leung et al., 2007). Furthermore, the ash residue in e-waste incineration sites contains increased quantities of polluting metals such as cadmium and lead, along with PCDDs and PCDFs which are deposited into the soil from the incineration effluents released. These species could be detrimental to the surrounding terrestrial area (Ni et al., 2010; Luo et al., 2011). However, researchers have different views on the environmental viability of the incineration of electronic waste. Stewart & Lemieux (2003) stated that one method of handling e-waste is the incineration of its combustible fraction, either to achieve volume reduction before landfilling or to concentrate the valuable metallic species in the residual ash so that they can be extracted through additional recovery techniques. They conducted preliminary tests aimed at providing data on the potentially toxic emissions involved in the incineration of e-waste. Experiments were conducted in a pilot-scale rotary kiln incinerator over a range of temperatures. The flue gas was tested for metals, halogens, volatile and semi-volatile organics, and PCDDs and PCDFs. The results indicated significant metals emissions, mostly consisting of copper, lead, and antimony, with trace amounts of other toxic metals such as cadmium, barium, arsenic, chromium and beryllium. Volatile organic emissions consisted mainly of bromobenzene, with tiny quantities of other brominated hydrocarbons. Emissions of PCDDs and PCDFs were below regulatory levels, possibly inhibited due to the presence of bromine originating from the combustion of brominated flame retardants in the waste. The authors suggested that e-waste incineration may be a viable recycling technique, provided that an appropriate method is used to control the emissions.

### 2.3.2 Energy and Resource Conservation

Another incentive for e-waste recycling through metal recovery is related to the potential for energy savings. Energy can be saved significantly by using recycled materials compared to mining new products because most of the metals in PCBs have high chemical energy compared to the energy required for PCB treatment (Khaliq et al., 2014). The chemical energy available in mobile phones has been reported to approximate 10.65 MJ/kg, whereas the energy required for the extractive treatment of this waste is about 7.43 MJ/kg (Szałatkiewicz, 2014). In addition, the treatment of e-waste will decrease the intricacies of digging ores for primary metals. Therefore, scarce resources, particularly those containing precious metals, could be saved (Khaliq et al., 2014). The energy savings of some of the common metals used in the industry are provided in Table 2-2.

**Table 2-2: Energy savings of recycled metals over virgin metals (Khaliq et al., 2014)**

| Metals | Energy Savings (%) |
|---|---|
| Aluminium | 95 |
| Copper | 85 |
| Iron and steel | 74 |
| Lead | 65 |
| Zinc | 60 |

### 2.3.3 Economic Value of Precious Metals in E-Waste

The market value of the metals recovered from waste PCBs can be used to assess the financial aspect of metal extraction from this waste. The market values of the extractable metals of interest in 1 metric ton of PCB are given in Table 2-3.

**Table 2-3: Current market value of various metals contained in 1 ton of PCBs (Baba et al., 2010; Zhang et al., 2016)**

| Recovered Metal | Weight (kg) | Approximate Market Value | |
|---|---|---|---|
| | | USD* | ZAR* |
| Au | 0.298 | 14,070 | 210,905 |
| Pd | 0.093 | 5,294 | 79,352 |
| Cu | 308.8 | 1,804 | 27,043 |
| Pb | 30.84 | 61 | 907 |
| Ag | 0.450 | 247 | 3,697 |

* USD: US Dollars; ZAR: South African Rand

Table 2-3 indicates that gold, copper and palladium have a significantly high market value compared to other metals contained in PCBs. Furthermore, despite the high amount of extractable copper (309 kg/ton of PCB), the market value of this metal is significantly smaller than that of gold or palladium although their masses are tiny in the PCB (gold mass being 1040 times lower than copper, and palladium mass being 3320 times smaller than copper). In fact, gold and palladium alone represent approximately 80% of the total market value of the extractable metals in PCBs (Szałatkiewicz, 2014; Baba et al., 2010). Gu et al. (2019) supported this claim by suggesting that the monetary value proportion of gold in PCBs can reach as high as 60%. This consideration adds to the incentives for gold extraction from electronic waste, mainly waste mobile phones.

## 2.4 General Waste PCBs Treatment Scheme

Waste PCBs recycling incorporates three major stages (Cui & Forssberg, 2003; Khaliq et al., 2014; Lu & Xu, 2016): (i) *dismantling:* aimed at separating the PCB from any mounted component, (ii) *pre-treatment/beneficiation:* involves the removal of the non-metallic fraction in order to upgrade the waste to the desired metal content, and (iii) *refining/end-treatment:* whereby the metal-concentrated waste is subjected to chemical (metallurgical) treatment for extracting the metals of interest and increasing their purity. The general treatment operations used for the recovery of precious metals from e-waste is provided in Figure 2-1.

The pre-treatment of waste PCBs is crucial because it allows the waste to be concentrated in metals before the extraction steps. Therefore, the pre-treatment process is said to entail beneficiation or metal enrichment steps. PCBs are known to be coated with different plastic and ceramic materials which make up most of the non-metallic fraction of the boards (J. Guo et al., 2015; X. Guo et al., 2015). To increase metal exposure, the removal of all non-metals is a prerequisite. In this regard, mechanical-physical separation, praised for its high efficiency and simple operation, is employed. This technology is based on the difference in physical properties – such as density, magnetic properties and electric conductivities – of the materials to be segregated (Huang et al., 2009).

The schematic diagram of a beneficiation process for waste PCBs is provided in Figure 2-2. This treatment route is currently employed at Shanghai Xinjinqiao Environmental Company Ltd. and Yangzhou Ningda Precious Metal Company Ltd., with a throughput of 5000 tons of waste PCBs per year (Wang & Xu, 2015). It encompasses two-step crushing and cyclone air separation-corona electrostatic separation (CAS-CES) (Wang & Xu, 2015).

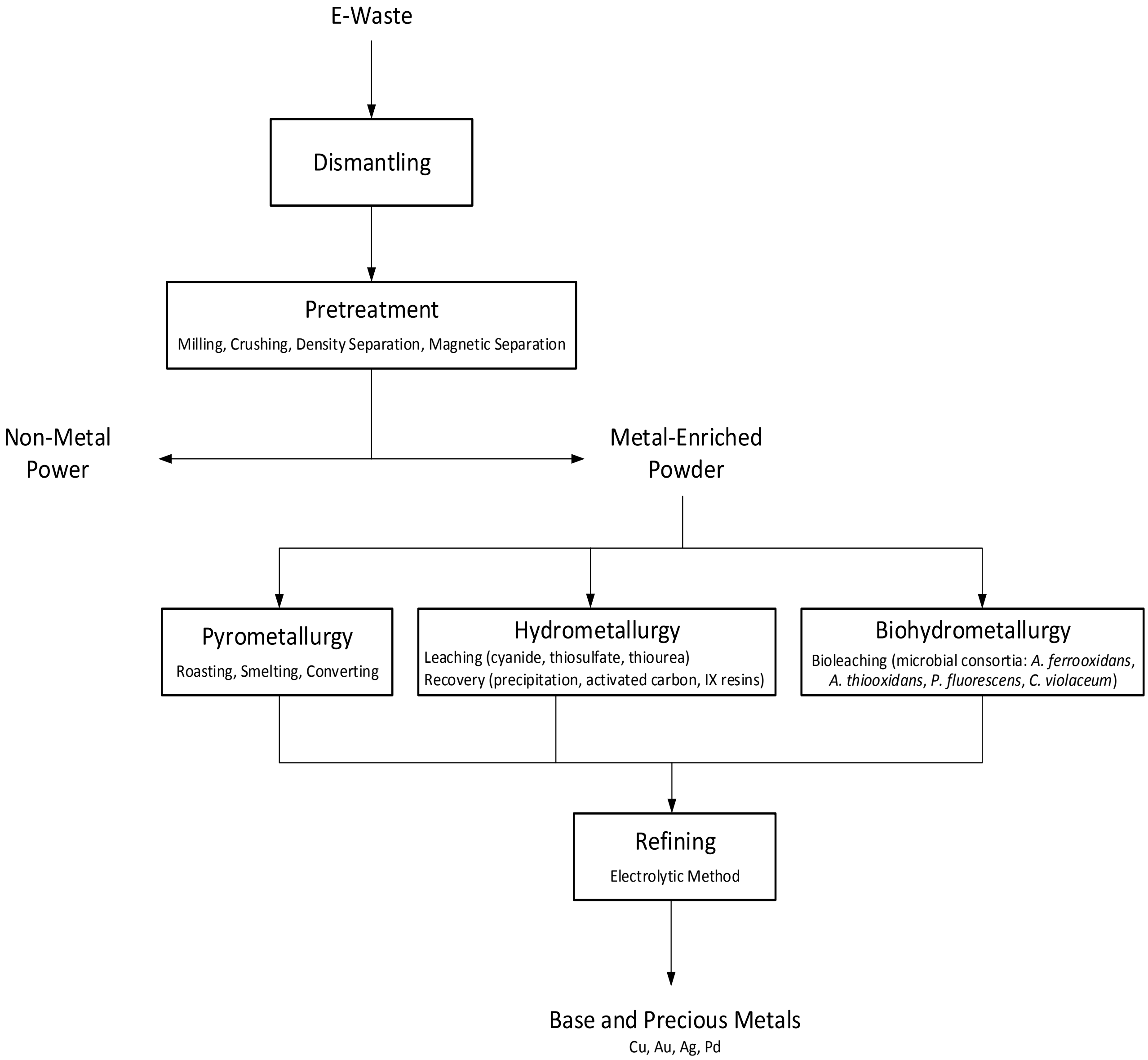


**Figure 2-1: General e-waste processing scheme (Hanafi et al., 2012; Syed, 2012; Lu & Xu, 2016)**

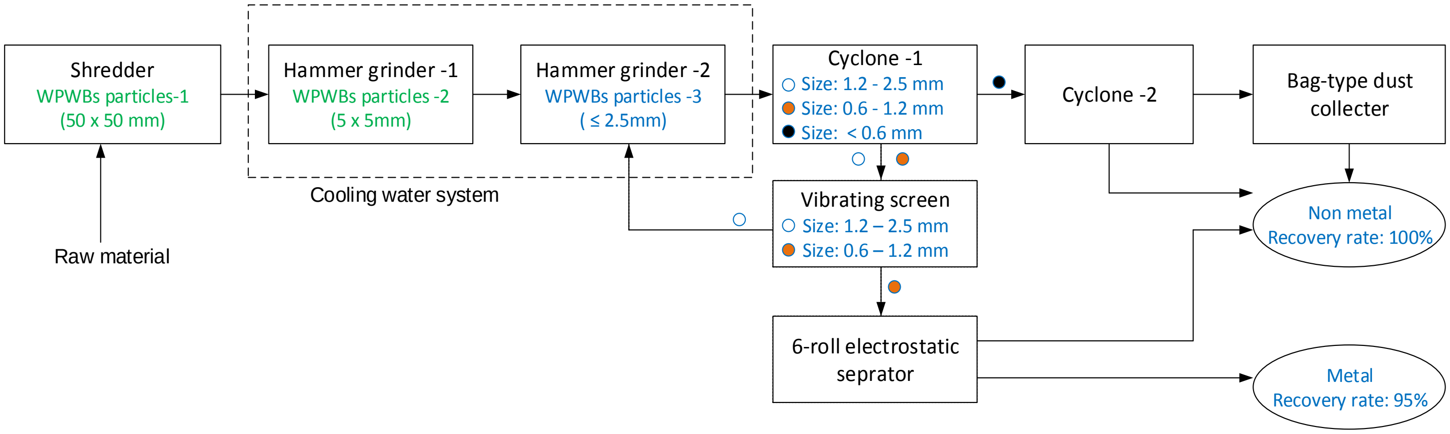


**Figure 2-2: Beneficiation process steps for waste PCBs (Wang & Xu, 2015)**

## 2.5 Gold Extraction by Hydrometallurgy

The underlying principle of any hydrometallurgical process involves the dissolution of metals from ores and wastes in a solution. The solution is referred to as a leaching agent or lixiviant or leachant (Gupta, 2003). The most common lixiviants used in the recovery of base metals and precious metals from ores are cyanide, halide, thiourea and thiosulphate (Gupta, 2003). The second step in hydrometallurgy involves the recovery of the metal(s) of interest from the pregnant leach liquor. Some of the metal recovery technologies in use include cementation, solvent extraction, carbon adsorption and ion-exchange resin adsorption (Safarzadeh et al., 2007; Makaka et al., 2010; Syed, 2012; Khaliq et al., 2014). At this stage, a careful choice of the recovery method is crucial to ensure an efficient and selective metal extraction.

### 2.5.1 Cyanide Leaching

Cyanide is amongst the oldest leaching reagents used in the gold mining industry. It has been used for more than 100 years for gold extraction. It is estimated that 13-20% of the global production of cyanide is directed towards mining operations for gold extraction (Ilyas & Lee, 2018). The dominant plant setups for cyanidation include tank leaching and heap leaching processes as the centre of operations (Cui & Zhang, 2008; Syed, 2012).

Cyanide leaching is an electrochemical process involving the complexation of gold in the feed with cyanide resulting in a pregnant solution containing the dissolved metal. The cyanidation process for the extraction of gold proceeds according to the following reactions (Dorin & Woods, 1991; Logsdon et al., 1999):

$$4\,Au + 8\,CN^- \longrightarrow 4\,Au(CN)_2^- + 4\,e^- \qquad (1)$$

$$O_2 + 2\,H_2O + 4\,e^- \longrightarrow 4\,OH^- \qquad (2)$$

*Overall:* $$4\,Au + 8\,CN^- + O_2 + 2\,H_2O \longrightarrow 4\,Au(CN)_2^- + 4\,OH^- \qquad (3)$$

Most of the studies conducted in this field have been directed towards the recovery of precious metals (PMs) and platinum group metals (PGMs), predominantly gold (Costello et al., 1992; Schmitz et al., 2001; Tan et al., 2005; Chen & Huang, 2006; Parga et al., 2007; Celep et al., 2009; Yazici et al., 2017; Rabieh et al., 2017; Khosravi et al., 2017). Cyanidation is carried out in alkaline media (pH 10) to avoid the hazardous evolution of HCN gas (Birich et al., 2019). Gold extractions ranging from 50 to 80% in heap leaching and up to 99% in conventional leaching have been reported (Habashi, 1966; Jeffrey, 2001; Marsden & House, 2006; Ilyas & Lee, 2018).

Cyanide leaching incurs selectivity issues when used in the extraction of gold from waste PCBs. This problem is driven by the variety of metals found in this waste, especially the high amount of copper which is known to interfere significantly with gold dissolution in cyanide solutions (Akcil et al., 2015). Bas et al. (2015) indicated that when the copper content of a gold-bearing ore exceeds 0.5%, the cyanide consumption can increase from 1.6 kg/t-ore to a range of 30 to 51.5 kg/t-ore for every 1% of extractable copper, with a significant reduction in gold extraction. This means that for waste PCBs containing high amounts of copper (up to 40%), cyanidation would incur unreasonably high reagent consumption levels. Hence the need for pre-treatment methods targeting copper removal or the use of additives to impede the effect of copper on gold extraction. These measures could have a detrimental impact on the economic viability of the process.

Although little research has been conducted on the cyanide leaching of gold from waste printed circuit boards, the available literature indicates gold extractions neighbouring 50% with no pre-treatment targeting copper removal, and gold dissolutions reaching as high as 97% with acid pre-treatment for copper removal and an associated cyanide consumption of 17.5 kg/t-PCB (Quinet et al., 2005; Montero et al., 2012).

The current use of cyanidation for the extraction of gold raises multiple environmental concerns. As a result, its use is highly restricted or banned in various regions. Cyanide leaching in the gold mining industry incurs the production of a significant quantity of cyanide-bearing wastewater, which is detrimental to the wellbeing of operators and the environment (Grosse et al., 2003; Zhang et al., 2012). There have been numerous reports on incidents related to cyanide leakages at gold mining sites, and the most recent occurred in 2015 at Barrick Gold/Veladero mine in Argentina (Hynes et al., 1998; Eisler & Wiemeyer, 2004; Noller & Saulep, 2004; MiningWatch, 2006; Guerra, 2010; Holland, 2015; Jamasmie, 2015).

Based on its reactivity, cyanide can follow various transformative paths when discharged into nature. In general, metal-cyanide complexes are less toxic than cyanide. However, copper and zinc complexes are more unstable owing to their weak acidity and thus will discharge cyanide into the earth. Despite the stability of iron cyanide complexes under various environmental conditions, iron cyanides can undergo photochemical disintegration and will, therefore, release cyanide if subjected to UV light. Furthermore, iron cyanide complexes react with Ni, Mg, Pb, Zn, Cd and Ag to form insoluble precipitates. The adsorption of cyanide and metal cyanide complexes on organics present in the soils is also predominant and results from the strong affinity of these species for organic matter. When released to the environment, free cyanide can also follow the volatilisation pathway by the slow evolution of gaseous hydrogen. It is noteworthy that the formation of HCN can be exacerbated by a decrease in pH, increased aeration of the solution and temperature (Eisler, 2000; International Cyanide Management Code, 2015; Jaszczak et al., 2017).

The acute toxicity of cyanide is the result of its lethal nature and ability of rapid diffusion and attachment to the human tissue. Liquid and gaseous hydrogen cyanide access to the human body occurs through various routes, mainly inhalation, ingestion or assimilation through the eyes and skin. The assimilation rate through the skin is exacerbated when the skin is cut, abraded or moist (Eisler & Wiemeyer, 2004; Leung & Lu, 2016).

Currently, more studies are focusing on the use of alternative non-cyanide lixiviants such as thiourea, thiocyanate, iodine and thiosulphate for gold extraction from e-waste.

### 2.5.2 Thiourea Leaching

The use of thiourea in the leaching of precious metals – predominantly gold and silver – from primary and secondary sources has gained interest over the years. Thiourea leaching is carried out in acidic solutions in a pH range of 1 to 2 due to its instability in alkaline environments (Hilson & Monhemius, 2006; Cui & Zhang, 2008; Syed, 2012). In acidic solutions, the thiourea leaching of gold involves the formation of a cationic complex; the reaction is rapid, and gold extractions are expected to reach as high as 99% (Yannopoulos, 1991).

Air and oxygen are inappropriate for thiourea leaching. The most suitable oxidants include Fe(III), $H_2O_2$ (Ranjbar et al., 2017). When the oxidant used is a ferric ion, the overall reactions of the acid-thioureation of gold and silver are as follows (Murthy et al., 2003; Gönen et al., 2007; Jing-ying et al., 2012):

$$Au + 2CS(NH_2)_2 + Fe^{3+} \longrightarrow Au[CS(NH_2)_2]_2^+ + Fe^{2+} \tag{4}$$

$$Ag + 3CS(NH_2)_2 + Fe^{3+} \longrightarrow Ag[CS(NH_2)_2]_3^+ + Fe^{2+} \tag{5}$$

However, the oxidation of thiourea by ferric ion in an acidic medium also produces formamidine disulphide:

$$2CS(NH_2)_2 + 2Fe^{3+} \longrightarrow (SCN_2H_3)_2 + 2Fe^{2+} + 2H^+ \tag{6}$$

Formamidine disulphide is unstable in acidic solutions, and thus undergoes an irreversible disproportion reaction to form elemental sulphur and cyanamide:

$$(SCN_2H_3)_2 \longrightarrow CS(NH_2)_2 + NH_2CN + S \tag{7}$$

In addition, thiourea is consumed through the formation of a stable ferric sulphate complex:

$$Fe^{3+} + SO_4^{2-} + CS(NH_2)_2 \longrightarrow [FeSO_4\,.\,CS(NH_2)_2]^+ \tag{8}$$

Therefore, careful control of the oxidation of thiourea is required to achieve optimum leaching performance.

Compared to cyanidation, thiourea leaching offers several advantages including lower toxicity, greater reagent handling, higher gold dissolution rates and recoveries (Brent Hiskey & Atluri, 1988; Ubaldini et al., 1998; Gönen et al., 2007; Cui & Zhang, 2008; Syed, 2012). Also, thioureation has been praised due to its overall higher leaching efficiency in acidic environments.

Although in a limited amount, previous studies have successfully applied thiourea leaching for the extraction of gold from electronic waste. Among them, others have examined pre-treatment techniques including thermal processing after size reduction for the removal of the non-metallic fraction, and acid leaching for the removal of base metals such as copper (Birloaga et al., 2014; Behnamfard et al., 2013; Gurung et al., 2013).

The main challenges encountered with thioureation are high reagent consumption (reaching as high as 140.7 kg/t-PCB) and poor stability (Quinet et al., 2005). Attempts have been made to tackle these issues. To overcome the instant thiourea complexation with base metals such as copper-nickel and iron in acidic media, Wei et al. (1999) proposed alkaline thioureation, which would improve the passivation of these unwanted metals. The alkaline thiourea leaching system was inclusive of sodium sulphite, and sodium persulphate used as the oxidant. However, it is worth noting that the stability of thiourea in alkaline solutions needs to be substantiated through more research to ascertain the process viability since most of the available literature on gold thioureation involves the more favoured acidic environments. The presence of formamidine disulphide in the leaching environment also has a deleterious effect on reagent consumption. Sulphur production is incurred in fine adhesive form and has the potential of inhibiting metal dissolution by passivation of the feed material.

### 2.5.3 Thiocyanate Leaching

Thiocyanate was first reported as a possible alternative lixiviant to cyanide for gold leaching by White (1905). Subsequent research on the topic, including its thermodynamic aspect, was conducted by Fleming (1986), Barbosa-Filho & Monhemius (1989) and Broadhurst & Du Perez (1993). Thereafter, Li et al. (2012a; 2012b; 2012c; 2012d; 2012e) built upon previous knowledge and outlined a comprehensive approach involving all treatment steps from pre-treatment to purification, and concluded their study with a conceptual flowsheet for gold extraction by thiocyanate leaching.

The thermodynamic studies conducted on the leaching of gold using thiocyanate indicated that, based on the Pourbaix diagram of the gold/iron/thiocyanate/sulphate/water system, thiocyanate is a stable and possible leaching reagent combination for gold extraction (Broadhurst & Du Perez, 1993; Li et al., 2012b). When the ferric ion is used as the oxidizing agent, leaching is carried out in a pH range of 1 to 3.5 (Li et al., 2012b; Barbosa-Filho & Monhemius, 1994b).

$$3Fe(SCN)_4^- + Au \longrightarrow 3Fe^{2+} + Au(SCN)_4^- + 8SCN^- \tag{9}$$

$$Fe(SCN)_4^- + Au \longrightarrow Fe^{2+} + Au(SCN)_4^- + 2SCN^- \tag{10}$$

The mechanism of the thiocyanate leaching of gold with $Fe^{3+}$ as an oxidant is based on an electrochemical process involving the reduction of $Fe^{3+}$ and oxidation of $\mathrm{SCN}^-$. This spontaneous redox process was referred to as ‘auto-reduction’ by Betts & Dainton (1953). Thiocyanate is oxidised by ferric ion through the formation of intermediates, predominantly trithiocyanate $(\mathrm{SCN})_3^-$ and thiocyanogen $(\mathrm{SCN})_2$, which behave as oxidants and, when reduced back to $\mathrm{SCN}^-$, as complexants for gold. This formation is thus considered the most critical feature of the auto-reduction process (Barbosa-Filho & Monhemius, 1994c). However, these intermediate species do not just increase the gold dissolution rate but are also subject to a rapid decomposition by hydrolysis which is considered as a major issue in the mechanistic analysis of the ferric-oxidised thiocyanate leaching of gold (Barbosa-Filho & Monhemius, 1994d). Therefore, the overall efficiency of the leaching process can be greatly improved by using solution concentrations such that the rates of auto-reduction and gold dissolution concur. This will ensure a continuous supply of $(\mathrm{SCN})_3^-$ and $(\mathrm{SCN})_2$ (Barbosa-Filho & Monhemius, 1994d).

Thiocyanate is mostly used in conjunction with other lixiviants such as thiourea to achieve a synergistic effect on the leaching process. For instance, Barbosa-Filho & Monhemius (1994a) studied the iodide-thiocyanate leaching and established that the synergistic effect of the dual-lixiviant system was ascribed to the formation of relatively stable mixed iodine-thiocyanate species such as $I_2SCN^-$ and $I(SCN)^{2-}$ which could partake in the mechanism of gold leaching.

Currently, no research has been reported on the thiocyanate leaching of gold from waste mobile phones. However, it is noteworthy that, based on the established process mechanism applied to primary sources, more research into this leaching technique with e-waste as raw material would provide additional insights into possible industrial upscale. Furthermore, an assessment of the environmental aspects of thiocyanate leaching has been described by Li et al. (2012b). Although thiocyanate is reported to be significantly less toxic than cyanide, more research is required to investigate the toxicity of thiocyanate degradation products in waste streams to comply with environmental discharge regulations.

### 2.5.4 Halide Leaching

Most halogens, except for fluorine and astatine, have been applied to the extraction of gold (Hilson & Monhemius, 2006; Calgaro et al., 2015). Halogens are praised for their high leaching kinetics and overall performance compared to conventional cyanidation. They are known to form stable complexes with gold due to their ability to produce highly polarised anions in aqueous media (Sahin et al., 2015). Iodine has been reported to have a higher affinity for gold compared to bromine and chlorine, with a dissolution rate close to that of aqua regia (Birich et al., 2019). Furthermore, iodine is praised for its low volatility and low hazardousness.

The mechanism of gold leaching by iodine, bromine and chlorine involves the formation of an Au(I)-compound which is readily converted to the most stable Au(III)-halide complex.

$$2\,Au + I_3^- + I^- \;\Leftrightarrow\; 2\,AuI_2^- \tag{11}$$

$$Au + 4\,Br^- \;\Leftrightarrow\; AuBr_4^- + 3\,e^- \tag{12}$$

$$Au + 4\,Cl^- \;\Leftrightarrow\; AuCl_4^- + 3\,e^- \tag{13}$$

Iodine is praised not only for its stable complexation with gold but also because it requires the least oxidising conditions and can coexist with iodide in aqueous solution. The triiodide ion $\mathrm{I_3^-}$, formed from $\mathrm{I^-}$, is the major oxidant even at relatively high pH values. It triggers the oxidation of elemental gold to gold(I)-iodide complex (Qi & Hiskey, 1991; Angelidis et al., 1993; Davis et al., 1993; Konyratbekova et al., 2015). The iodine-iodide leaching system is unaffected by pH in a wide range; i.e. 2 to 7 (Angelidis et al., 1993) and 2 to 10 (Qi & Hiskey, 1991).

Iodine leaching has been successfully used in the recovery of precious metals from electronic waste. Satisfactory results were obtained in the $H_2O_2$-oxidized iodine leaching of gold from waste PCBs, with pre-leaching procedures aimed at copper removal. Recent research has shown potential in the use of iodine in dual-lixiviant systems (Isaia et al., 2017).

Despite their potential as lixiviants, chlorine and bromine are highly corrosive and volatile, which impede their industrial application to gold extraction. Furthermore, bromine leaching still suffers from high reagent consumption and is susceptible to high capital costs and health risks because bromine can form toxic compounds with other elemental species which would require unique construction materials (Syed, 2012). More research on chlorine leaching should target the feasibility of the in-situ production of bromide and address the potential hazards associated with the storage and transportation of bromine (Sousa et al., 2018). Iodine is a relatively expensive reagent which mostly explains the lack of interest in using this reagent as a lixiviant for gold extraction. Chloride qualifies mostly as a pre-treatment method for the removal of competing metals such as Cu, Ni, Fe, Ag, Pt and Pd which have shown satisfactory digestion levels in this lixiviant. Gold can then be dissolved more selectively using an alternative lixiviant.

### 2.5.5 Thiosulphate Leaching

An in-depth description of the thiosulphate leaching of gold from waste PCBs is provided in section 2.6. Thiosulphate has been praised as a suitable non-cyanide leaching agent for the extraction of gold and other metals from primary and secondary sources. According to Birich et al. (2019), it is the only reagent that has seen industrial application for gold extraction from a highly carbonaceous preg-robbing gold ore at Barrick Gold. Thiosulphate liquors are favoured for their diversity and lesser environmental imprint. They are less prone to fouling of undesirable metal ions and can be applied in the processing of various types of ores and wastes. The types of thiosulphate salts commonly encountered ($Na^+$, $K^+$, $Ca^{2+}$ and $NH_4^+$) are known to be biodegradable, and thus are considered to be nonhazardous in various countries (NOHSC, 2004; Langhans et al., 1992).

It is understood that gold dissolution is slow in alkaline thiosulphate, but the leaching rate is greatly improved in ammoniacal thiosulphate solution with a metal oxidant such as copper (II) ion and ammonia as the stabilising agent. It is a complex reactive system involving multiple reactions (gold oxidation, copper reduction, the formation of copper-amine and copper-thiosulphate complexes).

Furthermore, as an electrochemical process, thiosulphate leaching is strongly dependent on pH (Grosse et al., 2003; Cui & Zhang, 2008; Syed, 2012; Akcil et al., 2015). As such, the factors influencing the process include: thiosulphate consumption, ammonia concentration, copper concentration, pulp density, temperature, pH, stirring speed and reaction time (Ha et al., 2010; Ha et al., 2014; Camelino et al., 2015; Xu et al., 2017).

There have been numerous reports on the application of thiosulphate leaching to extract gold from waste PCBs with metal dissolution levels ranging from 50 to 98% depending on the reagent concentrations and conditions used (Ha et al., 2010; Ficeriová et al., 2011; Tripathi et al., 2012; Kasper & Veit, 2015; Isildar et al., 2017; Kasper & Veit, 2018; Xiang et al., 2018; Gámez et al., 2019). The major concern of this process is related to metal selectivity and high reagent consumption which has been reported to exceed 100 kg/t-PCB (Aylmore & Muir, 2001; Xu et al., 2017), compared to the low reagent consumption (about 17.5 kg/t-PCB) reported in cyanidation (Quinet et al., 2005). This phenomenon is brought by the inference of other metals such as copper, silver and palladium present in PCBs. Even though thiosulphate has a lower market price compared to cyanide, its industrial implementation as a substitute for cyanidation in gold extraction will be financially attractive depending on the proper control and enhancement of the operating conditions in such a way as to minimise reagent consumption and increase gold extraction.

### 2.5.6 Bioleaching

The use of biotechnology for metal extraction is gaining interest in the field of hydrometallurgy. Bacteria-assisted leaching is currently targeting copper sulphides primarily and as a pre-treatment technique for refractory gold ores, but it is also applied to the extraction of other base metals, such as nickel and zinc (Rohwerder et al., 2003). Recent developments have been directed towards the use of acidophilic microorganisms to treat electronic waste, recover metals from oxidised ores, and selectively retrieve metals from process waters and waste streams (Johnson, 2014). In general, bioleaching is acknowledged for the following advantages: (i) moderate capital investment with low operating costs, (ii) metal extraction from low-grade ores and wastes and (iii) does not require intricate equipment or operating techniques (Watling, 2006; Gentina & Acevedo, 2013).

Various microorganisms have been used for metal extraction from e-waste, namely chemolithotrophic, heterotrophic and thermophilic bacteria for the mobilisation of base and precious metals (Brandl et al., 2001; Ilyas et al., 2007; Xiang et al., 2010; Chi et al., 2011). However, most of the studies in the bioleaching of e-waste are targeting gold and copper as the primary metals of interest (Baniasadi et al., 2019).

Chemolithotrophic (mesophilic) and heterotrophic cyanogenic microorganisms have found increased use in the extractions of copper and gold from waste PCBs. Microbial pre-treatment for copper removal has been successfully used to improve gold bioleaching. Various studies have reported the use of acidophilic bacteria as single strains or in mixed consortia to achieve Cu digestion (Arshadi & Mousavi, 2015; Li et al., 2015; Işıldar et al., 2016).

The bioleaching of waste PCBs is subject to significant challenges, including the toxicity and precipitation of the metal of interest due to jarosite formation. Valix (2017) indicated that unwanted jarosite could be formed as a result of the saturation of metals present in the leaching system as well as the occurrence of precipitating agents. Toxicity is brought about by the presence of heavy metals in the waste which is reported to impede the growth and activity of microorganisms. Hence the need for gradual sub-culturing for microbial adaption to the PCBs before proceeding with the metal solubilisation process (Ruan et al., 2014; Baniasadi et al., 2019). Toxicity is also related to the non-metallic fraction of PCBs (plastics and brominated flame retardants) which cannot be digested by bacteria and can be detrimental to these organisms at specific concentrations (Valix, 2017).

### 2.5.7 Comparison between Lixiviants used in Gold Extraction from E-waste

Table 2-4 compares the various lixiviants used in gold extraction from waste PCBs. This assessment is based on the leaching rate, reagent cost (consisting of the unit price and consumption), the environmental impact and level of knowledge and commercialisation in the field. It is worth mentioning that any treatment solution used to address the proliferation of e-waste is likely to lose its relevance if it incurs additional environmental risks or it is not financially appealing. As such, when selecting a process for e-waste treatment, environmental and financial considerations must be applied.

**Table 2-4: Basic assessment of cyanide and non-cyanide lixiviants used in gold extraction from waste PCBs (Quinet et al., 2005; Zhang et al., 2012; Akcil et al., 2015; Cui & Anderson, 2016)**

| Lixiviant | Gold Extraction | Reagent Cost | Corrosive | Toxicity | Research Level | Extent of Commercialization |
|---|---|---|---|---|---|---|
| Cyanide | High | Low | None | High | Extensive | Fully established for ores |
| Thiourea | Average | High | Low | Low | Extensive | Limited to Ores |
| Thiocyanate | Low | Moderate | Low | Moderate | Low | None reported |
| Chloride | High | Moderate | High | Moderate | Low | Electrolytic copper slimes |
| Bromine | High | High | High | Moderate | Low | None reported |
| Iodide | Above average | High | Moderate | Low | Low | None reported |
| Thiosulphate | Above average | Moderate | None | Low | Extensive | Semi-commercial |

A detailed description of the thermodynamic aspects of the formation of various gold(I/III) complexes and compounds was outlined by Senanayake (2004). The stability constants ($\beta_2$ or $\beta_4$) and corresponding standard reduction potentials of the complexes are provided in Table 2-5. It is evident that the stability of cyanide is significantly higher than that of alternative lixiviants. Furthermore, many ligands, such as thiosulphate and thiourea, are known to be oxidised at a lower potential than the corresponding Au(I) complex, which increases the likelihood of interference driven by competing metals present in the feed material. This phenomenon ultimately leads to high reagent consumption which is the most common impeding factor of these lixiviants (Aylmore, 2016).

**Table 2-5: Stability constants and standard reduction potentials for various gold complexes (Aylmore, 2016; Birich et al., 2019)**

| Ligand | Complex | *Log βᵢ* | *E°* | pH |
|---|---|---|---|---|
| $S_2O_3^{2-}$ | $Au(S_2O_3)_2^{3-}$ | 28.7 | 0.17 | 8 – 10 |
| $SCN^-$ | $Au(SCN)_2^-$ | 17.1 | 0.66 | < 3 |
| | $Au(SCN)_4^-$ | 43.9 | 0.66 | |
| $I^-$ | $AuI_2^-$ | 18.6 | 0.58 | 5 – 9 |
| | $AuI_4^-$ | 47.7 | 0.69 | |
| $Br^-$ | $AuBr_2^-$ | 12.0 | 0.98 | 5 – 8 |
| | $AuBr_4^-$ | 32.8 | 0.97 | |
| $Cl^-$ | $AuCl_2^-$ | 9.1 | 1.11 | < 3 |
| | $AuCl_4^-$ | 25.3 | 0.99 | |
| $CN^-$ | $Au(CN)_2^-$ | 38.3 | - 0.57 | > 9 |

Figure 2-3 shows that the gold dissolution into alternative lixiviants can be achieved in narrow operating regions. Again, reagent consumption is worsened by the high oxidising potentials involved with some leaching agents, indicating that the appropriate control of leaching conditions is required to sustain the use of alternative lixiviants for gold extraction.

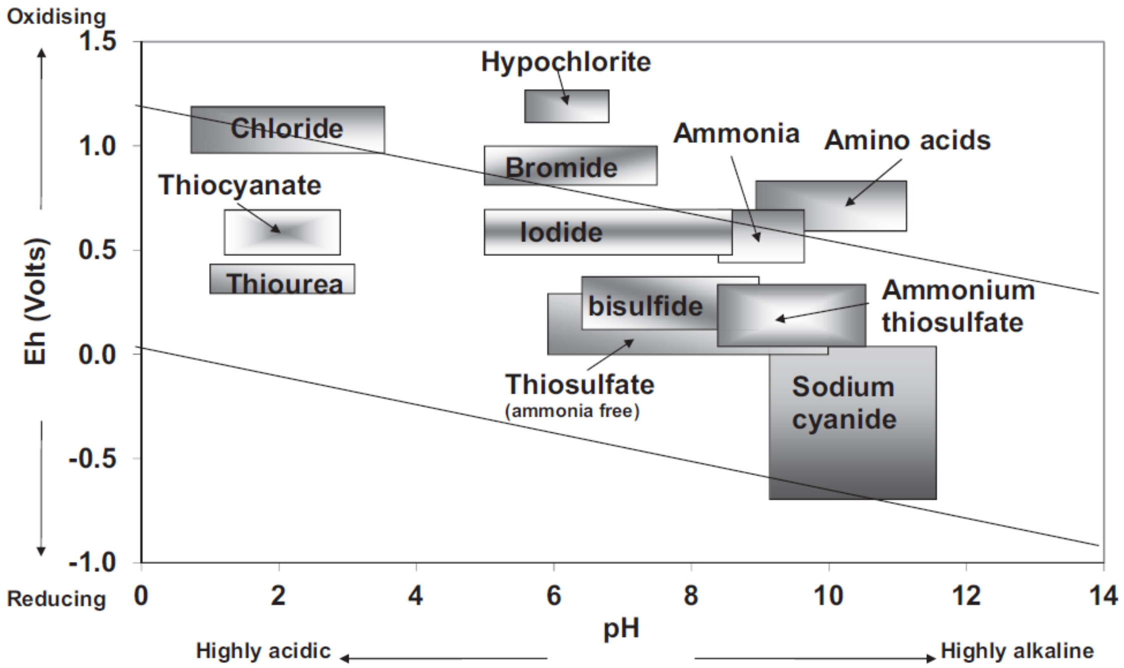


**Figure 2-3: Pourbaix diagram comparing the stability regions of lixiviants used for gold extraction (Aylmore, 2016)**

## 2.6 Ammonium Thiosulphate Leaching of Gold from E-waste

### 2.6.1 Thermodynamics of the Ammonium Thiosulphate Leaching of Gold

The main reaction of the thiosulphate leaching involves gold oxidation at the anode with the reduction of oxygen at the cathode, as per equation (14). However, this reaction alone is slow and incomplete without the use of appropriate catalysts. Copper and ammonia are known to improve the thiosulphate leaching of gold by a factor of 18 to 20 (Xu et al., 2017). The main reactions involved in gold extraction by the copper-ammonia-thiosulphate system occur as per equations (15) to (19). Reactions (15) to (17) occur on the anodic side whereas (18) and (19) occur on the cathodic side.

$$Net\ Reaction:\ 4Au + 8S_2O_3^{2-} + O_2 + 2H_2O \longrightarrow 4[Au(S_2O_3)_2]^{3-} + 4OH^- \tag{14}$$

$$Au \longrightarrow Au^+ + e^- \tag{15}$$

$$Au^+ + 2NH_3 \longrightarrow Au(NH_3)_2^+ \tag{16}$$

$$Au(NH_3)_2^+ + 2S_2O_3^{2-} \longrightarrow Au(S_2O_3)_2^{3-} + 2NH_3 \tag{17}$$

$$Cu(NH_3)_4^{2+} + 3S_2O_3^{2-} + e^- \longrightarrow Cu(S_2O_3)_3^{5-} + 4NH_3 \tag{18}$$

$$4Cu(S_2O_3)_3^{5-} + 16NH_3 + O_2 + 2H_2O \longrightarrow 4Cu(NH_3)_4^{2+} + 4OH^- + 12S_2O_3^{2-} \tag{19}$$

The above mechanism is further illustrated schematically in Figure 2-4. On the anodic side, gold is dissolved with subsequent complexation into two possible thiosulphate complexes $[\mathrm{Au(S_2O_3)}]^-$ and $[\mathrm{Au(S_2O_3)_2}]^{3-}$, of which the latter is the most stable.

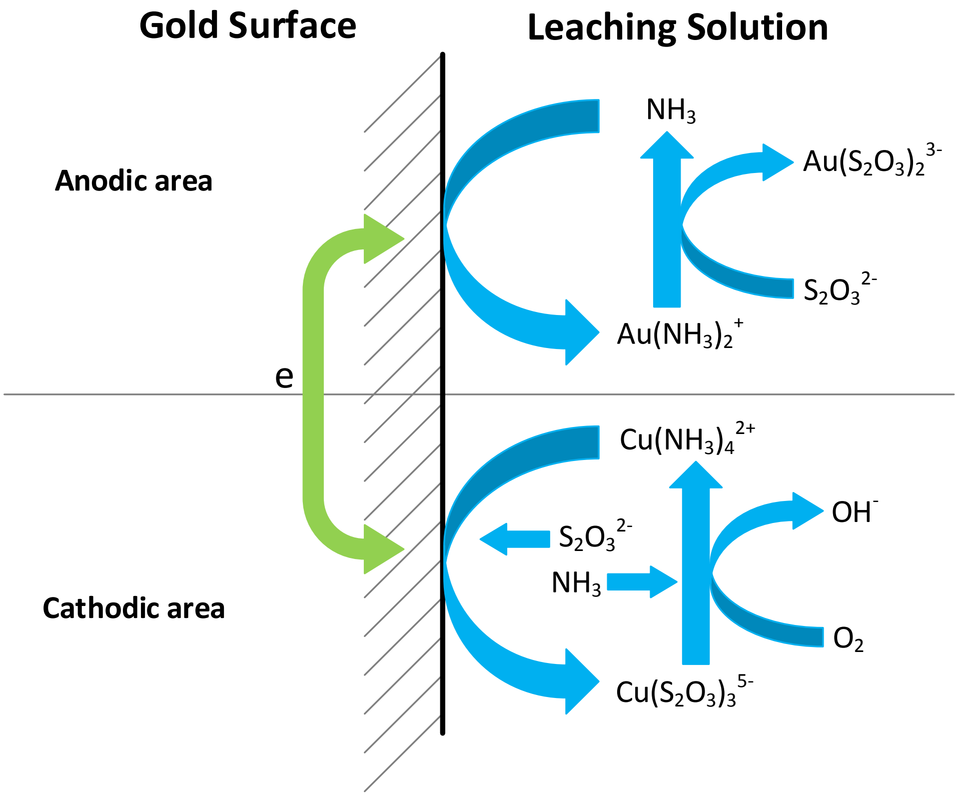


**Figure 2-4: Electrochemical-catalytic mechanism of the copper-thiosulphate leaching of gold (Aylmore & Muir, 2001; Camelino et al., 2015; Xu et al., 2017)**

Ammonia is used in the leaching system to prevent gold passivation driven by the formation of sulphur coatings on the surface. This is done by bringing gold into solution as the amine complex $[\mathrm{Au(NH_3)_2}]^+$ (equation 16), which is further converted into the thiosulphate complex $[\mathrm{Au(S_2O_3)_2}]^{3-}$, as per equation (17). The most important role played by ammonia is to stabilise copper(II) in the thiosulphate solution (Abbruzzese et al., 1995). Copper(II) ions are included in the leaching system to promote the process by providing grounds for the redox reaction (20) that drives the dissolution of gold as the aurous thiosulphate complex.

$$Au + 5S_2O_3^{2-} + [Cu(NH_3)_4]^{2+} \longrightarrow [Au(S_2O_3)_2]^{3-} + 4NH_3 + [Cu(S_2O_3)_3]^{5-} \qquad (20)$$

The redox equilibrium in the cuprous-cupric couple in the ammoniacal thiosulphate leaching system is provided by equation (19). This reaction indicates the use of oxygen to induce the "re-oxidation" of cuprous ions back to cupric ions to ensure the continuous supply of Cu(II) ions and further gold leaching (Aylmore & Muir, 2001).

The Pourbaix diagrams of the gold-ammonia-thiosulphate and copper-ammonia thiosulphate systems are depicted in Figures Figure 2-5 and Figure 2-6. The stability region of the cupric amine complex $\mathrm{Cu(NH_3)_4^{2+}}$ has been shown to broaden with an increase in ammonia and copper ions in the leaching system. Hence the significance of the copper and ammonia concentrations on the efficiency of the thiosulphate leaching of gold. Based on the Eh-pH diagrams, the $\mathrm{Cu(NH_3)_4^{2+}}/\ \mathrm{Cu(S_2O_3)_3^{5-}}$ pair can work for gold oxidation in a pH range of 8.7 to 9.8, although this pH range is expected to widen with a higher copper intake. Furthermore, the pH should be kept above 9 to maintain the stability of the aurous amine complex $\mathrm{Au\ (NH_3)_2^{+}}$. Based on the stability constants investigated by Smith and Martell (1976), the most predominant thiosulphate complexes are for gold(I), silver(I), iron(II), mercury(II) and lead(II). The rest of the metals present are thought to appear mainly as amine complexes. Gold in its high oxidation state Au(III) is mostly absent in thiosulphate solutions because it is readily reduced to its most stable oxidation state Au(I) (Grosse et al., 2003).

Despite its positive contribution to the gold oxidation, the cupric amine complex also increases the potential for thiosulphate degradation through reactions (21) and (22), thereby increasing the thiosulphate consumption through the conversion of thiosulphate to tetrathionate (Arima et al., 2004). This is the main factor that prevents the industrial adoption of ammonium thiosulphate for gold extraction.

$$2\ Cu(NH_3)_4^{2+} + 8S_2O_3^{2-} \ \longrightarrow\ 2Cu(S_2O_3)_3^{5-} + S_4O_6^{2-} + 8NH_3 \qquad (21)$$

$$2Cu(NH_3)_4^{2+} + 6S_2O_3^{2-} \ \longrightarrow\ 2Cu(S_2O_3)_2^{3-} + S_4O_6^{2-} + 8NH_3 \qquad (22)$$

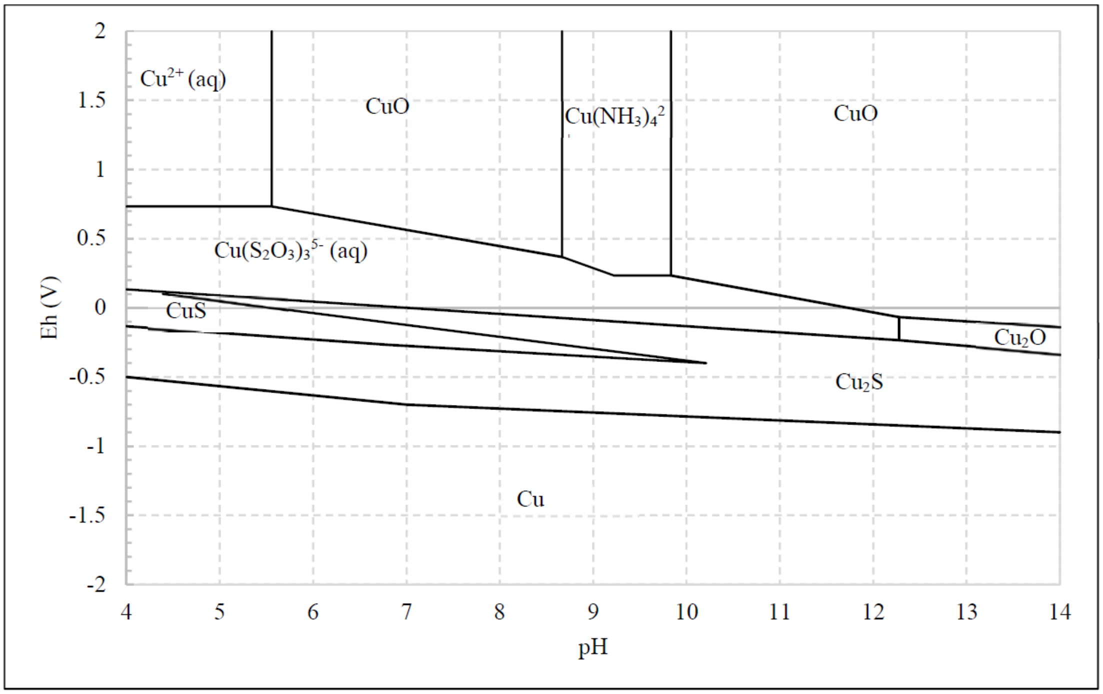


**Figure 2-5: Pourbaix diagram of the copper-ammonia-thiosulphate system at low reagent concentrations [0.1 M thiosulphate, 0.1 M ammonia, 0.0005 M Cu] (Aylmore & Muir, 2001)**

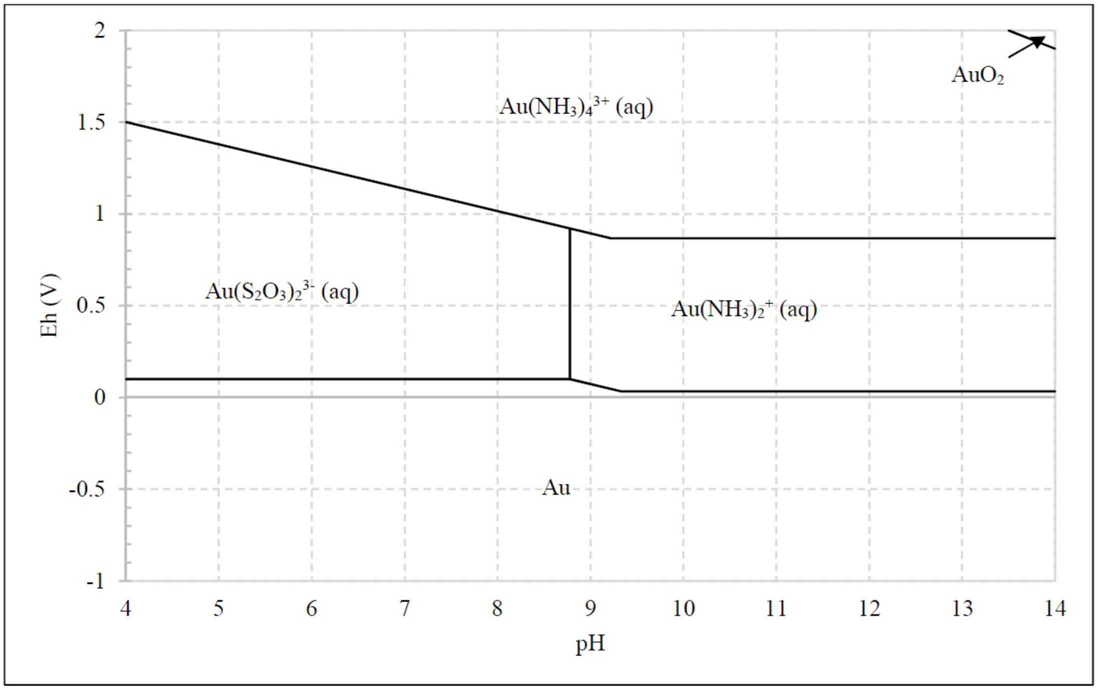


**Figure 2-6: Pourbaix diagram of the gold-ammonia-thiosulphate system at low reagent concentrations [0.1 M thiosulphate, 0.1 M ammonia, 0.0005 M Au] (Aylmore & Muir, 2001)**

### 2.6.2 Previous Research on Thiosulphate Leaching of Gold from Waste PCBs

Extensive research has been conducted on the applicability of thiosulphate leaching to recover precious metals from primary and secondary sources. Table 2-6 provides a summary of some of the studies conducted on the thiosulphate leaching of gold from waste PCBs. The most common variables of concern in the leaching process are ammonia, thiosulphate and copper concentrations, along with temperature, pulp density, pH and Eh of the system, as discussed in section 2.6.1. Previous research conducted in field (Table 2-6) highlights gold extraction levels of 50 to 98% at thiosulphate concentrations of 0.1 - 0.5 M, ammonia concentrations of 0.2 - 1 M, copper ion concentrations of 0.1 – 0.5 M, pH 9.5 - 10.5 and temperatures of 25 - 40°C. Numerous studies have reported gold extractions exceeding 70% at 0.1 M thiosulphate, 0.2 M ammonia, 0.03 M Cu(II) ion concentrations, pH 10.5 and 25°C, showing that the thiosulphate leaching process can produce satisfactory results at relative low initial reagent concentrations and mild conditions. However, a concise assessment of the thiosulphate consumption for insights into the economic feasibility of the process has not been established explicitly.

The kinetics of the ammoniacal thiosulphate leaching are adversely affected by the passivation of the gold surface due to the precipitation or adsorption of species contained in the feed. Some of these species include sulphur compounds such as tetrathionate, trithionate and sulphide which are produced inevitably through thiosulphate decomposition (Breuer & Jeffrey, 2000; Muir & Aylmore, 2002; Feng & Van Deventer, 2007; Aylmore et al., 2014). Furthermore, when using thiosulphate leaching for gold extraction from waste PCBs, the use of copper ion as the metal oxidant would have an adverse impact on downstream recovery processes such as resin adsorption due to its interference on the adsorptive process (Grosse et al., 2003; Chaparro et al., 2015; Dong et al., 2017). Jeon et al. (2019) further emphasised that the presence of copper would impede the leaching process by inducing re-deposition of the extracted gold ions through galvanically induced cementation.

Meanwhile, some studies have reported an increase in the leaching efficiency when extracting gold from full-size PCBs instead of PCB granules (Kasper & Veit, 2018; Ha et al., 2014; Tripathi et al., 2012; Kasper et al., 2011). It was suggested that since PCBs are designed with distinct metal layers, with the gold-nickel alloy layer on the outer side, any mechanical treatment and size reduction step will expectedly increase the surface area for gold leaching, but will also disrupt the PCB layer configuration and increase the contact area of competing metals with the liquid phase, thereby interfering with gold leaching.

However, the trade-off between the PCB size reduction and the preservation of the PCB layer configuration, in terms of thiosulphate consumption, was not established.

**Table 2-6: Studies on thiosulphate leaching of gold from waste PCBs**

| **Raw material** | **Reagents and Conditions** | **Metal Recovery** | **References** |
|---|---|---|---|
| MP-PCBs (0.12% Au, 35.1% Cu) | 0.12 M $S_2O_3^{2-}$, 0.2 M $NH_3$, 0.02 M $Cu^{2+}$, 25°C, 2h, 6.67% S/L ratio | 90% Au | (Ha et al., 2010) |
| Waste PCBs (0.014% Au, 0.08% Ag, 47.5% Cu) | 0.5 M $S_2O_3^{2-}$, 1.0 M $NH_3$, 0.2 M $Cu^{2+}$, 40°C, 48h, 8.89% S/L ratio | 98% Au, 93% Ag | (Ficeriová et al., 2011) |
| MP-PCBs (0.021% Au, 0.1% Ag, 56.68% Cu) | 0.1 M $(NH_4)_2S_2O_3$, 0.040 M $Cu^{2+}$, room temp, 8h, 10 g/L S/L ratio | 56.7% Au (ground PCB),<br>78.8% Au (full-size PCBs) | (Tripathi et al., 2012) |
| MP-PCBs | 0.1 M $S_2O_3^{2-}$, 0.3 M $NH_3$, 0.01 M $Cu^{2+}$, 30°C, pH 8.5-11.5, 4h, 1/25 S/L ratio<br>Full-size PCBs used | 50% Au | (Kasper & Veit, 2015) |
| PC-PCBs (21 g/t Au) | 0.3 M $S_2O_3^{2-}$, 0.38 M $NH_3$, 0.038 M $Cu^{2+}$, 23°C, pH 8.5-11.5, 6.73h, 10.79% S/L ratio | 92.2% Au | (Isildar et al., 2017) |
| MP-PCBs (142-700 g/t Au) | 0.12 M $(NH_4)_2S_2O_3$, 0.12 M $Na_2S_2O_3$<br>0.2M $NH_3$, 0.020 M $Cu^{2+}$, 30°C, pH 10, 4h, 1/25 S/L ratio<br>Full-size PCBs used | 70% Au with $Na_2S_2O_3$<br>75 Au with $(NH_4)_2S_2O_3$ | (Kasper & Veit, 2018) |
| MP-PCBs | 0.5 M $S_2O_3^{2-}$, 1.2 M $NH_3$, 0.04 M $Cu^{2+}$, 25°C, pH 10, 4h, 1/4 S/L ratio<br>0.1 M $Na_2SO_3$ | 95.3% Au | (Xiang et al., 2018) |
| MP-PCBs (453.4 g/t Au, 1968.9 g/t Ag, 237 kg/t Cu) | 0.7 M $S_2O_3^{2-}$, room temp, pH 10.5, 6h, 5% S/L ratio<br>No $Cu^{2+}$ ions added | 81% Au<br>88% Ag<br>32% Cu | (Gámez et al., 2019) |

* MP-PCBs: waste mobile phone printed circuit boards

* PC-PCBs: waste computer printed circuit boards

### 2.6.3 Thiosulphate Stabilization and Reagent Consumption

#### 2.6.3.1 Additives

Various additives have been used to stabilise thiosulphate in the leaching system and lower its consumption. Multiple studies have used humic acid (HA), sodium carboxymethyl (CMC), ethylenediaminetetraacetic acid (EDTA), sodium hexametaphosphate (SHMP), sulphite, sulphate, carbonate and chloride (Li & Kuang, 1998; Feng & Van Deventer, 2010; Feng & Van Deventer, 2011a; Feng & Van Deventer, 2011b; Senanayake, 2012; Aazami et al., 2014; Xu et al., 2015; Yang et al., 2015; Xu et al., 2017). The additives reduce the adverse effect of sulphide minerals on the leaching process by lowering the affinity of cupric ions for thiosulphate by complexation of the additive's functional groups with thiosulphate (Aazami et al., 2014; Yang et al., 2015; Xu et al., 2017). The effects of sulphite on the leaching process have been shown to reduce the consumption of thiosulphate by converting tetrathionate to thiosulphate in an alkaline environment (Guerra & Dreisinger, 1999; Senanayake, 2012; Xu et al., 2017). Sodium chloride was shown to improve gold leaching by inducing the formation of $\mathrm{AuCl_2^-}$ which enhanced the leaching kinetics (Li & Kuang, 1998). Phosphate and carbonate were reported to counteract the adverse effect of PbS due to $Pb(OH)_2$ precipitation (Senanayake, 2012). Satisfactory results were obtained by using SHMP, EDTA and CMC in low amounts in the thiosulphate leaching of gold from sulphide ores, as substantiated by Feng & Van Deventer (2010, 2011a, 2011b). Meanwhile, Xu et al. (2015) reported a reduction of thiosulphate consumption from 42.4 to 13.2% and increase in gold extraction from 72.7 to 81.4% when using humic acid as an additive in the gold extraction from a refractory calcined gold concentrate.

#### 2.6.3.2 Cobalt Oxidant

The use of cobalt instead of copper in ammonium thiosulphate leaching was first reported in a patent by Bin et al. (2016). This technique was used to extract gold from a quartz vein-type ore containing 5.60 g Au/t-ore, 5.33% Fe, 0.03% S, 0.03% Cu and 0.01% Pb. The inventors used a lixiviant solution consisting of 0.1 - 1.0 M $S_2O_3^{2-}$, 0.3 - 1.0 M $NH_3$ and 0.01 - 0.05 M $CoSO_4$ with a pulp concentration of 15 - 35%, pH 9 - 11, temperature of 45°C, stirring speed of 100 - 300 rpm and leaching time of 4 - 12 h. They reported a thiosulphate consumption reduction from 20 - 40 kg/t-ore to 8 kg/t-ore. However, the cost implications of replacing copper with cobalt in the leaching system were not established.

Furthermore, there is still no report of this technique applied to electronic waste. Considering that cobalt is more expensive than copper, proper economic evaluation of such a process on a pilot scale would be required to ascertain upgradability for industrial implementation.

### 2.6.3.3 Nickel Oxidant

The use of nickel ion as an alternative to copper ion for the stabilisation of thiosulphate was first reported by Arima et al. (2004). The researchers investigated the thiosulphate leaching of gold oxidised by nickel. The nickel-oxidised leaching of gold from a feed material containing 16 g/t Au and 0.2 mass% of Fe and C was found to achieve 95% gold extraction with 1.2 kg/t-solid of thiosulphate consumption in 24 hours at the optimum reagents combination of 0.0001 M $NiSO_4$, 0.05 M $(NH_4)_2S_2O_3$ and 0.5 M $NH_4OH$ at a pH of 9.5. This result was considered promising because of the conventional copper-thiosulphate leaching, at $Cu^{2+}$ concentrations from 0.0001 M to 0.001 M, incurred a thiosulphate consumption ranging between 3 to 21 kg/t-solid whereas the nickel-thiosulphate leaching, operating at $Ni^{2+}$ concentrations from 0.0001 to 0.005 M, resulted in thiosulphate consumptions of 1 to 5 kg/t-solid. Also, the researchers established the possibility of recovering gold from the nickel-thiosulphate pregnant leach solution by cementation and resin adsorption. Although the recovery of gold from nickel-assisted leaching incurred 30-50% nickel co-precipitation with gold, the overall cementation process with zinc powder, involving four stages of solution recycling with nickel addition, could yield 95% gold extraction with 1-3 kg/t-solid of thiosulphate consumption. Furthermore, the $[\mathrm{Ni(NH_3)_6}]^{2+}$ complex was found to be more stable thermodynamically than $[\mathrm{Ni(S_2O_3)_2}]^{2-}$ in solution, and would not co-adsorb alongside gold on anion-exchange resins, and thus did not interfere with the resin adsorption process in the nickel-thiosulphate system compared to the copper-thiosulphate system (Arima et al., 2003). Despite its significance in gold extraction from gold ore, there has been no report on the use of nickel as an oxidant gold leaching from waste PCBs.

The anodic and cathodic reactions involved in the nickel-thiosulphate leaching of gold are shown in equations (23) to (27). These reactions add up to the same overall reaction (14).
Nickelous oxide $\mathrm{Ni_3O_4}$, previously produced through the half-reactions (23) and (24), is reduced back to the nickel amine complex $\mathrm{Ni(NH_3)_6^{2+}}$ which, in turn, triggers the oxidation of gold, as per equations (25) and (26) (Arima et al., 2004).

$$3Ni(NH_3)_6^{2+} + OH^- \longrightarrow Ni_3O_4 + 18NH_3 + 4H_2O + 2e^- \qquad (23)$$

$$1/2\ O_2 + H_2O\ + 2e^- \ \longrightarrow\ 2OH^- \tag{24}$$

$$Ni_3O_4 + 18NH_3 + 4H_2O + 2e^- \ \longrightarrow\ 3Ni(NH_3)_6^{2+} + OH^- \tag{25}$$

$$2Au + 4NH_3 \ \longrightarrow\ 2Au(NH_3)_2^+ + 2e^- \tag{26}$$

$$Au(NH_3)_2^+ + 2S_2O_3^{2-} \ \longrightarrow\ Au(S_2O_3)_2^{3-} + 2NH_3 \tag{27}$$

Figure 2-7 illustrates the mechanism of the nickel-thiosulphate leaching of gold. Based on the electrochemistry of the nickel-ammonia-thiosulphate system (Figure 2-8), the $\mathrm{Ni_3O_4/Ni(NH_3)_6^{2+}}$ pair can be used to oxidise gold in a pH range of 9.5 to 10.5.

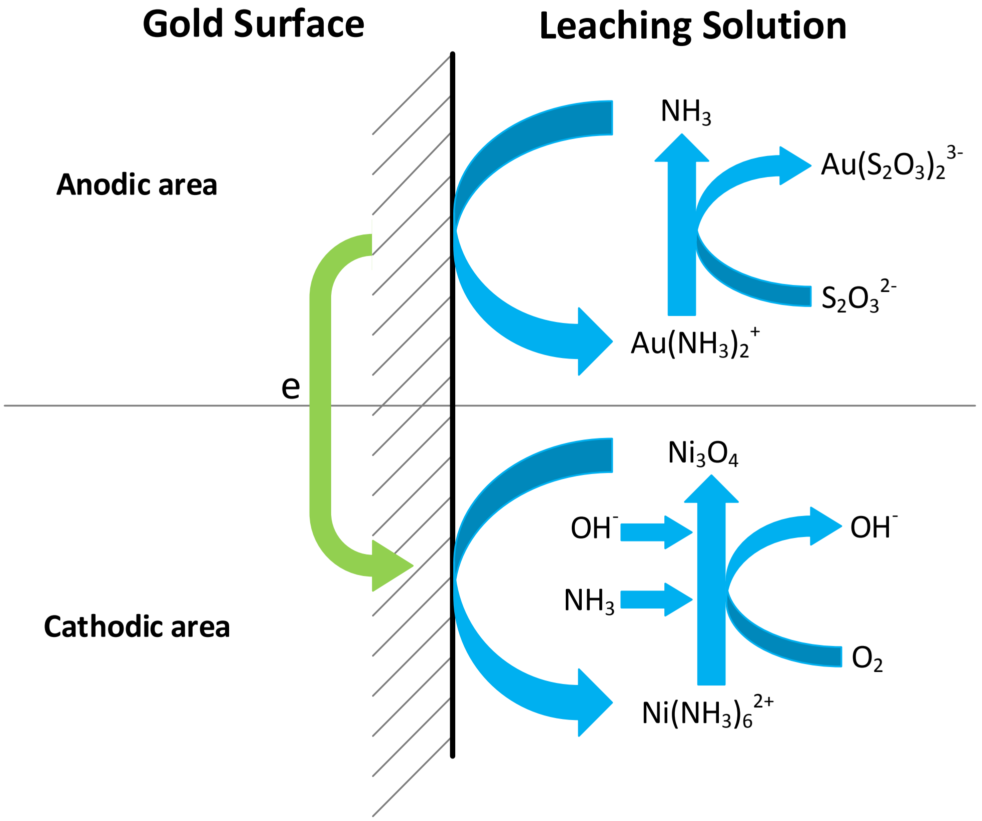


**Figure 2-7: Electrochemical-catalytic mechanism of the nickel-thiosulphate leaching of gold (Arima et al., 2004; Aylmore & Muir, 2001)**

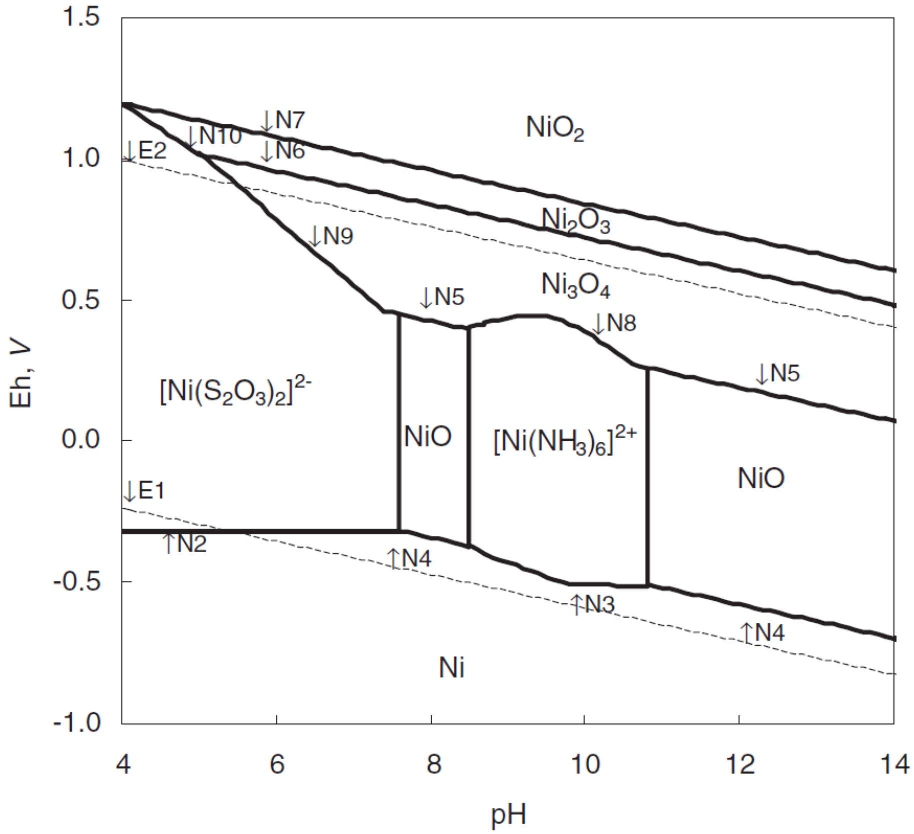


**Figure 2-8: Pourbaix diagram of the nickel-ammonia-thiosulphate system at low reagent concentrations [0.5 M thiosulphate, 0.5 M ammonia, 0.0005 M Ni] (Arima et al., 2004)**

## 2.7 Shrinking-Core Model and Mechanism of Leaching Process

The shrinking-core model (SCM) is a simple idealised model that has been successfully used to describe solid-liquid reactive systems, with application in leaching processes (Gbor & Jia, 2004; Othusitse & Muzenda, 2015). The model assumes that the reaction occurs at the outermost surface of the solid particle and progresses inwards while leaving behind a fully converted inert solid (Figure 2-9). This inert material is referred to as the ash layer. The unreacted material in the centre of the particle will thus shrink in size as the reaction proceeds (Levenspiel, 1999). The shrinking-core model can be applied to two types of particles: (i) shrinking particles (varying size) and (ii) unshrinking particles (constant size). The fundamental difference between these models, from a mechanistic standpoint, is that, as the reaction progresses, there is no ash formation in shrinking particles whereas unshrinking particles will incur the formation of this inert solid. The determination of the rate-limiting step of a solid-liquid reaction is dependent on this consideration.

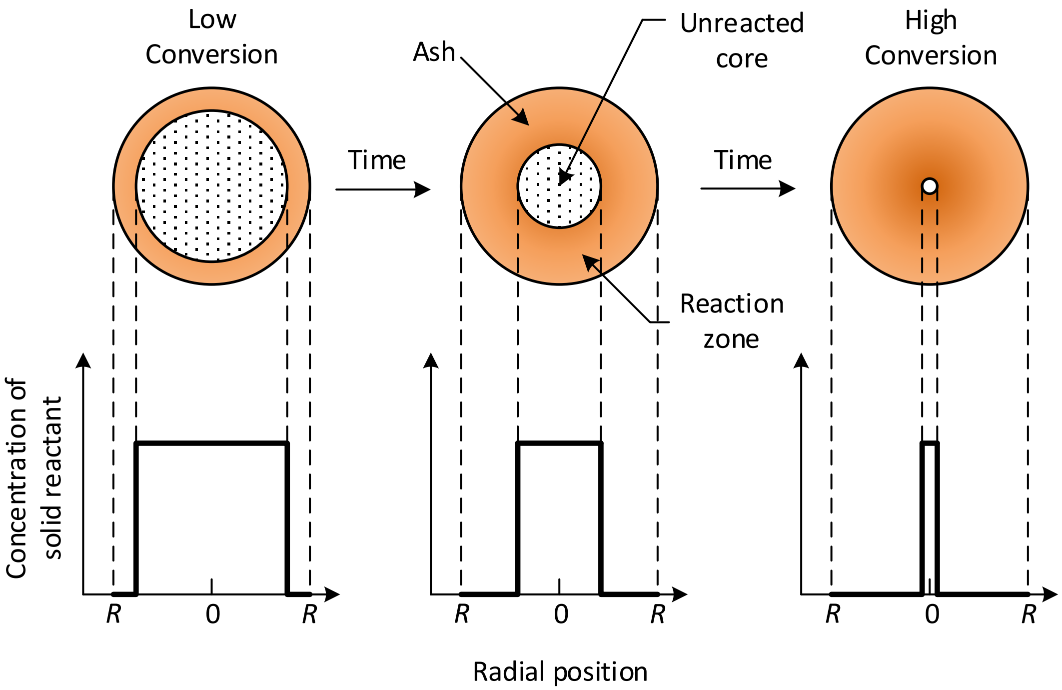


**Figure 2-9: Illustration of unreacted core shrinking as the reaction takes place from the outer layer (Levenspiel, 1999)**

Considering the following reaction between a solid A and surrounded by a fluid B:

$$A(f) + bB(s) \ \longrightarrow \ products \tag{28}$$

The model is developed by visualizing five basic steps occurring during the reaction (Figure 2-10):

Step 1: Diffusion of fluid reactant A through the film layer surrounding the particle to the surface of the solid.

Step 2: Penetration and diffusion of A through the blanket of ash to the surface of the unreacted core.

Step 3: Reaction of fluid A with solid at this reaction surface.

Step 4: Diffusion of fluid products through the ash back to the exterior surface of the solid.

Step 5: Diffusion of fluid products through the film layer back into the main body of the solution.

Therefore, a solid-fluid reaction can be controlled by fluid diffusion, ash diffusion and chemical reaction.

The resistance is known to change more significantly from one step to the other, and thus the rate-limiting step will be the one with the highest resistance. In some situations, it can be assumed that steps 4 and 5 involving products do not control the reaction significantly. Furthermore, considering particles shrinking in size while reacting with a fluid, no ash forms (Figure 2-11), and thus the solid-fluid reaction can proceed according to steps 1, 3 and 5.

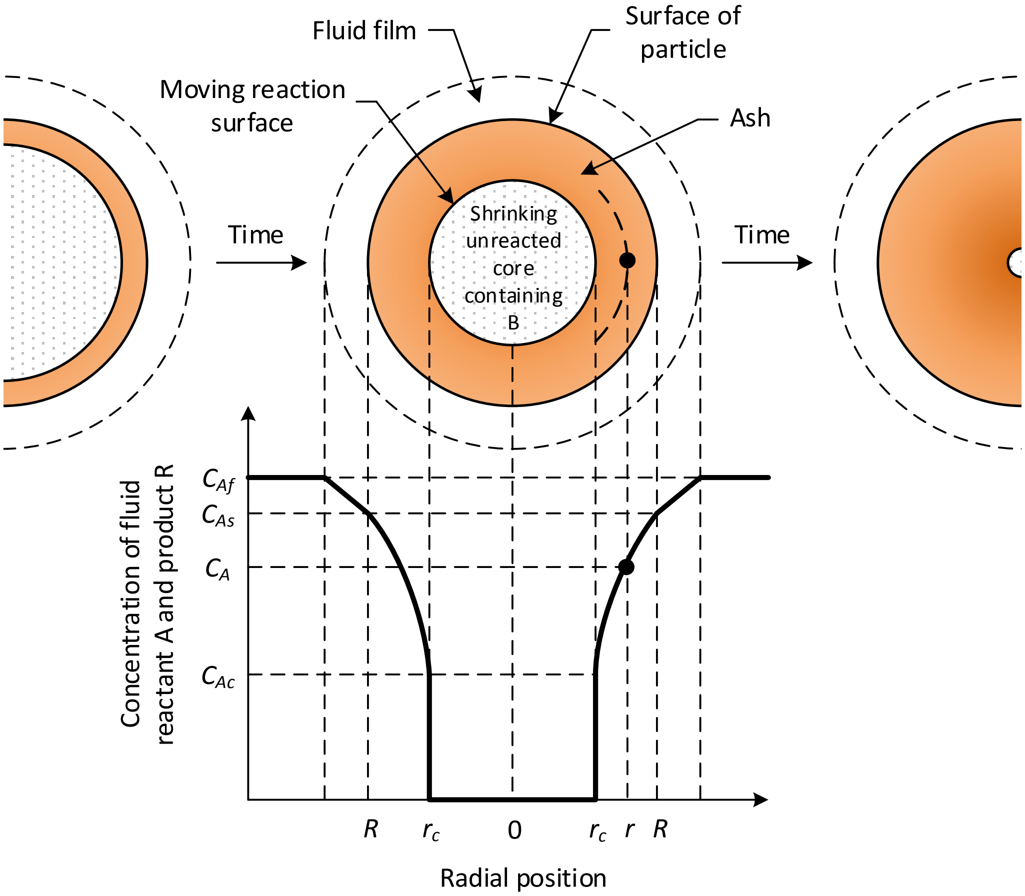


**Figure 2-10: Representation of concentration profiles of reactants and products for the reaction of fluid and solid with unchanging particle size (Levenspiel, 1999)**

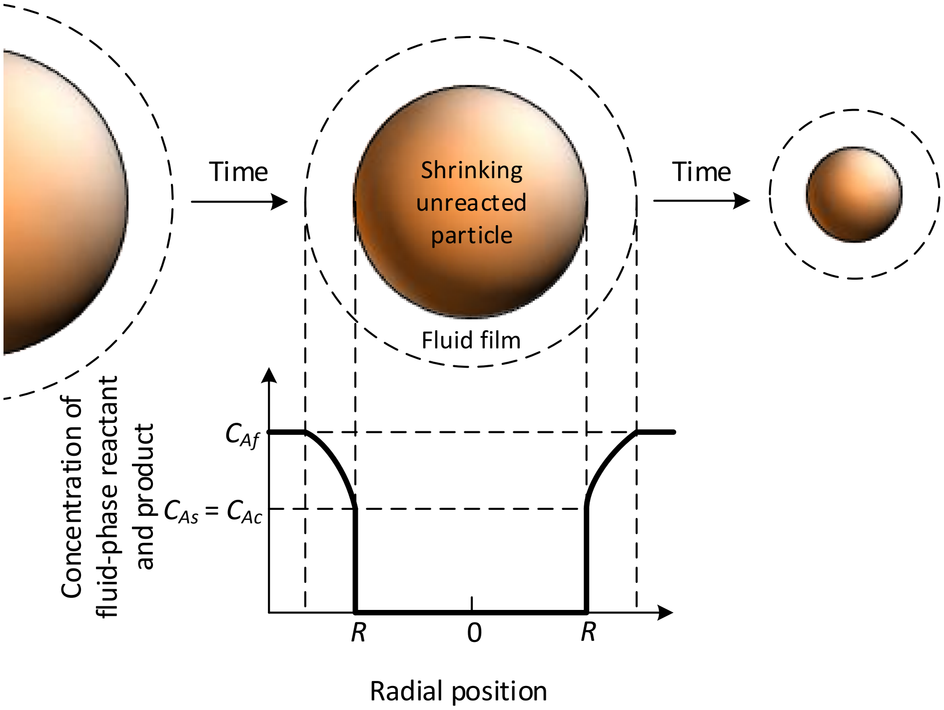


**Figure 2-11: Representation of concentration profiles of reactants and products for the reaction of fluid and solid with changing particle size (Levenspiel, 1999)**

The shrinking-core models outlined in Table 2-7 and plotted in Figure 2-12 are provided as conversion-time expressions for particles of spherical shape. $X$ represents conversion, $(1 - X)$ denotes the shrinking of the unreacted core, and $t/\tau$ is another means of expressing conversion in terms of reaction time $t$ and time for complete conversion $\tau$. $t/\tau$ is also referred to as the fractional time for total conversion. The shrinking-core model can thus be expressed in terms of the shrinking of the unreacted core and fractional time for full conversion. This is done to assist in modelling a solid-fluid reaction to determine the rate-limiting step. As such, experimental kinetic data (concentration change with time) is required along with an estimation of the time for complete conversion (Levenspiel, 1999). The mathematical derivations of the SCMs are provided in Appendix G (section G.6).

**Table 2-7: Shrinking-core model for shrinking and unshrinking particles (Levenspiel, 1999)**

| | **Sphere** | **Film Diffusion Control** | **Ash Diffusion Control** | **Reaction Control** |
|---|---|---|---|---|
| *Constant Size* | $X_B = 1 - \left(\frac{r_c}{R}\right)^3$ | $\frac{t}{\tau} = X_B$ (29)<br>$\tau = \frac{\rho_B R}{3bk_f C_{Af}}$ (30) | $\frac{t}{\tau} = 1 - 3(1 - X_B)^{2/3} + 2(1 - X_B)$ (31)<br>$\tau = \frac{\rho_B R^2}{6b\mathcal{D}_e C_{Af}}$ (32) | $\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$ (33)<br>$\tau = \frac{\rho_B R}{bk"C_{Af}}$ (34) |
| *Shrinking Sphere* | **Small particle**<br>Stokes regime | $\frac{t}{\tau} = 1 - (1 - X_B)^{2/3}$ (35)<br>$\tau = \frac{\rho_B R_0^2}{2b\mathcal{D}C_{Af}}$ (36) | Not applicable | $\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$<br>$\tau = \frac{\rho_B R_0}{bk"C_{Af}}$ |
| | **Large particle**<br>Turbulent regime | $\frac{t}{\tau} = 1 - (1 - X_B)^{1/2}$ (37)<br>$\tau = (const)\frac{R_0^{3/2}}{C_{Af}}$ | Not applicable | $\frac{t}{\tau} = 1 - (1 - X_B)^{1/3}$<br>$\tau = \frac{\rho_B R}{bk"C_{Af}}$ |

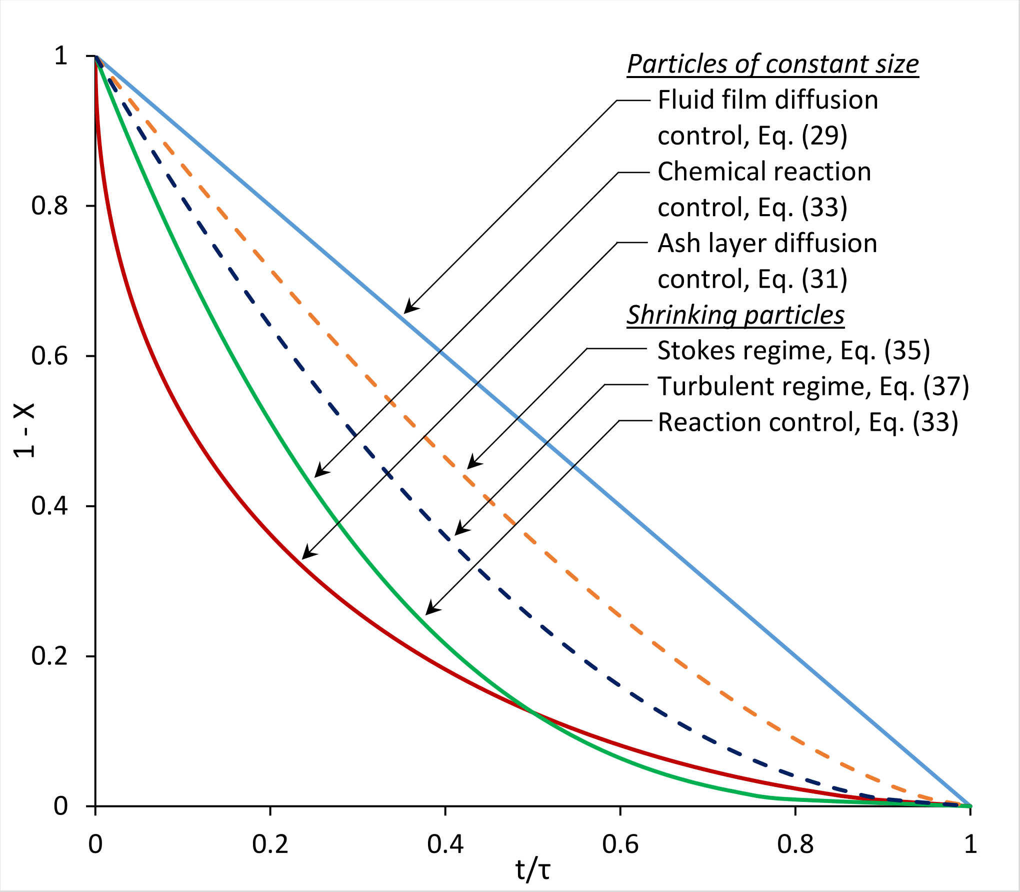


**Figure 2-12: Progression of a solid-fluid reaction in terms of fractional time for complete conversion: SCM for shrinking and unshrinking particles (Levenspiel, 1999)**

The conversion-time expressions assume that a single mechanism or rate-limiting step governs the solid-fluid reaction. However, in actual cases, the reaction can progress with variations in the significance of the individual reaction control stages, with possible combinations of the different driving forces (Levenspiel, 1999).

# CHAPTER 3

## RESEARCH METHODOLOGY

# CHAPTER 3 : RESEARCH METHODOLOGY

This chapter outlines the experimental methods and procedures used in this study. Descriptions of the experimental setup and instrumentation are also provided.

## 3.1 Research Design

This research involved the use of a quantitative technique to achieve its objectives. The experiments were grouped into three categories, as shown in Figure 3-1: PCB size reduction, metal characterisation and leaching experiments. The leaching experiments consisted of acid pre-treatment for copper removal and ammonium thiosulphate leaching for gold extraction.

### 3.1.1 PCB Size Reduction

The PCBs were removed from mobile phones through dismantling. After that, they were subjected to a size reduction process involving cutting and crushing. The PCBs were first cut to a 10 x 10 mm size, then crushed using a hammer mill to further reduce their size to < 3 mm. After crushing, the actual particle size distribution was determined with the aid of mechanical sieves of predetermined sizes.

### 3.1.2 PCB Characterization and Aqua Regia Leaching

The metal content of the mobile phone PCBs was determined by subjecting the crushed PCBs to aqua regia leaching. The metal characterisation was limited to copper and gold only. The aqua regia solution was prepared by mixing nitric acid and hydrochloric acid in a molar ratio of 1:3. To prepare 100 mL of lixiviant, 55 wt% $HNO_3$ and 32 wt% HCl stock solutions were used. 79.4 mL of HCl solution was first transferred into an empty flask, followed by the dropwise addition of a total $HNO_3$ solution volume of 20.6 mL. The lixiviant was then heated to the set point of 60°C before slowly adding 5 g of ground PCB and allowing the reaction to proceed for 24 hours. No stirring was required during aqua regia leaching since the reaction mixture already induced turbulence. The aqua regia preparation and leaching process were carried out under a fume hood with all the necessary safety precautions related to acid handling. The leaching process was replicated five times, and metal analyses were conducted with collected samples using the AAS.

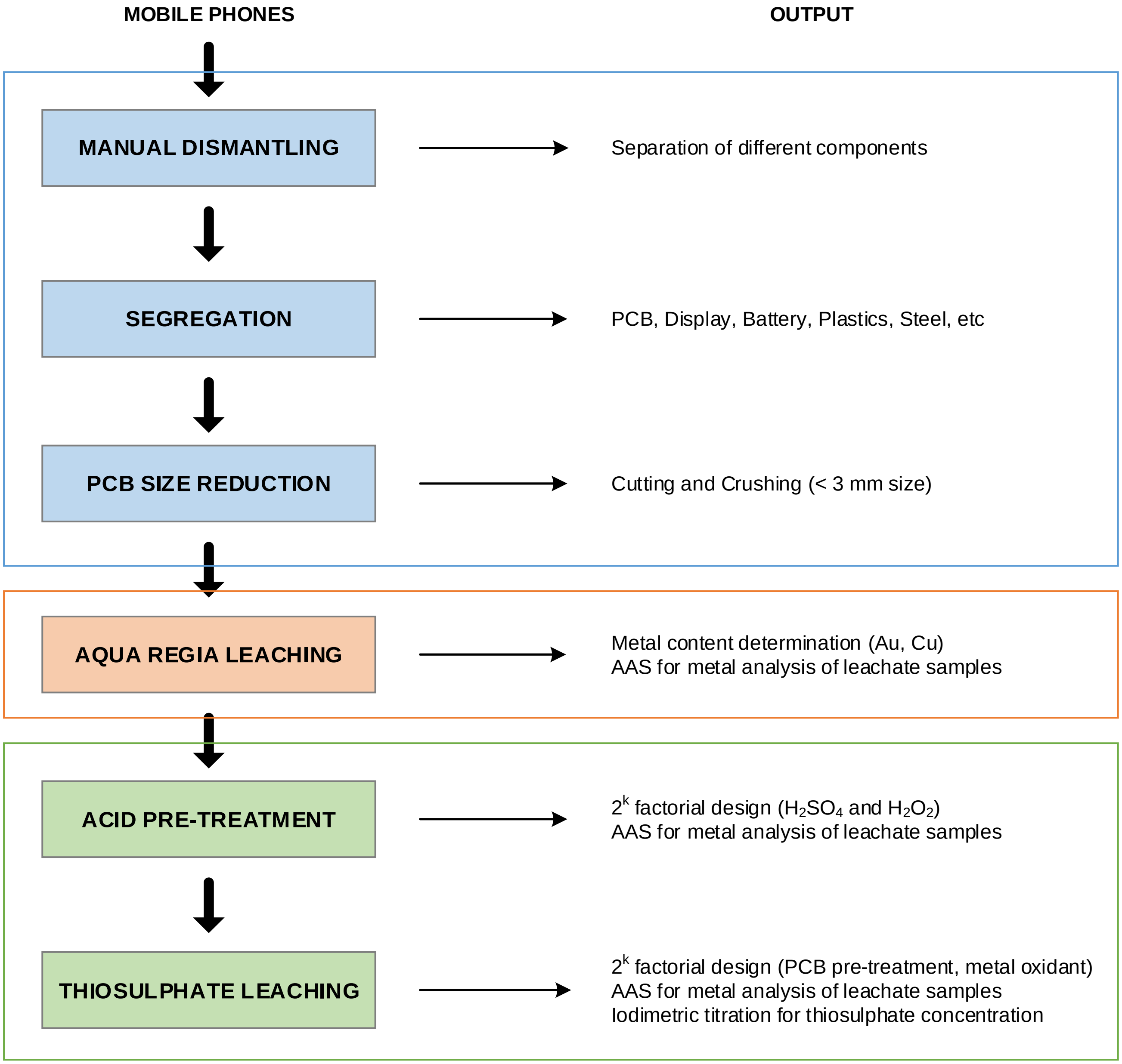


**Figure 3-1: Flow diagram of the research methodology**

### 3.1.3 Acid Pre-treatment

*Experimental Conditions*

The acid pre-treatment (leaching) experiments were carried out according to a $2^k$ factorial design (Table 3-1) consisting of two numerical factors (k = 2), namely sulphuric acid concentration and hydrogen peroxide concentration, and the factor levels were 2 M and 3 M (Birloaga et al., 2013; Behnamfard et al., 2013). The copper extraction and gold extraction were the responses investigated in the acid pre-treatment. Each experimental run was replicated twice to test for experimental repeatability and, more importantly, to assess factor interactions. The other parameters such as pulp density, reaction time, stirring speed and temperature were kept constant, as shown in Table 3-2.

**Table 3-1: Factorial experimental design of acid pre-treatment**

| | Factor 1 | Factor 2 | Response 1 | Response 2 |
|---|---|---|---|---|
| Run | $H_2SO_4$ (M) | $H_2O_2$ (M) | Cu Extraction (%) | Au Extraction (%) |
| 1 | 2 | 3 | | |
| 2 | 3 | 2 | | |
| 3 | 2 | 3 | | |
| 4 | 3 | 3 | | |
| 5 | 3 | 2 | | |
| 6 | 3 | 3 | | |
| 7 | 2 | 2 | | |
| 8 | 2 | 2 | | |

**Table 3-2: Fixed conditions used in acid pre-treatment (Birloaga et al., 2013; Behnamfard et al., 2013)**

| Pulp density (g/L) | Temp (°C) | Time (h) | Stirring Speed (rpm) |
|---|---|---|---|
| 50 | 25 | 3 | 350 |

*Experimental Procedure*

The acid leaching experiments were conducted in the jacketed reactor as shown in the experimental rig setup in Figure 3-2. The lixiviant solution was prepared by transferring a pre-determined volume of deionized water to the reactor, followed by the dropwise addition of the required amount of $H_2SO_4$.

The selected volume of $H_2O_2$ was then added in small quantities while gently stirring the mixture. The temperature of the lixiviant solution was allowed to stabilise at 25°C before adding PCBs to the mixture in a slow manner. The reaction was carried out under the fume hood for 3 hours. Samples were collected every 30 minutes for metal analysis (Cu and Au) by AAS. At the end of the experiment, the solid residue was filtered, dried and its mass was recorded.

### 3.1.4 Ammonium Thiosulphate Leaching

*Experimental Conditions*

The ammonium thiosulphate (ATS) leaching experiments were designed following a $2^k$ factorial design (Table 3-3) consisting of two categorical factors (k = 2), namely PCB pre-treatment and metal oxidant. The PCB pre-treatment factor had two levels: (i) without acid pre-treatment (w/o AP) and (ii) with acid pre-treatment (with AP). The acid pre-treatment was carried out at the optimum reagent combination. The metal oxidant had two levels: (i) copper and (ii) nickel. The reagent concentrations (ATS, ammonia, metal oxidant) and other parameters were fixed, as shown in Tables Table 3-4 and Table 3-5. The gold extraction and thiosulphate consumption were the responses investigated in the ATS leaching.

**Table 3-3: Factorial experimental design of ammonium thiosulphate leaching**

| | Factor 1 | Factor 2 | Response 1 | Response 2 |
|---|---|---|---|---|
| Run | PCB Pretreatment | Metal Oxidant | Au Extraction (%) | ATS Consumption (kg/t-PCB) |
| 1 | w/o AP | Ni | | |
| 2 | with AP | Cu | | |
| 3 | with AP | Ni | | |
| 4 | with AP | Ni | | |
| 5 | with AP | Cu | | |
| 6 | w/o AP | Cu | | |
| 7 | w/o AP | Ni | | |
| 8 | w/o AP | Cu | | |

**Table 3-4: Fixed conditions used in copper-thiosulphate leaching (Petter et al., 2015; Kasper & Veit, 2015; Tripathi et al., 2012; Ha et al., 2010)**

| Pulp density (g/L) | ATS (M) | $NH_3$ (M) | $CuSO_4$ (M) | Temp (°C) | pH | Time (h) | Stirring Speed (rpm) |
|---|---|---|---|---|---|---|---|
| 50 | 0.1 | 0.2 | 0.03 | 25 | 10.5 | 6 | 350 |

**Table 3-5: Fixed condition used in nickel-thiosulphate leaching (Petter et al., 2015; Kasper & Veit, 2015; Tripathi et al., 2012; Ha et al., 2010)**

| Pulp density (g/L) | ATS (M) | $NH_3$ (M) | $NiSO_4$ (M) | Temp (°C) | pH | Time (h) | Stirring Speed (rpm) |
|---|---|---|---|---|---|---|---|
| 50 | 0.1 | 0.2 | 0.03 | 25 | 10.5 | 6 | 350 |

*Experimental Procedure*

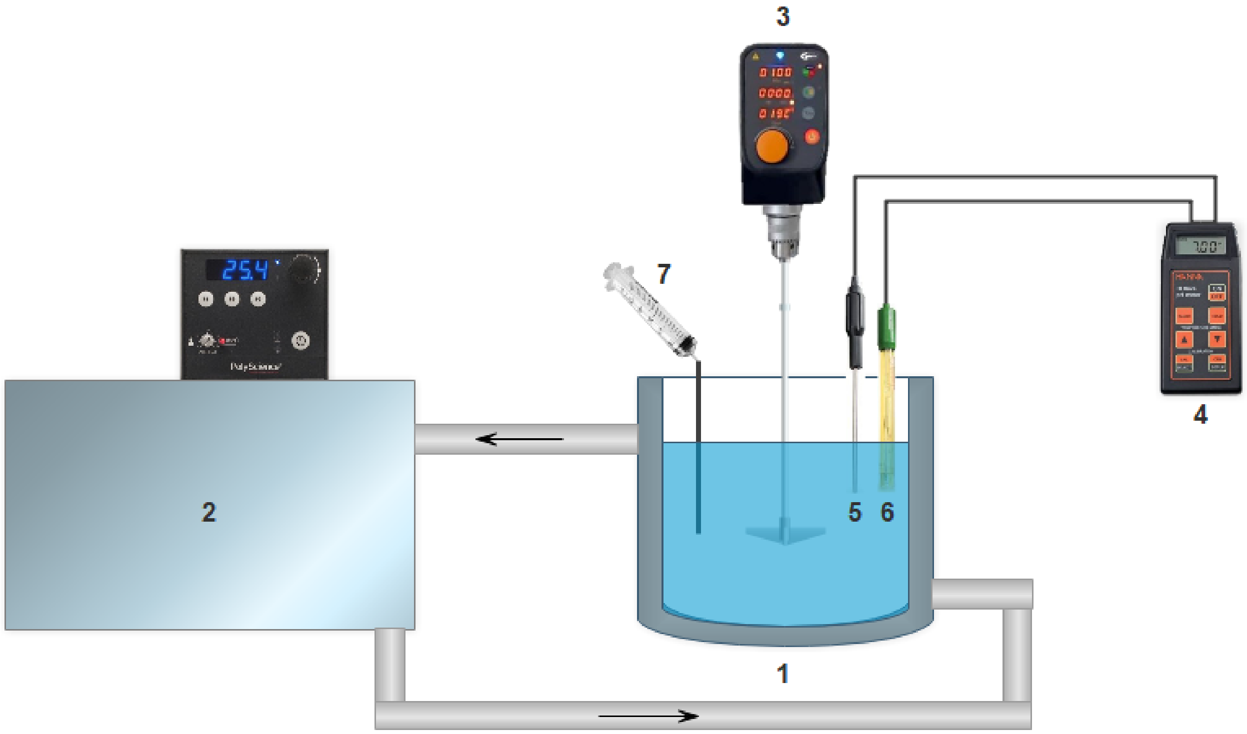
The ATS leaching experiments were conducted in the same jacketed reactor described in Figure 3-2. The lixiviant solution was prepared by transferring the pre-determined volume of deionised water to the reactor, followed by the required reagent quantities. For the copper-thiosulphate leaching system, the order of reagent addition was copper(II) sulphate, ammonium hydroxide and ammonium thiosulphate. For the nickel-thiosulphate leaching system, the order of reagent addition was nickel(II) sulphate, ammonium hydroxide and ammonium thiosulphate. Atluri (1987) suggested that this order of reagent addition aided in preventing unwanted side reactions and the formation of precipitation products during the lixiviant preparation, which would ultimately impede the gold leaching. The PCBs were then added, and the leaching process was allowed to proceed for 6h, with the temperature and pH maintained at 25°C and 10.5, respectively. The pH was controlled throughout the experimental runs using 10% NaOH and 10% $H_2SO_4$ solutions. For ATS leaching experimental runs involving acid pre-treatment, the acid leaching step was first carried out at the optimum reagent combination ($H_2SO_4$ and $H_2O_2$) and fixed conditions shown in Table 3-2. After that, the solid residue was filtered, dried and weighed before subjecting it to the ammonium thiosulphate leaching step. Samples were collected every 60 minutes for gold analysis by AAS and thiosulphate analysis by iodimetric titration.

### 3.1.5 Iodimetric Titration of Thiosulphate

The thiosulphate consumption in the ATS leaching (with copper and nickel oxidants) was determined by iodimetric titration as outlined by Arima et al. (2004). A 20 mL leachate sample was acidified with 10% v/v $H_2SO_4$ to a pH range of 7 - 7.5 prior to titration against a solution consisting of 5 mL of 0.05M (0.1N) iodine to which 2 mL of 2g/L starch solution and 2 mL of 5% acetate buffer solution (pH 5.5) were added. Starch was used as the indicator, and the endpoint of the titration was observed when the colour changed from dark brown to milky-white in the copper-thiosulphate leaching, and from dark brown to colourless for the nickel-thiosulphate leaching.

## 3.2 Experimental Setup and Instrumentation

The experimental setup used in the leaching studies is depicted in Figure 3-2. It included a 1-Liter jacketed reactor connected to a thermostatic water bath for temperature control of the reaction mixture. Mixing was achieved with the aid of a DragonLab OS20-S overhead stirrer. The pH of the leaching medium was monitored with a Hanna HI 8424 pH meter linked to the reactor through its temperature and pH probes. This pH meter was also used to monitor the reaction temperature. A Perkin-Elmer 3300 AAS instrument was used for the metal analysis of the leachate samples.



1. Jacketed reactor
2. Thermostatic water bath
3. Overhead stirrer
4. pH meter
5. Temperature probe
6. pH probe
7. Cylinder for sampling

**Figure 3-2: Schematic diagram of the leaching experimental setup**

## 3.3 Materials

All the chemicals (analytical grade) listed in this section were supplied by Merck, B & M Scientific and Cleansafe Labs.

- Nitric acid (55%)
- Hydrochloric acid (32%)
- Sulphuric acid (98%)
- Hydrogen peroxide (30%)
- Ammonium hydroxide (25%)
- Sodium hydroxide
- Sodium acetate
- Acetic acid (glacial, > 99%)
- Ammonium thiosulphate
- Copper(II) sulphate pentahydrate
- Nickel(II) sulphate hexahydrate
- Iodine (0.1 N)
- Soluble starch.

# CHAPTER 4

## RESULTS AND DISCUSSION

# CHAPTER 4 : RESULTS AND DISCUSSION

## 4.1 Metal Content of Mobile Phone PCBs

The metallic composition of the mobile phone PCBs was determined by aqua regia leaching, as detailed in chapter 3. Aqua regia leaching has been reported extensively in the existing literature as a method to estimate the metal content of a solid with relatively low levels of uncertainty. This mixture of hydrochloric acid and nitric acid in a molar ratio of 3:1 is known to dissolve most base and precious metals (Kasper & Veit, 2015; Vats & Singh, 2015).

**Table 4-1: Metal content of mobile phone PCBs**

| *Metal* | *Range* | *Average* | *units* |
|---|---|---|---|
| Cu | 43.53 - 48.07 | 46.18 | wt% |
| | 453.3 - 480.7 | 461.8 | kg/ton-PCB |
| Au | 0.0456 - 0.0607 | 0.0524 | wt% |
| | 456 - 607 | 524 | g/ton-PCB |

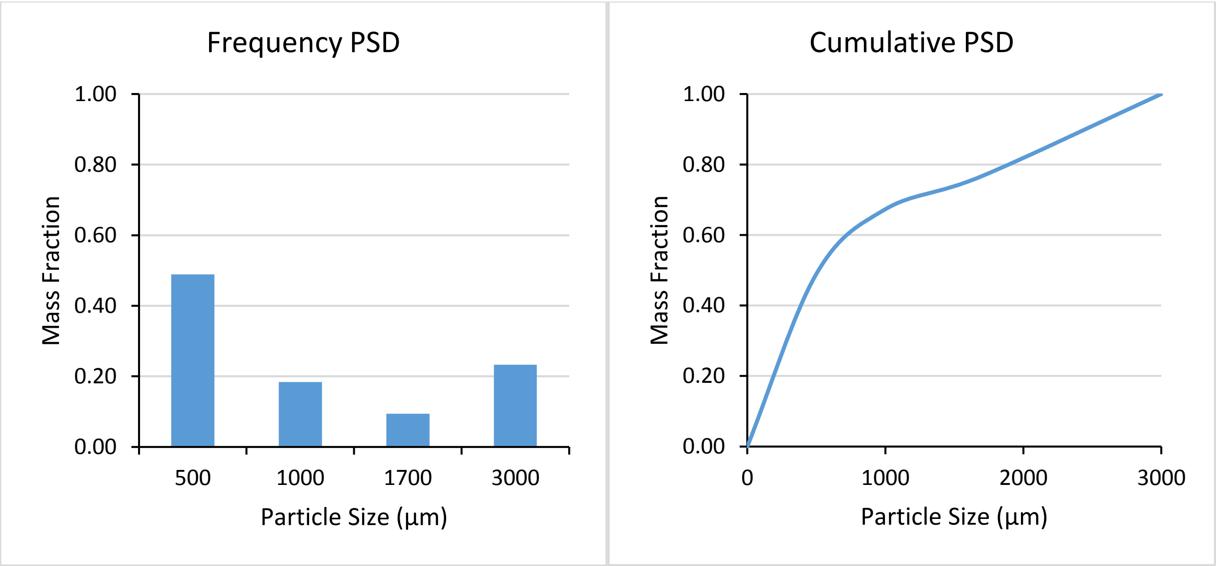
The gold and copper content of the mobile phone PCBs used in this research are provided in Table 4-1. The concentration ranges were found to be in accordance with the literature (Table 2-1). Copper was found to contribute to approximately 46.18 wt% of PCBs, or 461.8 kg/ton-PCB, almost half the total PCB mass. The average gold content was found to be 0.0524% or 524 g/ton-PCB. The amounts of gold and copper found in mobile phone PCBs are significantly large compared to naturally occurring minerals, as previously discussed (section 1.1), thus providing an economic incentive for the metallurgical treatment of waste mobile phones, and e-waste in general (Grosse et al., 2003; Montero et al., 2012; Cui & Anderson, 2016).

This research was concerned with mitigating the deleterious effect of copper, the most predominant base metal in mobile phone PCBs, on the thiosulphate leaching efficiency in terms of reagent consumption and gold extraction. Furthermore, ammonium thiosulphate is known to have a significant thermodynamic affinity for gold compared to other precious metals found in mobile phones such as silver, platinum and palladium (Grosse et al., 2003). Therefore, the metal characterisation of PCBs was limited to gold and copper in this research.

## 4.2 Particle Size Distribution of Ground PCBs

The PCB preparation stage involved size reduction to the microns scale. The PCBs were subjected to crushing and milling to reduce their size to less than 3 mm (3000 µm). The particle size distribution (PSD) obtained in this stage is provided in Figure 4-1, on the frequency basis (a) and cumulative basis (b). The $D_{50}$ was found to be 529 µm, as determined from the cumulative PSD, indicating that, after the size reduction stage, 50% of the PCB mass consisted of particles less than 529 µm in size. The PCB particle size distribution used in this study was in agreement with previous research involving the same type of feed and lixiviant (Ficeriová et al., 2011; Tripathi et al., 2012; Behnamfard et al., 2013; Birloaga et al., 2013; Isildar et al., 2017).

In general, reducing the particle size has an advantageous effect of increasing the effective surface area for the reaction. Furthermore, it can disrupt the multi-layer configuration of PCBs thereby releasing the trapped gold and improving the copper removal by acid pre-treatment.

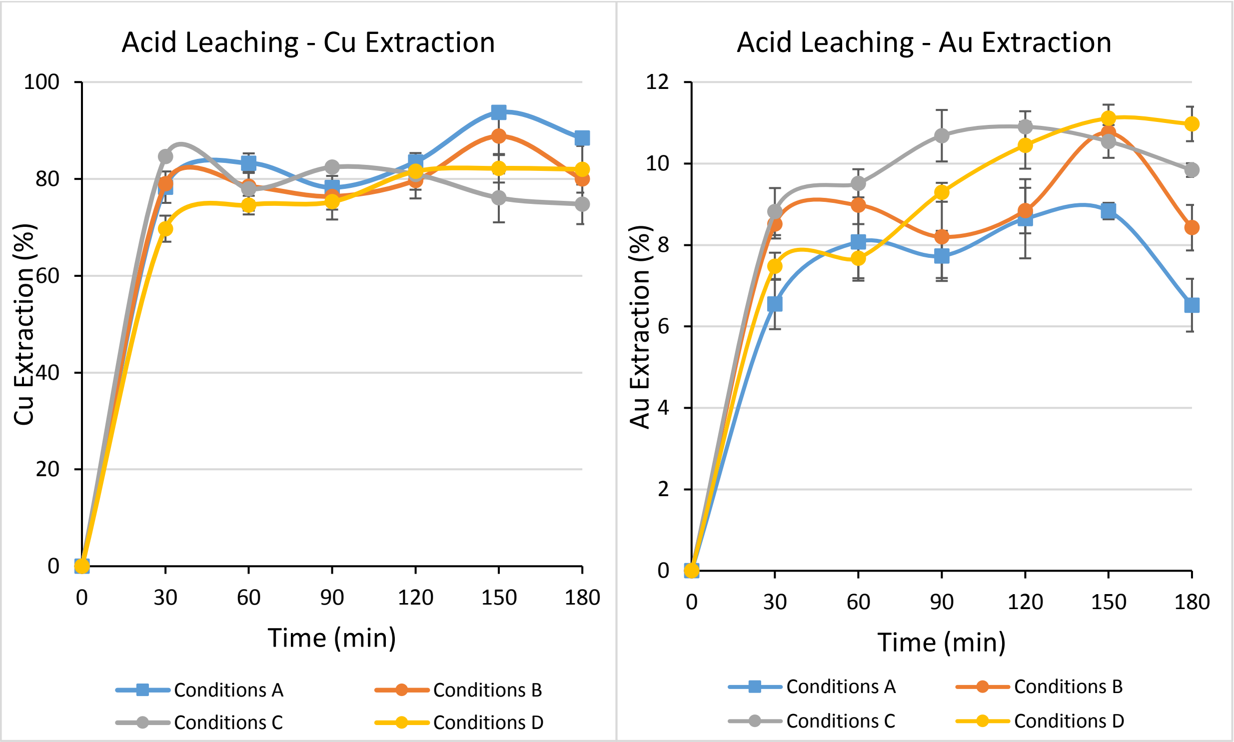


(a) (b)

**Figure 4-1: Particle size distribution of ground PCBs: (a) on frequency basis and (b) on cumulative basis**

## 4.3 Acid Pre-treatment

Figure 4-2(a) depicts the copper extraction profiles obtained at the four leaching conditions investigated. The factor combinations are provided in Table 4-2. It is apparent that the variability in copper extraction in all four conditions was not distinguishable up to 120 min of leaching time, with the metal extraction ranging from 70% and 85% between 30 min and 120 min. The variability in copper extraction was more apparent towards the end of the leaching process. The same observation was made for the gold extraction in Figure 4-2(b). The optimum factor combination that maximised copper extraction and minimised gold extraction was found to be 2 M $H_2SO_4$ and 3 M $H_2O_2$, yielding Cu and Au extractions of 93.72% and 8.83%, respectively in 150 min (Figure 4-3). More insight into the effect of sulphuric acid and hydrogen peroxide concentration variations on the copper and gold extraction was achieved by statistical means, as detailed in section 4.3.1.



(a) (b)

**Figure 4-2: Metal extraction by acid pre-treatment at four treatment combinations [50g/L pulp density, 350 rpm stirring speed, 25°C temperature, 3h reaction time]: (a) copper extraction and (b) gold extraction**

**Table 4-2: Factor combinations in acid pre-treatment**

| *Conditions* | *$H_2SO_4$ [M]* | *$H_2O_2$ [M]* |
|---|---|---|
| A | 2 | 3 |
| B | 3 | 2 |
| C | 3 | 3 |
| D | 2 | 2 |

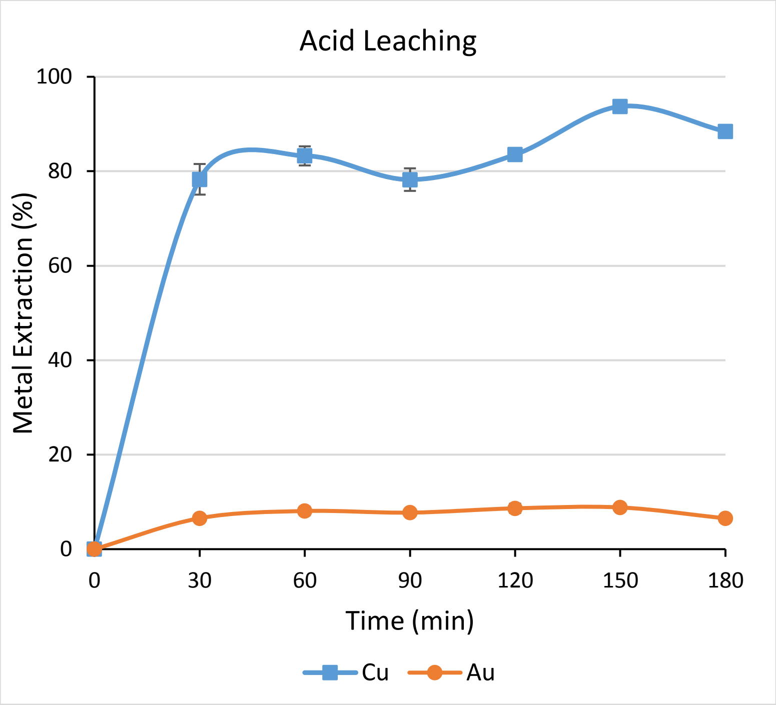


**Figure 4-3: Metal extraction by acid pre-treatment at best conditions: 2M $H_2SO_4$, 3M $H_2O_2$ [50g/L pulp density, 350 rpm stirring speed, 25°C temperature, 3h reaction time]**

In general, all runs achieved copper extractions exceeding 70% within the first hour of acid leaching, indicating the expected affinity of the acid solution for copper as a base metal. On the other hand, the gold extraction was capped at less than 12% irrespective of the conditions used, indicating a lower affinity of the acid lixiviant for gold. This property was exploited during the acid pre-treatment of PCBs to maximise the extraction of copper and minimise the extraction of gold, and to achieve a significant e-waste mass reduction.

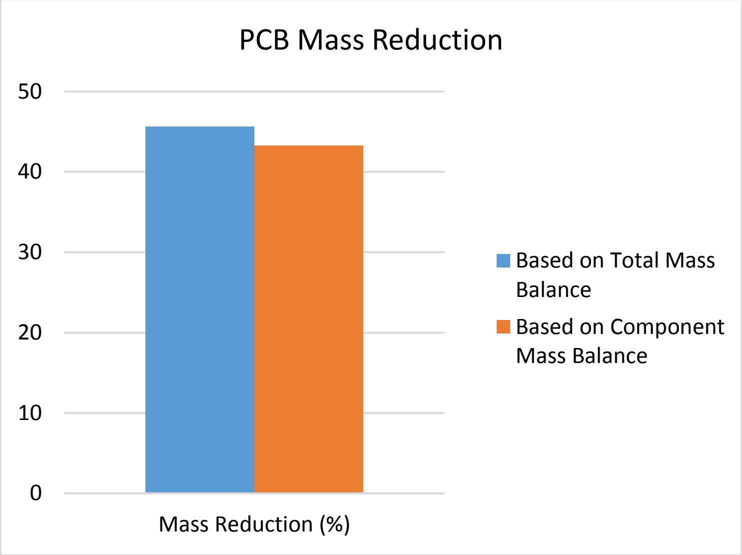


**Figure 4-4: Mobile phone PCB mass reduction after acid pre-treatment at best conditions: 2M $H_2SO_4$, 3M $H_2O_2$ [50g/L pulp density, 350 rpm stirring speed, 25°C temperature, 3h reaction time]**

An analysis of the material balance performed on the acid pre-treatment stage indicated that there was an agreement between the PCB mass reductions calculated from the total mass balance and component mass balance (Cu and Au extractions), as illustrated in Figure 4-4. This indicated that the PCB mass reduction achieved in acid leaching was mostly attributed to the copper extraction. This observation was further supported by the fact that any other base metals such as iron and aluminium that could have been dissolved in the acid pre-treatment stage did not contribute significantly to the overall PCB mass reduction due to their low occurrences in the mobile phone PCBs.

**Table 4-3: Metal content of PCBs before and after acid pre-treatment**

| *Metal* | *Before AP** | *After AP* | *units* |
|---|---|---|---|
| Cu | 46.18 | 5.11 | wt% |
| | 461.8 | 51.1 | kg/ton-PCB |
| Au | 0.0524 | 0.0842 | wt% |
| | 524 | 842 | g/ton-PCB |

*AP: acid pre-treatment

Table 4-3 shows the metal content of PCBs before and after acid pre-treatment. The copper content decreased from 461.8 kg/ton-PCB to 51.1 kg/ton-PCB, whereas the gold content increased from 524 g/ton-PCB to 842 g/ton-PCB, indicating a 60.8% gold concentration (beneficiation) of PCBs by acid pre-treatment. This is deemed beneficial for the subsequent gold extraction process by virtue of eliminating the interference on thiosulphate leaching brought about by an excessive initial amount of copper in the PCBs.

### 4.3.1 Statistical Analysis of Acid Pre-treatment Results

#### 4.3.1.1 Assumptions and Considerations for the t-Test and ANOVA

The experimental repeatability test was carried out by determining the closeness of the results of each experimental run and the corresponding duplicate. This was achieved by using a *two-sample t-test with matched samples*. The samples (run and duplicate) were matched because the data points were collected at equal time intervals. The null hypothesis $H_0$ for this t-test was that the two samples, i.e. experimental results of the run and duplicate, were indicative of the same experimental conditions (Montgomery, 2017). The null hypothesis for this test can also be expressed as follows:

- The two samples (data sets) have the same probability distribution.
- The two samples belong to the same population.

The *two-factor ANOVA (analysis of variance) with replication* was carried out to investigate the main factor effects and their interactions. The duplicates are specifically included to provide insights into factor interactions (DeCoursey, 2003). Finally, the *estimated marginal means* were used to add emphasis to the effect sizes of the factors investigated. The null hypothesis $H_0$ of ANOVA was that the factor variations would have no significant impact on the response variables. The alternative or research hypothesis $H_a$ was that varying the factors would have a statistically significant effect on the response variables.

The following assumptions and considerations were upheld for the t-test and ANOVA to provide simplicity and practicality to the statistical analysis:

- The t-tests and ANOVAs were based on response means for each run (Montgomery, 2017).
- All samples were drawn from normally distributed overall populations.
- No post hoc testing was carried out for the ANOVA because the factors investigated in acid pre-treatment and ammonium thiosulphate leaching had two levels only. In general, post hoc tests, aimed at determining the most significant factors, are carried out for factors with more than two levels (Weinberg & Abramowitz, 2008).
- Performing multiple ANOVAs is known to be detrimental to the data analysis because it increases the experiment-wise error. However, for this research, two ANOVAs were carried out to accommodate two responses, i.e. Cu and Au extractions in acid pre-treatment, and Au extraction and thiosulphate consumption in ammonium thiosulphate leaching. Therefore, to maintain the experiment-wise error or type I error (alpha) at 0.05, the *Bonferroni correction* $\alpha = 1 - (1 - \alpha_1)(1 - \alpha_2) \ldots (1 - \alpha_3)$ was used, whereby the alpha value was adjusted to $\alpha_1 = \alpha_2 = 0.0253$ for both Anovas (Norman & Streiner, 2008).

The above assumptions and considerations were adopted for both the acid pre-treatment results and ammonium thiosulphate leaching results.

#### 4.3.1.2 Experimental Repeatability Test

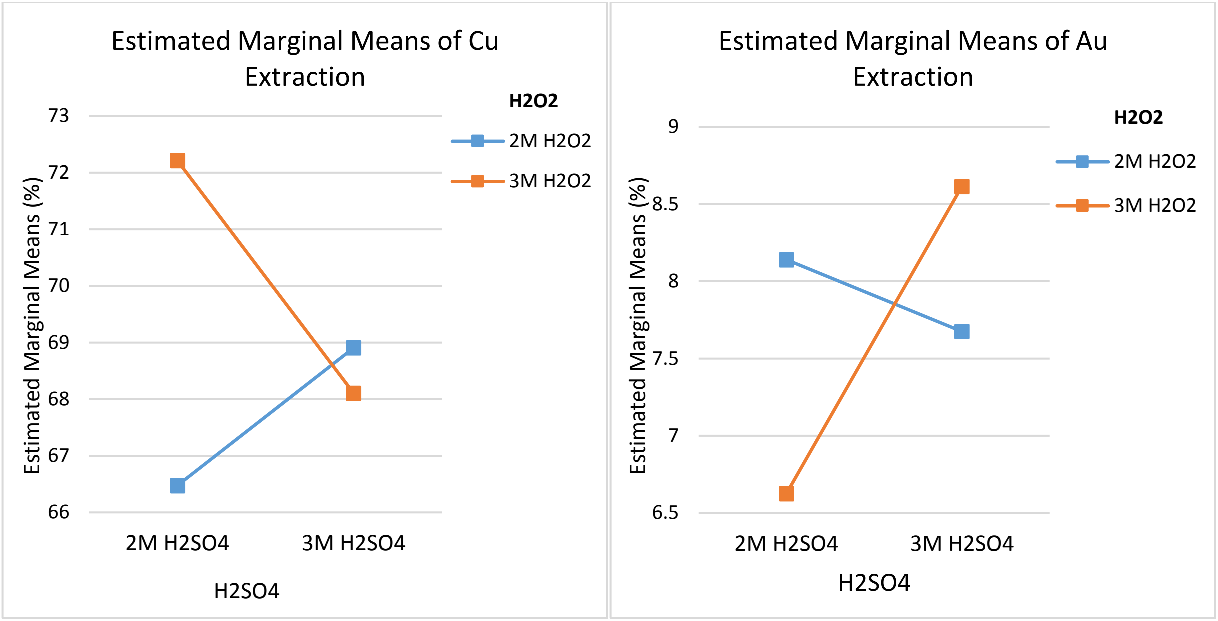
Detailed t-test results are tabulated in Appendix C (Tables Table C-7 and Table C-8). The alpha values for all four conditions and both responses were less than 0.05, indicating that there were no statistical grounds for rejecting the null hypothesis that the run and duplicate results were indicative of the same experimental conditions. The following two observations further supported this result: (i) the t-statistic was less than the t-critical in the t-distribution and (ii) the Pearson correlation coefficients were close to 1 for all conditions. Therefore, the experimental repeatability was confirmed statistically.

#### 4.3.1.3 Analysis of Variance (ANOVA) – Acid Pre-treatment

The ANOVA results for the acid pre-treatment experiments are fully provided in Appendix C (Table C-11). The factor significance and interactions can be assessed with the aid of three statistical variables, namely the p-value, F-statistic and partial eta squared. Furthermore, since a dual analysis of variance was carried out for the Cu extraction (response 1) and Au extraction (response 2), the alpha value was adjusted to 0.0253 to maintain the threshold of the overall experiment-wise error at 0.05.

The effect of varying $H_2SO_4$ concentration was not statistically significant for copper extraction but was significant for gold extraction based on the p-value and F-statistic which were found to be 0.208 and 2.255, respectively for copper extraction, and 0.006 and 28.115, respectively for gold extraction. The variation in $H_2O_2$ concentration, on the other hand, was found to be significant for Cu extraction and not statistically significant for Au extraction. Hydrogen peroxide was the oxidant involved in the acid leaching of copper and was thus expected to influence the extent of copper extraction. Therefore, based on these results, one can infer that varying sulphuric acid concentration had more statistical impact on the gold extraction, and varying hydrogen peroxide concentration had more effect on the copper extraction.

The most critical observation on the ANOVA results was the significant interaction between the sulphuric acid and hydrogen peroxide concentrations which was substantiated by the extremely low p-values (0.004 for Cu extraction and 0.001 for Au extraction), high F-statistics (34.214 for Cu extraction and 73.062 for Au extraction), and visually by the crossing of the estimated marginal means lines of the interaction plots in Figure 4-5. Elliott & Woodward (2014) suggested that when a significant interaction between factors has been established statistically, it becomes difficult to isolate the individual effects of each factor because the factors are too intertwined to be examined individually. The factor interaction was supported by the results plotted in Figure 4-2 which indicated that the variability in copper and gold extraction were not apparent for the major part of the leaching process irrespective of the investigated conditions, with the difference showing towards the end of acid pre-treatment process (after 120 min of leaching time).



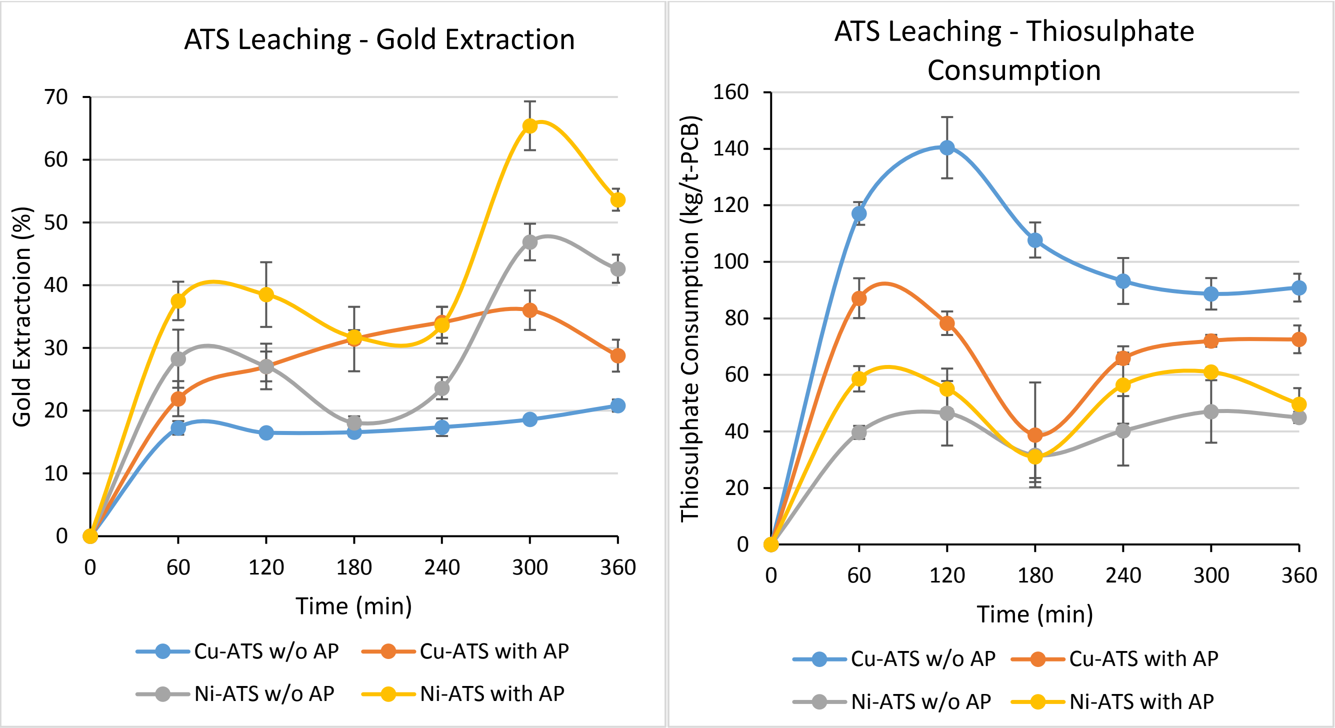
(a) (b)

**Figure 4-5: Factor interaction plots for acid pre-treatment: (a) Cu extraction and (b) Au extraction**

## 4.4 Ammonium Thiosulphate Leaching

### 4.4.1 Gold Extraction

Figure 4-6a depicts the gold extraction profiles obtained at the investigated conditions. The effects of acid pre-treatment and nickel oxidant are significantly noticeable. Firstly, replacing copper by nickel as the metal oxidant without any acid pre-treatment was found to improve the gold extraction drastically. The Au extraction reached a maximum of 18.61% with copper(II) ion as oxidant, and 46.89% with nickel(II) ion as oxidant after 5 hours of leaching time. Secondly, subjecting the mobile phone PCB to acid pre-treatment also improved the gold extraction extensively in both copper-thiosulphate (Cu-ATS) and nickel-thiosulphate (Ni-ATS) leaching systems. The acid pre-treatment increased gold extraction from 18.61% to 36.02% in Cu-ATS and from 46.89% to 65.41% in Ni-ATS after 5 hours of leaching time. Therefore, it was found that the acid pre-treatment improved the exposure of gold to the thiosulphate lixiviant by releasing it from copper trapping, and thus improving the kinetics of the leaching process. Finally, the combination of acid pre-treatment and nickel oxidant saw a significant improvement in gold extraction which increased from 18.61% in copper-thiosulphate leaching without acid pre-treatment to 65.41% in nickel-thiosulphate leaching with acid pre-treatment.



(a) (b)

**Figure 4-6: Ammonium thiosulphate leaching [0.1M ammonium thiosulphate, 0.2M ammonia, 0.03M copper sulphate, 0.03M nickel sulphate, pH 10, temperature 25°C, 6h reaction time, 350 rpm stirring speed]: (a) gold extraction and (b) thiosulphate consumption**

Therefore, the synergistic effect of combining these two factors was that the gold exposure to the lixiviant was improved and the Ni-ATS leaching system was more stable and efficient thermodynamically, and thus improved the kinetics of the leaching process.

A more detailed statistical assessment of the factor effect sizes and interaction between PCB pre-treatment and metal oxidant is provided in section 4.4.3.2.

### 4.4.2 Ammonium Thiosulphate Consumption

The ammonium thiosulphate consumption profiles obtained in this research are provided in Figure 4-6b. The first observation was that the copper-thiosulphate leaching system without acid pre-treatment incurred the highest thiosulphate consumption, reaching a peak value of 140.4 kg/ton-PCB before stabilising around 90.9 kg/t-PCB, although the resulting gold extraction reached a maximum of 20.82% only. The thermodynamics of Cu-ATS leaching outlined in chapter two (section 2.6.1) indicated that side reactions involving copper and thiosulphate, leading to the degradation of thiosulphate to tetrathionate, are among the main causes for this phenomenon.

The ATS consumption was found to improve significantly with the use of Ni(II) ion in place of Cu(II) ion. With untreated PCBs, the stabilised lixiviant consumption was reduced from 90.9 kg/t-PCB to 47.07 kg/t-PCB with an equivalent increase in gold extraction from 18.61% to 46.89%. With acid pre-treated PCBs, the stabilized reagent consumption decreased from 72.6 kg/t-PCB to 61.03 kg/t-PCB with a corresponding Au extraction increase from 36.02% to 65.41%. The thermodynamics of the process had thus shifted to the more stable Ni-ATS system which lessened the decomposition of thiosulphate. Another significant improvement in terms of the ATS consumption was observed in Cu-ATS leaching with acid-pretreated PCBs. The ATS consumption was reduced from a peak value of 140.4 kg/t-PCB to 87.2 kg/t-PCB, and the stabilized consumption was reduced from 90.9 kg/t-PCB to 72.6 kg/t-PCB. This consumption reduction was accompanied by an increase in gold extraction from 18.61% to 36.02% in 5 hours. The combined effect of PCB pre-treatment and nickel oxidant saw a decrease in thiosulphate consumption from a stabilised level of 90.9 kg/t-PCB to 61.03 kg/t-PCB with a resulting gold extraction increase from 18.61% to 65.41% in 5 hours, thus confirming the research hypotheses formulated for this project (section 1.4).

### 4.4.3 Statistical Analysis of Ammonium Thiosulphate Leaching Results

#### 4.4.3.1 Experimental Repeatability Test

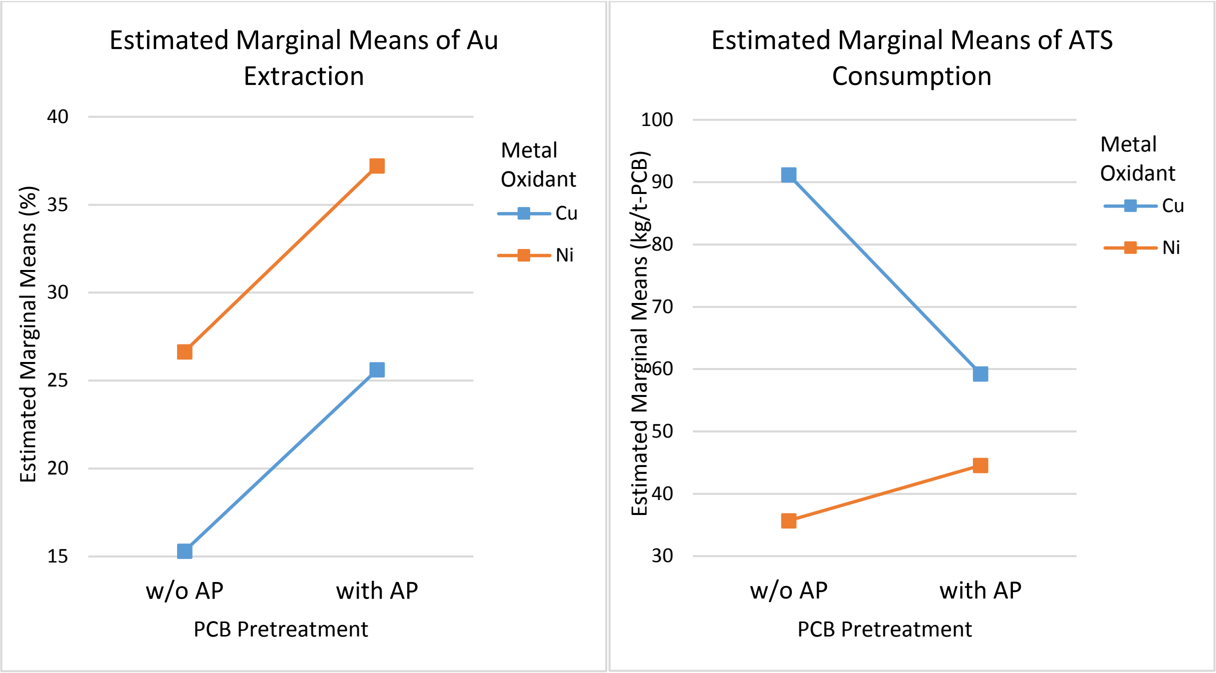
Based on the p-values, t-statistics and Pearson correlation coefficients of the t-tests tabulated in Appendix D (Table D-5 and Table D-6), there were no statistical grounds for rejecting the null hypothesis, and thus the runs and their respective duplicates were indicative of the same experimental conditions, which confirmed the experimental repeatability of ammonium thiosulphate leaching.

#### 4.4.3.2 Analysis of Variance (ANOVA) – ATS Leaching

The ANOVA results for the ammonium thiosulphate leaching experiments are fully provided in Appendix D (Table D-9). The p-values of the effect of PCB pre-treatment variation were extremely small compared to the adjusted alpha value of 0.0253 for both gold extraction (0.000) and ATS consumption (0.002), confirming the statistical significance of PCB pre-treatment. Similarly, the variation of the metal oxidant used in ATS leaching was found to be statistically significant for both gold extraction and ATS consumption based on the low p-values obtained.

For gold extraction, the effect of PCB pre-treatment and metal oxidant, in terms of the partial eta squared, indicated equal or close significance levels for both factors. However, the F-statistic provided more insight into the significance level of each factor. The F-critical of the metal oxidant (694.8) was greater than that of the PCB pre-treatment (574.9), indicating that the metal oxidant had a higher significance level than PCB pre-treatment with respect to gold extraction. This observation was in agreement with the previous discussion in section 4.4.2 which established that a significant improvement in gold extraction was achieved by first replacing copper(II) ion with nickel(II) ion as the metal oxidant which was found to increase the gold extraction from 18.61% to 46.89% (i.e. 152% increase) in 5 hours, whereas for each metal oxidant used, the PCB pre-treatment improved the gold extraction by a lower amount. Acid pre-treatment increased the gold extraction from 18.61% to 36.02% (i.e. 93.6% increase) in Cu-ATS leaching and from 46.89% to 65.41% (i.e. 39.5% increase) in Ni-ATS leaching. Replacing copper with nickel had a major effect in that it changed the chemistry and thermodynamic stability of the leaching system, as discussed in chapter two (section 2.6.3.3).

The interaction between PCB pre-treatment and metal oxidant were not statistically significant for gold extraction (p-value of 0.788 > 0.0253) but significant for ATS consumption (p-value <<< 0.0253). The interaction plots in Figure 4-7 indicate that the estimated marginal means of gold extraction exhibited parallel lines, indicating no interaction or correlation between the two factors with respect to gold extraction. On the other hand, the estimated marginal means of ATS consumption exhibited nonparallel lines, indicating a possible interaction or correlation between the two factors with respect to ATS consumption. Although no factor interaction was established statistically, the individual factor effects had proven significant in relation to Au extraction. For ATS consumption, since there was an intimate correlation between PCB pre-treatment and metal oxidant, the individual effects of these factors were also interrelated, expectedly in chemical and thermodynamic aspects.



(a) (b)

**Figure 4-7: Factor interaction plots for ammonium thiosulphate leaching: (a) Au extraction and (b) ATS consumption**

## 4.5 Shrinking-Core Model Fitting of Kinetic Data and Rate-Limiting Mechanism

In this section, the mathematical analysis of the kinetic data of acid pre-treatment and ammonium thiosulphate leaching of gold from mobile phone PCBs is provided in terms of the shrinking-core model (SCM). This model has been used extensively to provide a conceptual description of fluid-solid reactive systems (Levenspiel, 1999; Gbor & Jia, 2004; Othusitse & Muzenda, 2015). It is based on the premise that a fluid-solid reaction proceeds according to five steps, as outlined in chapter two (section 2.7). However, since the rate-controlling step has the highest resistance, the current study was limited to steps 1 through 3, from which the general mechanism of the leaching process could be established. Thus, the three mechanisms included film diffusion control, ash diffusion control and chemical reaction control.

### 4.5.1 Assumptions and Considerations for Modelling of Leaching Processes

The following assumptions and considerations were upheld when using the shrinking-core model to provide simplicity and practicality in the description of the acid pre-treatment and ammonium thiosulphate leaching. Levenspiel (1999) emphasised that when performing a mathematical analysis for the progression of a chemical reaction, it is useless to choose a model that closely describes the process but is too complex that it cannot be used for future predictions and design purposes.

- The PCB particles were spherical. Furthermore, the particles were assumed to conserve their spherical shape after acid pre-treatment.
- The SCM used for acid pre-treatment was that of shrinking particles because a PCB mass reduction was incurred in the pre-treatment process. Furthermore, the particles were assumed to shrink uniformly, thus maintaining their spherical shape.
- The SCM used for ammonium thiosulphate leaching was that of unshrinking (constant size) particles. This assumption was supported by the low amount of gold and other precious metals that could be extracted by ATS. Since gold was the target metal of the thiosulphate lixiviant, the PCB size reduction resulting from this metal extraction could be safely assumed to be negligible.
- The time for complete conversion $\tau$ was estimated from the final conversion and corresponding leaching time.
- The gold extraction was expressed as the shrinking of the unreacted solid (PCB) core. This meant that as the reaction progressed, an increasing metal conversion corresponded to a decreasing unreacted core, and that the highest gold conversion occurred at the smallest unreacted core size. This is supported by the fact that, under ideal conditions, a fluid-solid reaction with unshrinking particles progresses until all the solid reactant is used up and replaced with the reacted (inert) ash. At this point, the reaction is complete with a total conversion.
- In the conversion-time plots, the metal extraction was expressed as $(1 - X)$ representing the shrinking of the unreacted core, and the time was expressed as $t/\tau$ which indicated the fractional time for complete conversion.

### 4.5.2 Acid Pre-treatment – SCM with Shrinking Particles

For shrinking particles, it has been established that no ash formation occurs. Three mechanisms are incorporated into the shrinking-core model, namely: (1) film diffusion control under Stokes flow regime (FDC-SR), (2) film diffusion control under turbulent flow regime (FDC-TR) and (3) chemical reaction control (RC). The statistical analysis of the SCM fitting to the acid pre-treatment kinetic data involved the two-sample t-test with paired (matched) samples, and the results are tabulated in Appendix E (Table E-6).

A visual analysis of model fitting in Figure 4-8 indicated that, for all four leaching conditions investigated, any of the three SCMs fitted the kinetic data to an acceptable level. Furthermore, the examination of the kinetic results for conditions A, B and D indicated that the RC and FDC-TR exhibited a closer fit to the leaching data as the reaction progressed, with chemical reaction control having the highest impact level on the acid pre-treatment from a mechanistic viewpoint. The visual analysis of the model fitting was supported statistically in terms of the p-values and coefficients of determination ($R^2$ values) in Table E-6. The p-values of all paired-sample t-tests were greater than 0.05 for all conditions (A, B, C and D). However, the corresponding $R^2$ values exhibited a high level of variability. For the optimum conditions A (2M $H_2SO_4$, 3M $H_2O_2$), the p-values for FDC-SR, FDC-TR and RC were found to be 0.083, 0.20 and 0.58, respectively with corresponding $R^2$ values of 0.58, 0.65 and 0.75. This indicated that, although the p-values confirmed correlation, the coefficients of determination revealed that chemical reaction control (RC) was the best fit to kinetic data and predicted 75% of the variation in copper conversion with time. The film diffusion control with turbulent flow regime came second, predicting 65% of the variation in copper conversion with time.

Thus, the statistical analysis of SCM fitting to the experimental data was found to provide insight into the degrees of resistance (control) of the three mechanisms which were ranked as: RC > FDC-TR > FDC-SR. Therefore, the acid pre-treatment was found to be chemically controlled, with moderate control due to the mixing-driven turbulence.

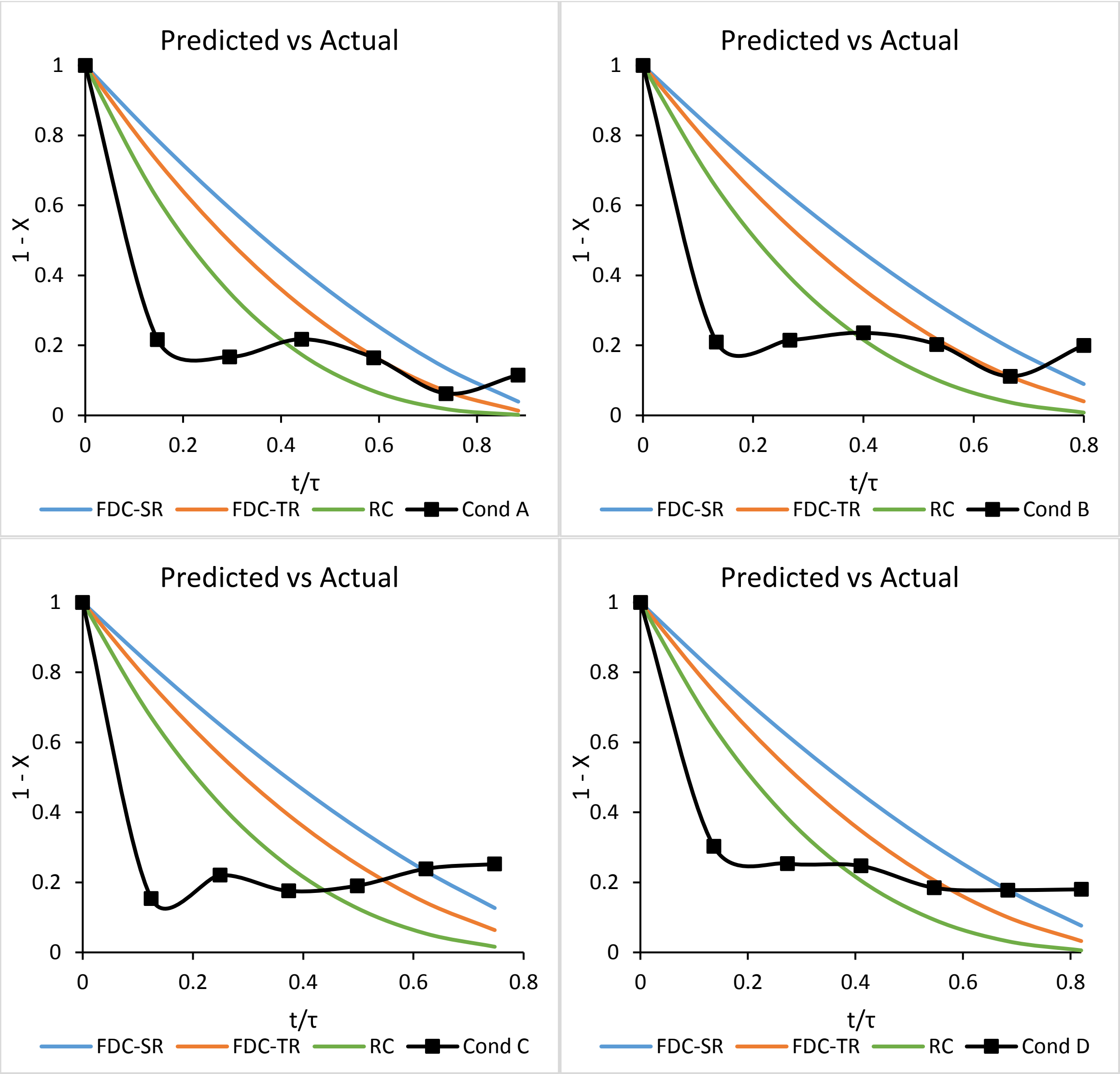


**Figure 4-8: SCM fitting to kinetic data for acid pre-treatment**

### 4.5.3 Ammonium Thiosulphate Leaching – SCM with Unshrinking Particles

For unshrinking particles, the three mechanisms investigated in terms of the shrinking-core model included: (1) film diffusion control (FDC), (2) ash diffusion control (ADC) and (3) chemical reaction control (RC). The statistical analysis of the SCM fitting to the ATS leaching kinetic data involved the two-sample t-test with paired (matched) samples, and the results are tabulated in Appendix E (Table E-12).

A visual analysis of model fitting in Figure 4-9 indicated that none of the three mechanisms described Cu-ATS leaching without acid pre-treatment. This was supported statistically by the fact that the p-values and $R^2$ values were not in agreement. For instance, the p-value for RC was 0.07 (> 0.05) with a corresponding $R^2$ of 0.58 (low correlation). In contrast, the other three leaching conditions, i.e. Cu-ATS with acid pre-treatment, Ni-ATS leaching (with and w/o AP) were described by chemical reaction control (RC) based on the fit of this model to the experimental data. The statistical analysis of model fitting confirmed this observation for the copper-thiosulphate leaching and nickel-thiosulphate leaching with acid pre-treatment. A p-value of 0.15 (> 0.05) and $R^2$ of 0.68 were obtained for Cu-ATS leaching with AP, and a p-value of 0.07 (> 0.05) and R-squared of 0.68 were obtained for Ni-ATS leaching with AP. This was an indication that chemical reaction control predicted 68% of the variation in gold extraction with time for the copper-thiosulphate and nickel-thiosulphate leaching with acid pre-treatment.

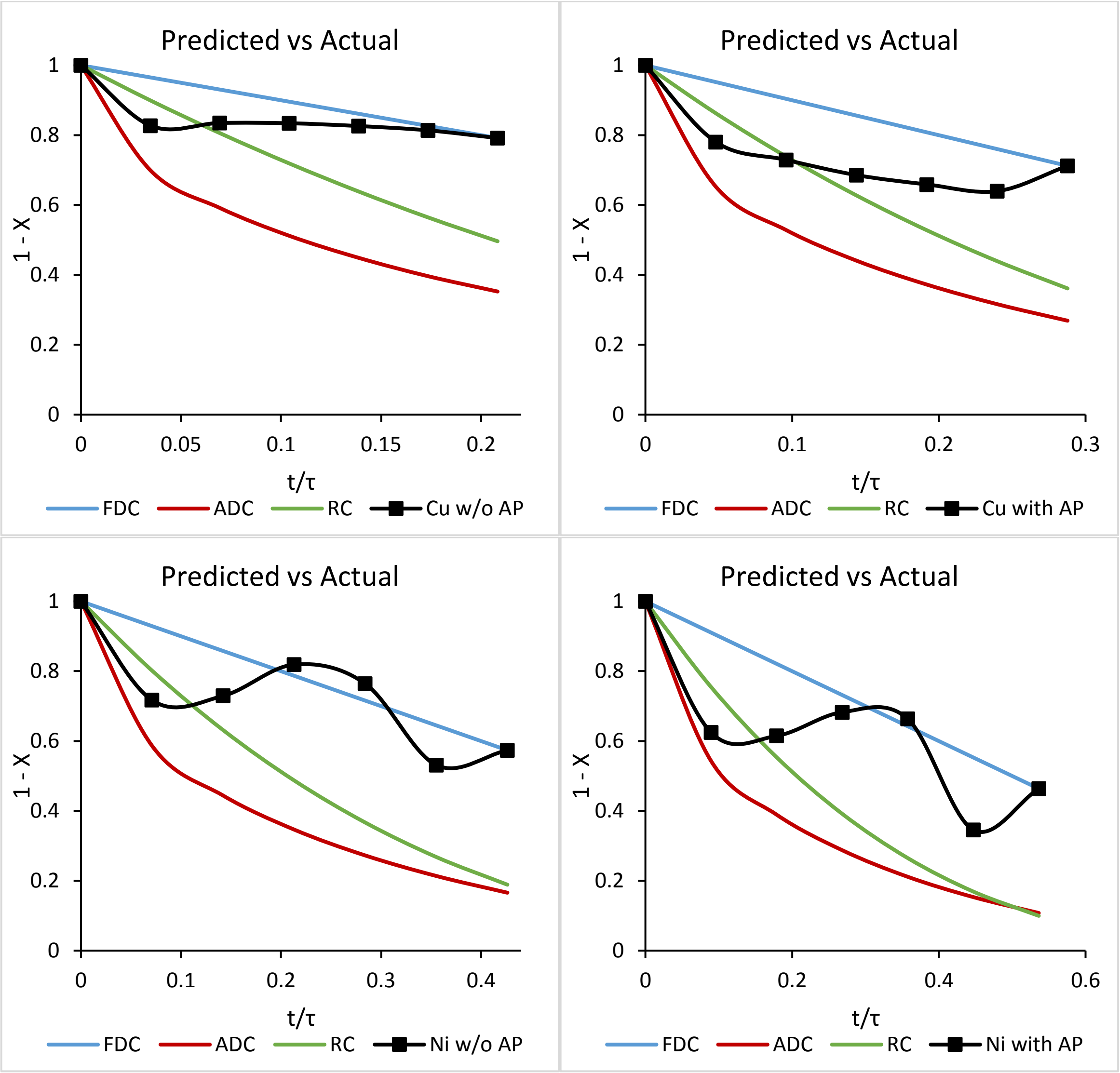


**Figure 4-9: SCM fitting to kinetic data for ammonium thiosulphate leaching**

## 4.6 Preliminary Economics Analysis

This section briefly compares the economics of the copper- and nickel-thiosulphate leaching and the conventional cyanidation for the gold extraction from acid-pretreated PCBs. Due to the limited data available for this analysis, the comparison was based on production costs only, with an emphasis on gross margin. A preliminary economic comparison of different processes based on their gross margins is significant since raw materials are known to contribute to more than 80% of the total cost of production (Towler & Sinnott, 2008).

The following considerations and simplifying assumptions were adopted:

- The production costs were related to the reagent (lixiviant and oxidant) consumptions obtained in the study. For cyanide leaching, the reference gold extraction and reagent consumption were obtained from the literature (Quinet et al., 2005).
- The cost of PCBs as raw materials was assumed to be negligible. Thus, the cost of raw materials was attributed to the reagents used in leaching.
- The revenue was related entirely to the amount of gold dissolved.
- The economics analysis was based on one metric ton of processed PCBs containing 524 g Au/t-PCB.

Figure 4-10 indicates that cyanidation had the highest gross margin of 22,066 USD and lowest raw materials cost of 2,112 USD, as a result of the highest gold extraction with low reagent consumption obtained. Furthermore, it adds to the reasons for the predominance of cyanidation in the gold mining industry. However, the margin of thiosulphate leaching was found to improve significantly by replacing copper with nickel, as a result of the higher revenue driven by the improved gold extraction and the reduced thiosulphate consumption. The gold extraction was increased from 36.02% in copper-thiosulphate leaching to 65.41% in nickel-thiosulphate leaching. In addition, the thiosulphate consumption was reduced from 72.06 to 47.7 kg/t-PCB. The raw materials cost decreased from 3,768 USD to 2,868 USD, approaching the previously reported cyanidation costs closely. The revenue and gross margin were increased from 8,969 and 5,201 USD in copper-thiosulphate leaching to 16,287 and 13,419 USD in nickel-thiosulphate leaching, respectively. Although nickel is almost triple the price of copper, its use in the leaching process as a substitute for copper reduced the overall raw materials cost because this cost was mostly attributed to the cost of thiosulphate (Figure 4-11) and using nickel caused a significant reduction in thiosulphate consumption.

Therefore, the use of thiosulphate as an environment-friendly non-cyanide lixiviant shows potential by virtue of the economics of the process. The calculations involved in the preliminary economics analysis are provided in Appendix G (section G.5).

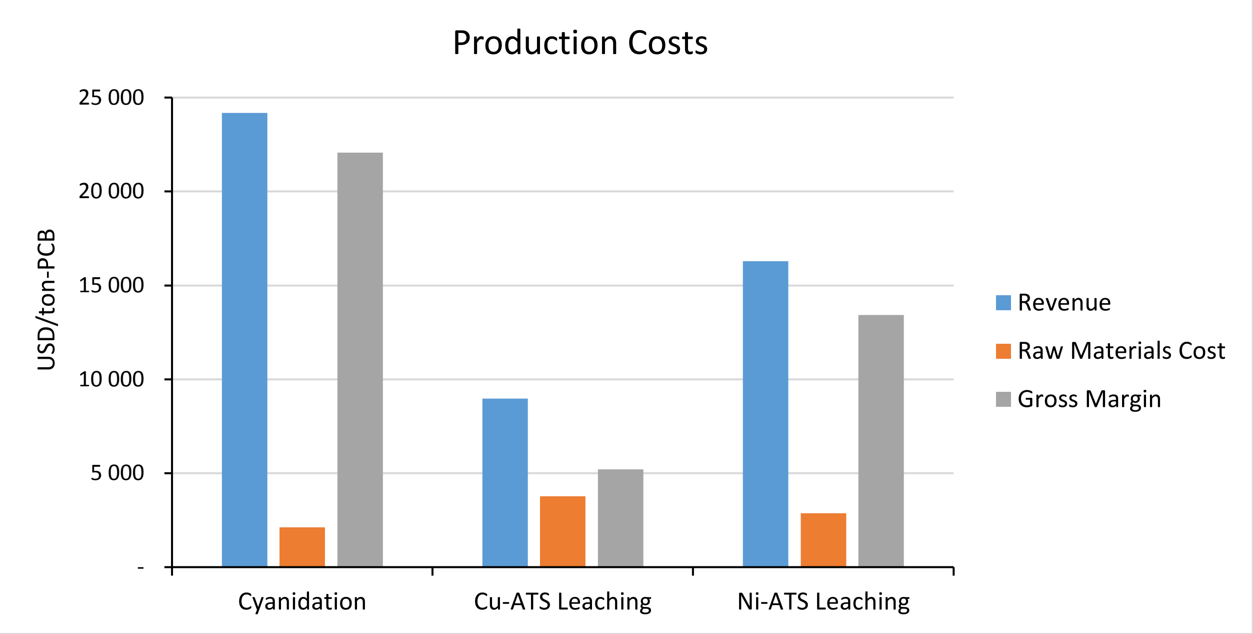


**Figure 4-10: Gross margins of three gold leaching process routes with a basis of one metric ton of processed PCBs**

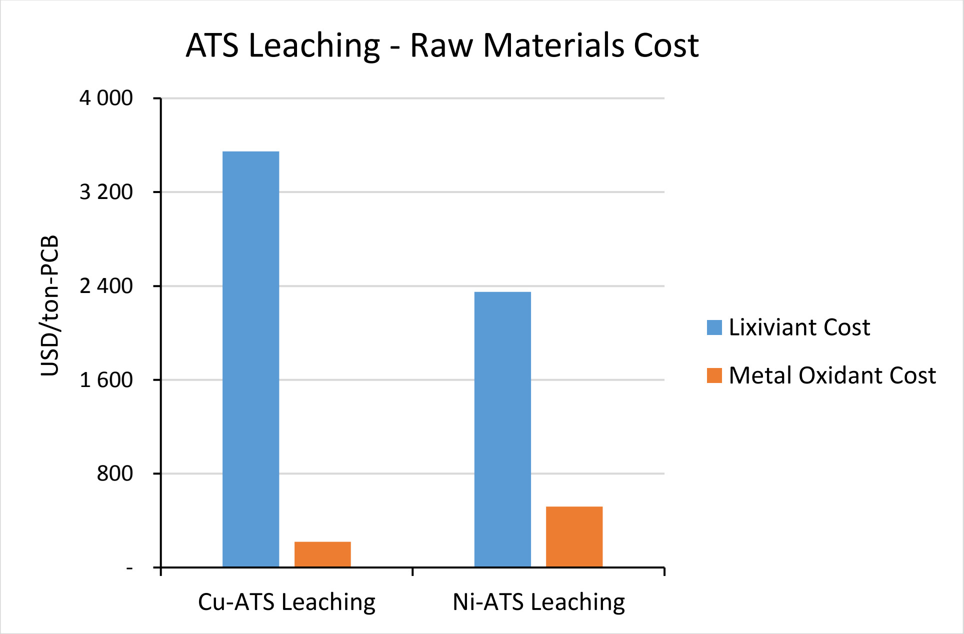


**Figure 4-11: Contributions of the lixiviant and metal oxidant to the overall raw materials costs in thiosulphate leaching**

# CHAPTER 5

## CONCLUSION AND RECOMMENDATION

# CHAPTER 5 : CONCLUSION AND RECOMMENDATION

## 5.1 Conclusion

The proliferation of electronic waste exacerbated by rapid technological growth is posing a predominant environmental challenge. Proper management of this waste is required to sustain the protection of our ecosystem. Recycling of e-waste is a promising route because not only does it allow the adequate handling of e-waste, but also it is attractive in economic aspects due to the high value of precious metals extractable from PCBs. Cyanide leaching has been used for many years as the traditional hydrometallurgical technology for the extraction of precious metals from refractory ores, concentrates and wastes. However, due to the adverse health and environmental impact of the process, alternative non-cyanide and less toxic lixiviants such as ammonium thiosulphate are gaining precedence over cyanide. To mitigate the operability issues of ammonium thiosulphate and improve the viability of the process, the effects of acid pre-treatment and nickel oxidant on the gold extraction and thiosulphate consumption were instigated.

The acid pre-treatment stage achieved 93.72% copper extraction and 8.83% gold loss in 150 minutes the optimum conditions of 2 M $H_2SO_4$, 3 M $H_2O_2$, 50 g/L pulp density, 25°C and 350 rpm mixing rate. This pre-processing stage was a beneficiation process that increased the extractable gold content from 524 to 842 g/ton-PCBs. The variation in $H_2SO_4$ was found to have a higher statistical impact on gold extraction and the variation in $H_2O_2$, the oxidant in the acid pre-treatment, was more statistically significant for copper extraction. The acid pre-treatment was found to be chemically controlled based on the shrinking-core model. The ammonium thiosulphate leaching stage achieved 65.41% gold extraction and 61.03 kg/ton-PCB thiosulphate consumption with the use of nickel as the metal oxidant in the gold extraction from acid-pretreated PCBs at 50 g/L pulp density, 0.1 M thiosulphate, 0.2 M $NH_3$, 0.03 M $Ni^{2+}$, pH 10.5 and stirring speed of 350 rpm. The variation in metal oxidant was found to have a more pronounced statistical effect on gold extraction compared to the PCB pre-treatment. The copper-thiosulphate and nickel-thiosulphate leaching processes were found to be chemically controlled based on the shrinking-core model.

A preliminary economic comparison between Cu-thiosulphate and Ni-thiosulphate leaching, based on production costs, indicated that a significant improvement in terms of gross margin was obtained with the use of nickel in thiosulphate leaching, and despite the higher margin of cyanidation, the improved process economics of the ammonium thiosulphate leaching shows potential for industrial implementation.

## 5.2 Recommendations for Future Research

In this research, the gold extraction and thiosulphate consumption were improved by altering the chemistry of the leaching process through acid pre-treatment and using nickel as the metal oxidant. In addition, based on the level of knowledge and experience acquired through this research, it is the author's view that future developments on the ammonium thiosulphate leaching of gold from waste PCBs should focus on the following aspects to envisage further improvements:

- The lixiviant recyclability through appropriate metal recovery techniques targeting copper removal (in acid pre-treatment) and gold (in thiosulphate leaching). The nickel oxidant used in thiosulphate leaching would have a positive impact on adsorptive recovery techniques such as resin adsorption because the positively-charged nickel amine complex formed in the leaching system would have no affinity for anion-exchange resins, thus decreasing the level of interference.

- The presence of non-metals (resin material, glass, and other plastics) is known to be detrimental to the gold leaching efficiency. Multiple studies have outlined the benefits of non-metal removal from the PCB prior to leaching (Hocheng et al., 2017; Rossouw, 2015; Havlik et al., 2010) while others have reported satisfactory gold extraction levels with no non-metallic fraction removal step (Ha et al., 2010; Ficeriová et al., 2011; Tripathi et al., 2012; Gámez et al., 2019). Furthermore, proper economics analysis should be carried out to confirm the economic viability of adding this processing stage.

- Since nickel was found to shift the thermodynamics of ammonium thiosulphate leaching towards the more stable nickel amine complex, an in-depth investigation into the effects of thiosulphate, ammonia and nickel(II) ion concentrations along with interactions among these factors should be undertaken through optimization experiments to envisage the possibility of further minimizing the starting reagent concentrations while maintaining or improving gold extraction. This will have a significant impact on the process economics.

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# APPENDICES

# APPENDIX A

## PCB CHARACTERIZATION AND AQUA REGIA LEACHING

# APPENDIX A : PCB Characterization & Aqua Regia Leaching

Aqua regia leaching was performed to determine the metal content of PCBs, as summarised in Table 4-1. The results of the five replicate runs are shown below. Since the initial samples were diluted 50 times, the actual ppm concentrations in the pregnant were calculated by multiplying the dilute concentration by 50.

**Table A-1: Dilute copper concentration (mg/L) of pregnant aqua regia leach solutions**

| | **Time (min)** | | | | | | | **Time (h)** |
|---|---|---|---|---|---|---|---|---|
| **Run** | **0** | **20** | **40** | **60** | **80** | **100** | **120** | **24** |
| **1** | 0 | 358.1 | 394.9 | 395 | 393.6 | 407.2 | 416.2 | 480.7 |
| **2** | 0 | 393.8 | 399.8 | 394.7 | 417.4 | 425.2 | 444.6 | 460.7 |
| **3** | 0 | 377.1 | 396.1 | 393 | 425.6 | 447.3 | 448.4 | 458.7 |
| **4** | 0 | 410.2 | 406.2 | 420.8 | 433.5 | 430 | 464.3 | 473.8 |
| **5** | 0 | 410 | 404.4 | 446.4 | 459.8 | 461.5 | 473.7 | 435.3 |

**Table A-2: Dilute gold concentration (mg/L) of pregnant aqua regia leach solutions**

| | **Time (min)** | | | | | | | **Time (h)** |
|---|---|---|---|---|---|---|---|---|
| **Run** | **0** | **20** | **40** | **60** | **80** | **100** | **120** | **24** |
| **1** | 0 | 0.347 | 0.383 | 0.400 | 0.425 | 0.439 | 0.470 | 0.607 |
| **2** | 0 | 0.414 | 0.410 | 0.411 | 0.433 | 0.437 | 0.488 | 0.456 |
| **3** | 0 | 0.309 | 0.332 | 0.349 | 0.352 | 0.387 | 0.375 | 0.534 |
| **4** | 0 | 0.325 | 0.364 | 0.375 | 0.401 | 0.397 | 0.439 | 0.472 |
| **5** | 0 | 0.375 | 0.389 | 0.435 | 0.447 | 0.445 | 0.465 | 0.550 |

**Table A-3: Actual copper concentration (mg/L) of pregnant aqua regia leach solutions**

| | Time (min) | | | | | | | Time (h) |
|---|---|---|---|---|---|---|---|---|
| **Run** | **0** | **20** | **40** | **60** | **80** | **100** | **120** | **24** |
| **1** | 0 | 17905 | 19745 | 19750 | 19680 | 20360 | 20810 | 24035 |
| **2** | 0 | 19690 | 19990 | 19735 | 20870 | 21260 | 22230 | 23035 |
| **3** | 0 | 18855 | 19805 | 19650 | 21280 | 22365 | 22420 | 22935 |
| **4** | 0 | 20510 | 20310 | 21040 | 21675 | 21500 | 23215 | 23690 |
| **5** | 0 | 20500 | 20220 | 22320 | 22990 | 23075 | 23685 | 21765 |

**Table A-4: Actual gold concentration (mg/L) of pregnant aqua regia leach solutions**

| | Time (min) | | | | | | | Time (h) |
|---|---|---|---|---|---|---|---|---|
| **Run** | **0** | **20** | **40** | **60** | **80** | **100** | **120** | **24** |
| **1** | 0.00 | 17.35 | 19.14 | 20.00 | 21.27 | 21.94 | 23.49 | 30.35 |
| **2** | 0.00 | 20.71 | 20.48 | 20.54 | 21.64 | 21.87 | 24.38 | 22.82 |
| **3** | 0.00 | 15.43 | 16.62 | 17.44 | 17.61 | 19.33 | 18.77 | 26.68 |
| **4** | 0.00 | 16.27 | 18.21 | 18.77 | 20.07 | 19.87 | 21.96 | 23.62 |
| **5** | 0.00 | 18.77 | 19.44 | 21.77 | 22.33 | 22.26 | 23.26 | 27.48 |

# APPENDIX B

## PARTICLE SIZE DISTRIBUTION

# APPENDIX B : Particle Size Distribution

The particle size distribution (PSD) of the ground PCBs (total mass of 828.32 g) plotted in Figure 4-1 was obtained from Table B-1 and Table B-2.

**Table B-1: Particle size distribution on frequency basis**

| Particle Size (µm) | Mass (g) | Mass Fraction |
|---|---|---|
| 500 | 405.28 | 0.49 |
| 500-1000 | 152.18 | 0.18 |
| 1000-1700 | 77.87 | 0.09 |
| 1700-3000 | 192.99 | 0.23 |

**Table B-2: Particle size distribution on cumulative basis**

| Particle Size (µm) | Mass Fraction |
|---|---|
| 0 | 0 |
| 500 | 0.49 |
| 1000 | 0.67 |
| 1700 | 0.77 |
| 3000 | 1.00 |

# APPENDIX C

## ACID PRE-TREATMENT

# APPENDIX C : Acid Pre-treatment

## C.1 Copper and Gold Extractions

The copper and gold concentrations of the pregnant leach solutions obtained in the acid pre-treatment runs designed in Chapter 3 (Table 3-1) are shown in Table C-2 and Table C-3. The corresponding gold and copper extractions are shown in Table C-4 and Table C-5.

**Table C-1: Dilute copper concentration (mg/L) of pregnant leach solutions in acid pre-treatment**

| | Reaction Time (min) | | | | | | |
|---|---|---|---|---|---|---|---|
| Run | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
| 1 | 0 | 372.2 | 377.9 | 353.5 | 387.7 | 431.4 | 412.1 |
| 2 | 0 | 361.1 | 372.1 | 343.9 | 380.2 | 397.5 | 372.2 |
| 3 | 0 | 351 | 391.1 | 369.1 | 383.8 | 434.3 | 404.7 |
| 4 | 0 | 390.5 | 345.3 | 383.2 | 378.7 | 367.9 | 358.6 |
| 5 | 0 | 368.4 | 352.6 | 361.7 | 355.9 | 422.9 | 366.5 |
| 6 | 0 | 390.8 | 374.5 | 378.2 | 369 | 334.9 | 331.9 |
| 7 | 0 | 313.2 | 350.8 | 359.6 | 364.3 | 370 | 362.9 |
| 8 | 0 | 330.8 | 338.2 | 335.7 | 389 | 389.2 | 394.4 |

**Table C-2: Actual copper concentration (mg/L) of pregnant leach solutions in acid pre-treatment**

| | Reaction Time (min) | | | | | | |
|---|---|---|---|---|---|---|---|
| Run | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
| 1 | 0 | 18610 | 18895 | 17675 | 19385 | 21570 | 20605 |
| 2 | 0 | 18055 | 18605 | 17195 | 19010 | 19875 | 18610 |
| 3 | 0 | 17550 | 19555 | 18455 | 19190 | 21715 | 20235 |
| 4 | 0 | 19525 | 17265 | 19160 | 18935 | 18395 | 17930 |
| 5 | 0 | 18420 | 17630 | 18085 | 17795 | 21145 | 18325 |
| 6 | 0 | 19540 | 18725 | 18910 | 18450 | 16745 | 16595 |
| 7 | 0 | 15660 | 17540 | 17980 | 18215 | 18500 | 18145 |
| 8 | 0 | 16540 | 16910 | 16785 | 19450 | 19460 | 19720 |

**Table C-3: Actual gold concentration (mg/L) of pregnant leach solutions in acid pre-treatment**

| | Reaction Time (min) | | | | | | |
|---|---|---|---|---|---|---|---|
| Run | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
| 1 | 0 | 1.829 | 2.281 | 1.911 | 2.084 | 2.276 | 1.828 |
| 2 | 0 | 2.295 | 2.437 | 1.960 | 2.213 | 2.761 | 2.103 |
| 3 | 0 | 1.601 | 1.950 | 2.139 | 2.444 | 2.351 | 1.588 |
| 4 | 0 | 2.203 | 2.556 | 2.681 | 2.785 | 2.687 | 2.608 |
| 5 | 0 | 2.164 | 2.265 | 2.334 | 2.420 | 2.873 | 2.310 |
| 6 | 0 | 2.417 | 2.428 | 2.915 | 2.926 | 2.836 | 2.546 |
| 7 | 0 | 1.897 | 2.113 | 2.477 | 2.843 | 2.972 | 2.952 |
| 8 | 0 | 2.020 | 1.908 | 2.391 | 2.630 | 2.849 | 2.795 |

**Table C-4: Copper extraction (%) by acid pre-treatment at four treatment combinations**

| Conditions | Time (min) | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|---|
| A (Run 1 - Run 3) | Run | 0.00 | 80.59 | 81.82 | 76.54 | 83.95 | 93.41 | 89.23 |
| | Dup | 0.00 | 76.00 | 84.68 | 79.92 | 83.10 | 94.04 | 87.63 |
| | Mean | 0.00 | 78.30 | 83.25 | 78.23 | 83.52 | 93.72 | 88.43 |
| | Std Dev | 0.00 | 3.25 | 2.02 | 2.39 | 0.60 | 0.44 | 1.13 |
| B (Run 2 - Run 5) | Run | 0.00 | 78.19 | 80.57 | 74.46 | 82.32 | 86.07 | 80.59 |
| | Dup | 0.00 | 79.77 | 76.35 | 78.32 | 77.06 | 91.57 | 79.36 |
| | Mean | 0.00 | 78.98 | 78.46 | 76.39 | 79.69 | 88.82 | 79.97 |
| | Std Dev | 0.00 | 1.12 | 2.99 | 2.73 | 3.72 | 3.89 | 0.87 |
| C (Run 4 - Run 6) | Run | 0.00 | 84.55 | 74.77 | 82.97 | 82.00 | 79.66 | 77.65 |
| | Dup | 0.00 | 84.62 | 81.09 | 81.89 | 79.90 | 72.51 | 71.86 |
| | Mean | 0.00 | 84.59 | 77.93 | 82.43 | 80.95 | 76.09 | 74.76 |
| | Std Dev | 0.00 | 0.05 | 4.47 | 0.77 | 1.49 | 5.05 | 4.09 |
| D (Run 7 - Run 8) | Run | 0.00 | 67.82 | 75.96 | 77.86 | 78.88 | 80.11 | 78.58 |
| | Dup | 0.00 | 71.63 | 73.23 | 72.69 | 84.23 | 84.27 | 85.40 |
| | Mean | 0.00 | 69.72 | 74.59 | 75.27 | 81.55 | 82.19 | 81.99 |
| | Std Dev | 0.00 | 2.69 | 1.93 | 3.66 | 3.78 | 2.94 | 4.82 |

**Table C-5: Gold extraction (%) by acid pre-treatment at four treatment combinations**

| Conditions | Time (min) | 0 | 30 | 60 | 90 | 120 | 150 | 180 |
|---|---|---|---|---|---|---|---|---|
| A (Run 1 - Run 3) | Run | 0.00 | 6.98 | 8.71 | 7.30 | 7.96 | 8.69 | 6.98 |
| | Dup | 0.00 | 6.11 | 7.45 | 8.17 | 9.33 | 8.98 | 6.06 |
| | Mean | 0.00 | 6.55 | 8.08 | 7.73 | 8.64 | 8.83 | 6.52 |
| | Std Dev | 0.00 | 0.62 | 0.89 | 0.62 | 0.97 | 0.20 | 0.65 |
| B (Run 2 - Run 5) | Run | 0.00 | 8.76 | 9.31 | 7.48 | 8.45 | 10.54 | 8.03 |
| | Dup | 0.00 | 8.26 | 8.65 | 8.91 | 9.24 | 10.97 | 8.82 |
| | Mean | 0.00 | 8.51 | 8.98 | 8.20 | 8.84 | 10.76 | 8.42 |
| | Std Dev | 0.00 | 0.35 | 0.46 | 1.01 | 0.56 | 0.30 | 0.56 |
| C (Run 4 - Run 6) | Run | 0.00 | 8.41 | 9.76 | 10.24 | 10.63 | 10.26 | 9.96 |
| | Dup | 0.00 | 9.23 | 9.27 | 11.13 | 11.17 | 10.83 | 9.72 |
| | Mean | 0.00 | 8.82 | 9.52 | 10.68 | 10.90 | 10.54 | 9.84 |
| | Std Dev | 0.00 | 0.58 | 0.35 | 0.63 | 0.38 | 0.40 | 0.17 |
| D (Run 7 - Run 8) | Run | 0.00 | 7.24 | 8.07 | 9.46 | 10.86 | 11.35 | 11.27 |
| | Dup | 0.00 | 7.71 | 7.29 | 9.13 | 10.04 | 10.88 | 10.67 |
| | Mean | 0.00 | 7.48 | 7.68 | 9.29 | 10.45 | 11.11 | 10.97 |
| | Std Dev | 0.00 | 0.33 | 0.55 | 0.23 | 0.58 | 0.33 | 0.42 |

**Table C-6: Material balance – acid pre-treatment**

| Metal | Initial Mass | Final Mass | Mass Removed | Metal Content After Acid Leaching (%) |
|---|---|---|---|---|
| Cu | 16.164 | 1.015 | 15.150 | 5.1119 |
| Au | 0.0183 | 0.017 | 0.0016 | 0.0842 |
| Total PCB Mass | 35 | | | |

## C.2 Statistical Analysis

The statistical analysis of the acid pre-treatment and ammonium thiosulphate leaching was performed with the aid of Microsoft Excel and IBM SPSS Statistics software packages.

### C.2.1 Experimental Repeatability Test

**Table C-7: Run-duplicate t-test: paired two-sample for means – Cu extraction**

| *Experimental Conditions* | | *Mean* | *Variance* | *n* | *Pearson Correlation* | *df* | *t Stat* | *P(T<=t) one-tail* | *t Critical one-tail* | *P(T<=t) two-tail* | *t Critical two-tail* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | *Run* | 72.22 | 1045.43 | 7 | 0.9965 | 6 | 0.0241 | 0.4908 | 1.9432 | 0.9816 | 2.4469 |
| | *Dup* | 72.20 | 1046.07 | 7 | | | | | | | |
| B | *Run* | 68.89 | 935.36 | 7 | 0.9917 | 6 | -0.0206 | 0.4921 | 1.9432 | 0.9842 | 2.4469 |
| | *Dup* | 68.92 | 949.88 | 7 | | | | | | | |
| C | *Run* | 68.80 | 931.40 | 7 | 0.9895 | 6 | 0.8338 | 0.2182 | 1.9432 | 0.4363 | 2.4469 |
| | *Dup* | 67.41 | 906.47 | 7 | | | | | | | |
| D | *Run* | 65.60 | 853.56 | 7 | 0.9894 | 6 | -1.0349 | 0.1703 | 1.9432 | 0.3406 | 2.4469 |
| | *Dup* | 67.35 | 919.05 | 7 | | | | | | | |

**Table C-8: Run-duplicate t-test: paired two-sample for means – Au extraction**

| *Experimental Conditions* | | *Mean* | *Variance* | *n* | *Pearson Correlation* | *df* | *t Stat* | *P(T<=t) one-tail* | *t Critical one-tail* | *P(T<=t) two-tail* | *t Critical two-tail* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| A | *Run* | 6.66 | 9.16 | 7 | 0.9500 | 6 | 0.1987 | 0.4245 | 1.9432 | 0.8490 | 2.4469 |
| | *Dup* | 6.59 | 10.06 | 7 | | | | | | | |
| B | *Run* | 7.51 | 11.92 | 7 | 0.9774 | 6 | -1.1438 | 0.1481 | 1.9432 | 0.2963 | 2.4469 |
| | *Dup* | 7.84 | 12.69 | 7 | | | | | | | |
| C | *Run* | 8.47 | 14.44 | 7 | 0.9911 | 6 | -1.4653 | 0.0966 | 1.9432 | 0.1932 | 2.4469 |
| | *Dup* | 8.76 | 15.64 | 7 | | | | | | | |
| D | *Run* | 8.32 | 16.01 | 7 | 0.9947 | 6 | 2.0714 | 0.0419 | 1.9432 | 0.0837 | 2.4469 |
| | *Dup* | 7.96 | 14.24 | 7 | | | | | | | |

### C.2.2 ANOVA

The null hypothesis of the Anova for the acid pre-treatment was formulated as follows:

- The effect of variations in $H_2SO_4$ and $H_2O_2$ concentrations were not statistically significant in terms of copper extraction and gold extraction.

The research (alternative) hypothesis, attempting to disprove the null hypothesis, was formulated as follows:

- The effect of variations in $H_2SO_4$ and $H_2O_2$ concentrations had a significant impact on copper and gold extractions.

It is worth noting that the effect of varying a factor was statistically significant if and only if the following conditions were fulfilled:

- The p-value of the effect of factor variation on the response (dependent) variable was less than 0.0253.
- The F-statistic of the effect of factor variation on the response variable was greater than the F-critical.

**Table C-9: Response means – Cu extraction (%)**

| | $H_2O_2$ Concentration | |
|---|---|---|
| $H_2SO_4$ Concentration | 2M $H_2O_2$ | 3M $H_2O_2$ |
| 2M $H_2SO_4$ | 65.60 | 72.22 |
| | 67.35 | 72.20 |
| 3M $H_2SO_4$ | 68.89 | 68.80 |
| | 68.92 | 67.41 |

**Table C-10: Response means – Au extraction (%)**

| | $H_2O_2$ Concentration | |
|---|---|---|
| $H_2SO_4$ Concentration | 2M $H_2O_2$ | 3M $H_2O_2$ |
| 2M $H_2SO_4$ | 8.32 | 6.66 |
| | 7.96 | 6.59 |
| 3M $H_2SO_4$ | 7.51 | 8.47 |
| | 7.84 | 8.76 |

**Table C-11: Anova: two-factor with replication – Acid pre-treatment**

| *Source of Variation* | *Dependent Variable* | *Sum of Squares (SS)* | *df* | *Mean Square (MS)* | *F* | *P-value* | *F crit* | *Partial Eta Squared* |
|---|---|---|---|---|---|---|---|---|
| $H_2SO_4$ | Cu Extraction | 1.405 | 1 | 1.405 | 2.255 | 0.208 | 7.709 | 0.360 |
| | Au Extraction | 1.164 | 1 | 1.164 | 28.115 | 0.006 | 7.709 | 0.877 |
| $H_2O_2$ | Cu Extraction | 12.186 | 1 | 12.186 | 19.557 | 0.011 | 7.709 | 0.830 |
| | Au Extraction | 0.166 | 1 | 0.166 | 4.012 | 0.116 | 7.709 | 0.502 |
| Interaction | Cu Extraction | 21.319 | 1 | 21.319 | 34.214 | 0.004 | 7.709 | 0.895 |
| | Au Extraction | 3.024 | 1 | 3.024 | 73.062 | 0.001 | 7.709 | 0.948 |
| Within (Error) | Cu Extraction | 2.492 | 4 | 0.623 | | | | |
| | Au Extraction | 0.166 | 4 | 0.041 | | | | |
| Corrected Total | Cu Extraction | 37.403 | 7 | | | | | |
| | Au Extraction | 4.519 | 7 | | | | | |

**Table C-12: Estimated marginal means – Factor interaction**

| **$H_2SO_4$ * $H_2O_2$** | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | 95% Confidence Interval | |
| Dependent Variable | $H_2SO_4$ | $H_2O_2$ | Mean | Std. Error | Lower Bound | Upper Bound |
| Cu Extraction (%) | 2M $H_2SO_4$ | 2M $H_2O_2$ | 66.475 | 0.559 | 64.924 | 68.026 |
| | | 3M $H_2O_2$ | 72.210 | 0.559 | 70.659 | 73.761 |
| | 3M $H_2SO_4$ | 2M $H_2O_2$ | 68.905 | 0.559 | 67.354 | 70.456 |
| | | 3M $H_2O_2$ | 68.105 | 0.559 | 66.554 | 69.656 |
| Au Extraction (%) | 2M $H_2SO_4$ | 2M $H_2O_2$ | 8.140 | 0.143 | 7.743 | 8.537 |
| | | 3M $H_2O_2$ | 6.625 | 0.143 | 6.228 | 7.022 |
| | 3M $H_2SO_4$ | 2M $H_2O_2$ | 7.675 | 0.143 | 7.278 | 8.072 |
| | | 3M $H_2O_2$ | 8.615 | 0.143 | 8.218 | 9.012 |

# APPENDIX D

## AMMONIUM THIOSULPHATE LEACHING

# APPENDIX D : Ammonium Thiosulphate Leaching

## D.1 Gold Extraction and ATS Consumption

**Table D-1: PCB mass recorded after acid pre-treatment (Cu-ATS and Ni-ATS with AP)**

|  |  | PCB Mass (g) |  |
|---|---|---|---|
| Conditions | Run | Before AP | After AP |
| Cu-ATS with AP | Run 2 | 35 | 19.06 |
|  | Run 5 | 35 | 17.97 |
| Ni-ATS with AP | Run 3 | 35 | 19.54 |
|  | Run 4 | 35 | 19.50 |

**Table D-2: Gold concentration (mg/L) of pregnant leach solutions in ATS leaching**

|  | Reaction Time (min) |  |  |  |  |  |  |
|---|---|---|---|---|---|---|---|
| Run | 0 | 60 | 120 | 180 | 240 | 300 | 360 |
| 1 | 0 | 8.267 | 7.758 | 4.554 | 5.852 | 12.82 | 10.75 |
| 2 | 0 | 10.06 | 12.10 | 11.70 | 13.62 | 16.10 | 12.87 |
| 3 | 0 | 14.88 | 17.75 | 13.04 | 13.29 | 28.70 | 23.10 |
| 4 | 0 | 16.70 | 14.68 | 13.69 | 15.03 | 26.38 | 22.06 |
| 5 | 0 | 8.40 | 10.69 | 14.76 | 15.09 | 14.23 | 11.36 |
| 6 | 0 | 4.321 | 4.367 | 4.223 | 4.291 | 4.956 | 5.274 |
| 7 | 0 | 6.552 | 6.413 | 4.927 | 6.504 | 11.74 | 11.58 |
| 8 | 0 | 4.722 | 4.275 | 4.462 | 4.814 | 4.793 | 5.633 |

**Table D-3: Gold extraction (%) by ATS leaching at four treatment combinations**

| Conditions | Time (min) | 0 | 60 | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|---|---|---|
| Cu-ATS w/o AP (Run 6 - Run 8) | Run | 0 | 16.50 | 16.67 | 16.12 | 16.38 | 18.92 | 20.14 |
| | Dup | 0 | 18.03 | 16.32 | 17.04 | 18.38 | 18.30 | 21.51 |
| | Mean | 0 | 17.26 | 16.50 | 16.58 | 17.38 | 18.61 | 20.82 |
| | Std Dev | 0 | 1.08 | 0.25 | 0.65 | 1.41 | 0.44 | 0.97 |
| Cu-ATS with AP (Run 2- Run 5) | Run | 0 | 23.90 | 28.74 | 27.79 | 32.35 | 38.25 | 30.58 |
| | Dup | 0 | 19.95 | 25.38 | 35.06 | 35.84 | 33.80 | 26.98 |
| | Mean | 0 | 21.92 | 27.06 | 31.42 | 34.09 | 36.02 | 28.78 |
| | Std Dev | 0 | 2.80 | 2.38 | 5.14 | 2.46 | 3.14 | 2.54 |
| Ni-ATS w/o AP (Run 1 - Run 7) | Run | 0 | 31.57 | 29.62 | 17.39 | 22.34 | 48.95 | 41.05 |
| | Dup | 0 | 25.02 | 24.49 | 18.81 | 24.83 | 44.83 | 44.22 |
| | Mean | 0 | 28.29 | 27.05 | 18.10 | 23.59 | 46.89 | 42.63 |
| | Std Dev | 0 | 4.63 | 3.63 | 1.01 | 1.76 | 2.92 | 2.24 |
| Ni-ATS with AP (Run 3 - Run 4) | Run | 0 | 35.33 | 42.16 | 30.98 | 31.57 | 68.16 | 54.87 |
| | Dup | 0 | 39.67 | 34.87 | 32.53 | 35.71 | 62.66 | 52.39 |
| | Mean | 0 | 37.50 | 38.51 | 31.75 | 33.64 | 65.41 | 53.63 |
| | Std Dev | 0 | 3.06 | 5.16 | 1.09 | 2.92 | 3.89 | 1.75 |

**Table D-4: ATS consumption (kg/t-PCB) in ATS leaching of gold at four treatment combinations**

| Conditions | Time (min) | 0 | 60 | 120 | 180 | 240 | 300 | 360 |
|---|---|---|---|---|---|---|---|---|
| Cu-ATS w/o AP (Run 6 - Run 8) | Run | 0 | 114.3 | 148.1 | 103.3 | 87.5 | 84.8 | 94.4 |
| | Dup | 0 | 120.0 | 132.7 | 112.1 | 99.0 | 92.6 | 87.4 |
| | Mean | 0 | 117.13 | 140.40 | 107.74 | 93.23 | 88.70 | 90.88 |
| | Std Dev | 0 | 4.02 | 10.83 | 6.21 | 8.12 | 5.57 | 4.92 |
| Cu-ATS with AP (Run 2- Run 5) | Run | 0 | 92.1 | 75.3 | 51.9 | 64.4 | 70.6 | 69.1 |
| | Dup | 0 | 82.2 | 81.2 | 25.7 | 67.3 | 73.5 | 76.1 |
| | Mean | 0 | 87.15 | 78.29 | 38.79 | 65.87 | 72.06 | 72.60 |
| | Std Dev | 0 | 7.05 | 4.17 | 18.54 | 2.03 | 2.10 | 4.92 |
| Ni-ATS w/o AP (Run 1 - Run 7) | Run | 0 | 38.0 | 54.5 | 37.3 | 48.9 | 39.2 | 46.4 |
| | Dup | 0 | 41.3 | 38.3 | 25.9 | 31.5 | 54.9 | 43.6 |
| | Mean | 0 | 39.66 | 46.42 | 31.59 | 40.22 | 47.07 | 44.97 |
| | Std Dev | 0 | 2.31 | 11.42 | 8.08 | 12.29 | 11.06 | 1.98 |
| Ni-ATS with AP (Run 3 - Run 4) | Run | 0 | 61.8 | 60.1 | 24.7 | 46.7 | 61.9 | 45.6 |
| | Dup | 0 | 55.5 | 50.0 | 37.5 | 66.1 | 60.2 | 53.7 |
| | Mean | 0 | 58.63 | 55.08 | 31.08 | 56.43 | 61.03 | 49.63 |
| | Std Dev | 0 | 4.49 | 7.17 | 9.02 | 13.69 | 1.20 | 5.69 |

## D.2 Statistical Analysis

### D.2.1 Experimental Repeatability Test

**Table D-5: Run-duplicate t-test: paired two-sample for means – Au extraction**

| *Experimental Conditions* | | *Mean* | *Variance* | *n* | *Pearson Correlation* | *df* | *t Stat* | *P(T<=t) one-tail* | *t Critical one-tail* | *P(T<=t) two-tail* | *t Critical two-tail* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu w/o AP | *Run* | 14.96 | 45.83 | 7 | 0.9903 | 6 | -1.7971 | 0.0612 | 1.9432 | 0.1224 | 2.4469 |
| | *Dup* | 15.65 | 50.29 | 7 | | | | | | | |
| Cu with AP | *Run* | 25.94 | 150.40 | 7 | 0.9347 | 6 | 0.3871 | 0.3560 | 1.9432 | 0.7120 | 2.4469 |
| | *Dup* | 25.29 | 158.34 | 7 | | | | | | | |
| Ni w/o AP | *Run* | 27.27 | 258.23 | 7 | 0.9694 | 6 | 0.8347 | 0.2179 | 1.9432 | 0.4359 | 2.4469 |
| | *Dup* | 26.03 | 236.42 | 7 | | | | | | | |
| Ni with AP | *Run* | 37.58 | 458.70 | 7 | 0.9795 | 6 | 0.4371 | 0.3387 | 1.9432 | 0.6774 | 2.4469 |
| | *Dup* | 36.83 | 382.95 | 7 | | | | | | | |

**Table D-6: Run-duplicate t-test: paired two-sample for means – ATS consumption**

| *Experimental Conditions* | | *Mean* | *Variance* | *n* | *Pearson Correlation* | *df* | *t Stat* | *P(T<=t) one-tail* | *t Critical one-tail* | *P(T<=t) two-tail* | *t Critical two-tail* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Cu w/o AP | *Run* | 90.33 | 2048.55 | 7 | 0.9768 | 6 | -0.4498 | 0.3343 | 1.9432 | 0.6687 | 2.4469 |
| | *Dup* | 91.98 | 1897.12 | 7 | | | | | | | |
| Cu with AP | *Run* | 60.50 | 857.80 | 7 | 0.9295 | 6 | 0.5580 | 0.2985 | 1.9432 | 0.5971 | 2.4469 |
| | *Dup* | 58.00 | 1031.31 | 7 | | | | | | | |
| Ni w/o AP | *Run* | 37.76 | 317.75 | 7 | 0.7759 | 6 | 0.9234 | 0.1957 | 1.9432 | 0.3914 | 2.4469 |
| | *Dup* | 33.64 | 304.47 | 7 | | | | | | | |
| Ni with AP | *Run* | 42.98 | 534.77 | 7 | 0.8906 | 6 | -0.7811 | 0.2322 | 1.9432 | 0.4644 | 2.4469 |
| | *Dup* | 46.12 | 493.11 | 7 | | | | | | | |

### D.2.2 ANOVA

The null hypothesis of the Anova for the ammonium thiosulphate leaching was formulated as follows:

- The effect of variations in PCB pre-treatment and metal oxidant were not statistically significant in terms of gold extraction and ammonium thiosulphate consumption.

The research (alternative) hypothesis, attempting to disprove the null hypothesis, was formulated as follows:

- The effect of variations in PCB pre-treatment and metal oxidant had a significant impact on gold extraction and ammonium thiosulphate consumption.

The effect of varying a factor was statistically significant if and only if the following conditions were fulfilled:

- The p-value of the effect of factor variation on the response (dependent) variable was less than 0.0253.
- The F-statistic of the effect of factor variation on the response variable was greater than the F-critical.

**Table D-7: Response means – Au extraction (%)**

| | Metal Oxidant | |
|---|---|---|
| PCB Pretreatment | Cu | Ni |
| w/o AP | 14.96 | 27.27 |
| | 15.65 | 26.03 |
| with AP | 25.94 | 37.58 |
| | 25.29 | 36.83 |

**Table D-8: Response means – ATS consumption (kg/t-PCB)**

| | Metal Oxidant | |
|---|---|---|
| PCB Pretreatment | Cu | Ni |
| w/o AP | 90.33 | 37.76 |
| | 91.98 | 33.64 |
| with AP | 60.50 | 42.98 |
| | 58.00 | 46.12 |

**Table D-9: Anova: two-factor with replication – ATS leaching**

| *Source of Variation* | *Dependent Variable* | *Sum of Squares (SS)* | *df* | *Mean Square (MS)* | *F* | *P-value* | *F crit* | *Partial Eta Squared* |
|---|---|---|---|---|---|---|---|---|
| PCB Pretreatment | Au Extraction | 217.615 | 1 | 217.615 | 574.935 | 0.000 | 7.709 | 0.993 |
| | ATS Consumption | 265.696 | 1 | 265.696 | 59.293 | 0.002 | 7.709 | 0.937 |
| Metal Oxidant | Au Extraction | 262.983 | 1 | 262.983 | 694.796 | 0.000 | 7.709 | 0.994 |
| | ATS Consumption | 2460.727 | 1 | 2460.727 | 549.141 | 0.000 | 7.709 | 0.993 |
| Interaction | Au Extraction | 0.031 | 1 | 0.031 | 0.083 | 0.788 | 7.709 | 0.020 |
| | ATS Consumption | 830.497 | 1 | 830.497 | 185.336 | 0.000 | 7.709 | 0.979 |
| Within (Error) | Au Extraction | 1.514 | 4 | 0.379 | | | | |
| | ATS Consumption | 17.924 | 4 | 4.481 | | | | |
| Corrected Total | Au Extraction | 482.144 | 7 | | | | | |
| | ATS Consumption | 3574.844 | 7 | | | | | |

**Table D-10: Estimated marginal means – Factor interaction**

| **PCB Pretreatment * Metal Oxidant** | | | | | | |
|---|---|---|---|---|---|---|
| | | | | | 95% Confidence Interval | |
| Dependent Variable | PCB Pretreatment | Metal Oxidant | Mean | Std. Error | Lower Bound | Upper Bound |
| Au Extraction (%) | w/o AP | Cu | 15.305 | 0.433 | 14.103 | 16.507 |
| | | Ni | 26.650 | 0.433 | 25.448 | 27.852 |
| | with AP | Cu | 25.615 | 0.433 | 24.413 | 26.817 |
| | | Ni | 37.205 | 0.433 | 36.003 | 38.407 |
| ATS Consumption (kg/t-PCB) | w/o AP | Cu | 91.155 | 1.496 | 87.002 | 95.308 |
| | | Ni | 35.700 | 1.496 | 31.547 | 39.853 |
| | with AP | Cu | 59.250 | 1.496 | 55.097 | 63.403 |
| | | Ni | 44.550 | 1.496 | 40.397 | 48.703 |

## D.3 Iodimetric Titration Results

**Table D-11: Iodimetric titration – Cu-ATS w/o AP (Run)**

| Run 6 | | | | | | | ATS Consumption (kg/t-PCB) |
|---|---|---|---|---|---|---|---|
| Time (min) | $V_1$ (mL) | $V_2$ (mL) | $V_{to}$ (mL) | $V_{tf}$ (mL) | $L_2$ (mL) | ATS (M) | |
| 0 | - | - | - | - | - | - | 0 |
| 60 | 14 | 16 | 41.3 | 50.6 | 9.3 | 0.061 | 114.3 |
| 120 | 13.5 | 15 | 43.5 | 54.6 | 11.1 | 0.050 | 148.1 |
| 180 | 22.5 | 25.5 | 33.1 | 41.8 | 8.7 | 0.065 | 103.3 |
| 240 | 18 | 20.3 | 38 | 46 | 8 | 0.070 | 87.5 |
| 300 | 19.5 | 22 | 37.2 | 45.1 | 7.9 | 0.071 | 84.8 |
| 360 | 19 | 21.5 | 38.7 | 47 | 8.3 | 0.068 | 94.4 |

**Table D-12: Iodimetric titration – Cu-ATS w/o AP (Duplicate Run)**

| Run 8 | | | | | | | ATS Consumption (kg/t-PCB) |
|---|---|---|---|---|---|---|---|
| Time (min) | $V_1$ (mL) | $V_2$ (mL) | $V_{to}$ (mL) | $V_{tf}$ (mL) | $L_2$ (mL) | ATS (M) | |
| 0 | - | - | - | - | - | - | 0 |
| 60 | 14 | 15.5 | 41.7 | 51 | 9.3 | 0.060 | 120.0 |
| 120 | 13 | 14.5 | 42.9 | 53 | 10.1 | 0.055 | 132.7 |
| 180 | 21 | 23.5 | 34.7 | 43.7 | 9 | 0.062 | 112.1 |
| 240 | 21 | 23.5 | 35.7 | 44.1 | 8.4 | 0.067 | 99.0 |
| 300 | 20 | 22 | 37 | 45 | 8 | 0.069 | 92.6 |
| 360 | 20 | 22 | 36.7 | 44.5 | 7.8 | 0.071 | 87.4 |

**Table D-13: Iodimetric titration – Cu-ATS with AP (Run)**

| Run 2 | | | | | | | ATS Consumption (kg/t-PCB) |
|---|---|---|---|---|---|---|---|
| Time (min) | $V_1$ (mL) | $V_2$ (mL) | $V_{to}$ (mL) | $V_{tf}$ (mL) | $L_2$ (mL) | ATS (M) | |
| 0 | - | - | - | - | - | - | 0 |
| 60 | 9 | 9.8 | 46.5 | 54.4 | 7.9 | 0.069 | 92.1 |
| 120 | 9 | 9.8 | 49.1 | 56.4 | 7.3 | 0.075 | 75.3 |
| 180 | 9 | 9.8 | 48.9 | 55.5 | 6.6 | 0.082 | 51.9 |
| 240 | 10 | 10.8 | 48.5 | 55.4 | 6.9 | 0.078 | 64.4 |
| 300 | 9 | 9.6 | 49.8 | 56.8 | 7 | 0.076 | 70.6 |
| 360 | 9 | 9.8 | 49.1 | 56.2 | 7.1 | 0.077 | 69.1 |

**Table D-14: Iodimetric titration – Cu-ATS with AP (Duplicate Run)**

| Run 5 | | | | | | | ATS Consumption (kg/t-PCB) |
|---|---|---|---|---|---|---|---|
| Time (min) | $V_1$ (mL) | $V_2$ (mL) | $V_{to}$ (mL) | $V_{tf}$ (mL) | $L_2$ (mL) | ATS (M) | |
| 0 | - | - | - | - | - | - | 0 |
| 60 | 9.5 | 10.3 | 49 | 56.5 | 7.5 | 0.072 | 82.2 |
| 120 | 9 | 9.8 | 48.7 | 56.2 | 7.5 | 0.073 | 81.2 |
| 180 | 9 | 9.7 | 49.6 | 55.5 | 5.9 | 0.091 | 25.7 |
| 240 | 9 | 9.6 | 49.6 | 56.5 | 6.9 | 0.077 | 67.3 |
| 300 | 9.5 | 10 | 49.4 | 56.4 | 7 | 0.075 | 73.5 |
| 360 | 9 | 9.5 | 49.7 | 56.8 | 7.1 | 0.074 | 76.1 |

**Table D-15: Iodimetric titration – Ni-ATS w/o AP (Run)**

| Run 1 | | | | | | | ATS Consumption (kg/t-PCB) |
|---|---|---|---|---|---|---|---|
| Time (min) | $V_1$ (mL) | $V_2$ (mL) | $V_{to}$ (mL) | $V_{tf}$ (mL) | $L_2$ (mL) | ATS (M) | |
| 0 | - | - | - | - | - | - | 0 |
| 60 | 19 | 21.2 | 37.8 | 44.2 | 6.4 | 0.087 | 38.0 |
| 120 | 20 | 22.2 | 37.4 | 44.2 | 6.8 | 0.082 | 54.5 |
| 180 | 18.5 | 20.7 | 38.6 | 45 | 6.4 | 0.087 | 37.3 |
| 240 | 18.5 | 20.7 | 38.6 | 45.3 | 6.7 | 0.084 | 48.9 |
| 300 | 19 | 21.1 | 38.4 | 44.8 | 6.4 | 0.087 | 39.2 |
| 360 | 18.5 | 20.6 | 38.2 | 44.8 | 6.6 | 0.084 | 46.4 |

**Table D-16: Iodimetric titration – Ni-ATS w/o AP (Duplicate Run)**

| Run 7 | | | | | | | ATS Consumption (kg/t-PCB) |
|---|---|---|---|---|---|---|---|
| Time (min) | $V_1$ (mL) | $V_2$ (mL) | $V_{to}$ (mL) | $V_{tf}$ (mL) | $L_2$ (mL) | ATS (M) | |
| 0 | - | - | - | - | - | - | 0 |
| 60 | 18.5 | 20.7 | 38.5 | 45 | 6.5 | 0.086 | 41.3 |
| 120 | 9 | 10.5 | 48.6 | 55.3 | 6.7 | 0.087 | 38.3 |
| 180 | 18.5 | 20.6 | 46.7 | 52.8 | 6.1 | 0.091 | 25.9 |
| 240 | 18.5 | 20.5 | 38.8 | 45 | 6.2 | 0.089 | 31.5 |
| 300 | 18.5 | 20.2 | 38.1 | 44.8 | 6.7 | 0.081 | 54.9 |
| 360 | 18.5 | 20.2 | 44.9 | 51.3 | 6.4 | 0.085 | 43.6 |

**Table D-17: Iodimetric titration – Ni-ATS with AP (Run)**

| Run 3 | | | | | | | **ATS Consumption (kg/t-PCB)** |
|---|---|---|---|---|---|---|---|
| Time (min) | $V_1$ (mL) | $V_2$ (mL) | $V_{to}$ (mL) | $V_{tf}$ (mL) | $L_2$ (mL) | ATS (M) | |
| 0 | - | - | - | - | - | - | 0 |
| 60 | 18.5 | 20.5 | 40.2 | 47.2 | 7 | 0.079 | 61.8 |
| 120 | 18 | 19.8 | 38.1 | 45 | 6.9 | 0.080 | 60.1 |
| 180 | 18 | 19.8 | 39.3 | 45.3 | 6 | 0.092 | 24.7 |
| 240 | 20 | 21.9 | 38.3 | 44.8 | 6.5 | 0.084 | 46.7 |
| 300 | 18.5 | 20.2 | 41.6 | 48.5 | 6.9 | 0.079 | 61.9 |
| 360 | 18 | 19.8 | 39.3 | 45.8 | 6.5 | 0.085 | 45.6 |

**Table D-18: Iodimetric titration – Ni-ATS with AP (Duplicate Run)**

| Run 4 | | | | | | | **ATS Consumption (kg/t-PCB)** |
|---|---|---|---|---|---|---|---|
| Time (min) | $V_1$ (mL) | $V_2$ (mL) | $V_{to}$ (mL) | $V_{tf}$ (mL) | $L_2$ (mL) | ATS (M) | |
| 0 | - | - | - | - | - | - | 0 |
| 60 | 18 | 19.9 | 40.3 | 47.1 | 6.8 | 0.081 | 55.5 |
| 120 | 18.5 | 20.3 | 39.9 | 46.5 | 6.6 | 0.083 | 50.0 |
| 180 | 18 | 19.5 | 39.5 | 45.7 | 6.2 | 0.087 | 37.5 |
| 240 | 18 | 19.3 | 40.9 | 47.8 | 6.9 | 0.078 | 66.1 |
| 300 | 15.5 | 16.8 | 42.9 | 49.7 | 6.8 | 0.080 | 60.2 |
| 360 | 18.5 | 20 | 40.4 | 47 | 6.6 | 0.082 | 53.7 |

# APPENDIX E

## SHRINKING-CORE MODEL AND RATE-LIMITING MECHANISM

# APPENDIX E : Shrinking-Core Model and Rate-Limiting Mechanism

## E.1 Acid Pre-treatment – SCM with Shrinking Particles

**Table E-1: Estimated time for complete conversion $\tau$ – Acid pre-treatment**

| *Conditions* | *$\tau$ (h)* |
|---|---|
| *A* | 3.4 |
| *B* | 3.8 |
| *C* | 4.0 |
| *D* | 3.7 |

**Table E-2: SCM-generated data and experimental data – Conditions A**

| | | | | | | **1 - X** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Shrinking Core Model** | | | **Data** |
| **Time (min)** | **Time (h)** | **Extraction (%)** | **Conversion (X)** | **1-X** | **t/τ** | **FDC-SR** | **FDC-TR** | **RC** | **Cond A** |
| 0 | 0 | 0 | 0 | 1 | 0.000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 30 | 0.5 | 78.30 | 0.7830 | 0.2170 | 0.147 | 0.7873 | 0.7270 | 0.6198 | 0.2170 |
| 60 | 1 | 83.25 | 0.8325 | 0.1675 | 0.295 | 0.5922 | 0.4974 | 0.3508 | 0.1675 |
| 90 | 1.5 | 78.23 | 0.7823 | 0.2177 | 0.442 | 0.4167 | 0.3112 | 0.1736 | 0.2177 |
| 120 | 2 | 83.52 | 0.8352 | 0.1648 | 0.590 | 0.2630 | 0.1685 | 0.0692 | 0.1648 |
| 150 | 2.5 | 93.72 | 0.9372 | 0.0628 | 0.737 | 0.1349 | 0.0692 | 0.0182 | 0.0628 |
| 180 | 3 | 88.43 | 0.8843 | 0.1157 | 0.884 | 0.0394 | 0.0134 | 0.0015 | 0.1157 |

**Table E-3: SCM-generated data and experimental data – Conditions B**

| | | | | | | **1 - X** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Shrinking Core Model** | | | **Data** |
| **Time (min)** | **Time (h)** | **Extraction (%)** | **Conversion (X)** | **1-X** | **t/τ** | **FDC-SR** | **FDC-TR** | **RC** | **Cond B** |
| 0 | 0 | 0 | 0 | 1 | 0.000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 30 | 0.5 | 78.98 | 0.7898 | 0.2102 | 0.133 | 0.8069 | 0.7512 | 0.6511 | 0.2102 |
| 60 | 1 | 78.46 | 0.7846 | 0.2154 | 0.267 | 0.6281 | 0.5379 | 0.3945 | 0.2154 |
| 90 | 1.5 | 76.39 | 0.7639 | 0.2361 | 0.400 | 0.4649 | 0.3602 | 0.2161 | 0.2361 |
| 120 | 2 | 79.69 | 0.7969 | 0.2031 | 0.533 | 0.3190 | 0.2179 | 0.1017 | 0.2031 |
| 150 | 2.5 | 88.82 | 0.8882 | 0.1118 | 0.666 | 0.1926 | 0.1113 | 0.0371 | 0.1118 |
| 180 | 3 | 79.97 | 0.7997 | 0.2003 | 0.800 | 0.0896 | 0.0401 | 0.0080 | 0.2003 |

**Table E-4: SCM-generated data and experimental data – Conditions C**

| | | | | | | 1 - X | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Shrinking Core Model | | | Data |
| **Time (min)** | **Time (h)** | **Extraction (%)** | **Conversion (X)** | **1-X** | **t/τ** | **FDC-SR** | **FDC-TR** | **RC** | **Cond C** |
| 0 | 0 | 0 | 0 | 1 | 0.000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 30 | 0.5 | 84.59 | 0.8459 | 0.1541 | 0.125 | 0.8191 | 0.7663 | 0.6709 | 0.1541 |
| 60 | 1 | 77.93 | 0.7793 | 0.2207 | 0.249 | 0.6506 | 0.5637 | 0.4233 | 0.2207 |
| 90 | 1.5 | 82.43 | 0.8243 | 0.1757 | 0.374 | 0.4956 | 0.3922 | 0.2456 | 0.1757 |
| 120 | 2 | 80.95 | 0.8095 | 0.1905 | 0.498 | 0.3553 | 0.2516 | 0.1262 | 0.1905 |
| 150 | 2.5 | 76.09 | 0.7609 | 0.2391 | 0.623 | 0.2315 | 0.1422 | 0.0536 | 0.2391 |
| 180 | 3 | 74.76 | 0.7476 | 0.2524 | 0.748 | 0.1268 | 0.0637 | 0.0161 | 0.2524 |

**Table E-5: SCM-generated data and experimental data – Conditions D**

| | | | | | | 1 - X | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Shrinking Core Model | | | Data |
| **Time (min)** | **Time (h)** | **Extraction (%)** | **Conversion (X)** | **1-X** | **t/τ** | **FDC-SR** | **FDC-TR** | **RC** | **Cond D** |
| 0 | 0 | 0 | 0 | 1 | 0.000 | 1.0000 | 1.0000 | 1.0000 | 1.0000 |
| 30 | 0.5 | 69.72 | 0.6972 | 0.3028 | 0.137 | 0.8022 | 0.7454 | 0.6435 | 0.3028 |
| 60 | 1 | 74.59 | 0.7459 | 0.2541 | 0.273 | 0.6195 | 0.5281 | 0.3838 | 0.2541 |
| 90 | 1.5 | 75.27 | 0.7527 | 0.2473 | 0.410 | 0.4533 | 0.3482 | 0.2054 | 0.2473 |
| 120 | 2 | 81.55 | 0.8155 | 0.1845 | 0.547 | 0.3053 | 0.2056 | 0.0932 | 0.1845 |
| 150 | 2.5 | 82.19 | 0.8219 | 0.1781 | 0.683 | 0.1783 | 0.1003 | 0.0318 | 0.1781 |
| 180 | 3 | 81.99 | 0.8199 | 0.1801 | 0.820 | 0.0764 | 0.0324 | 0.0058 | 0.1801 |

### Table E-6: Goodness of model fit – t-test: paired two sample for means (acid pre-treatment)

| *Pair* | *Mean* | *Variance* | *n* | *Pearson Correlation R* | Coeff. of Det. $R^2$ | *df* | *t Stat* | *P(T<=t) one-tail* | *t Critical one-tail* | *P(T<=t) two-tail* | *t Critical two-tail* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *FDC-SR - Cond A* | 0.4619 | 0.1232 | 7 | 0.7618 | 0.5804 | 6 | 2.0794 | 0.0414 | 1.9432 | 0.0828 | 2.4469 |
| *FDC-TR - Cond A* | 0.3981 | 0.1328 | 7 | 0.8041 | 0.6466 | 6 | 1.4536 | 0.0981 | 1.9432 | 0.1963 | 2.4469 |
| *RC - Cond A* | 0.3190 | 0.1383 | 7 | 0.8642 | 0.7469 | 6 | 0.5810 | 0.2912 | 1.9432 | 0.5824 | 2.4469 |
| *Cond A* | 0.2779 | 0.1044 | | | | | | | | | |
| *FDC-SR - Cond B* | 0.5002 | 0.1096 | 7 | 0.7069 | 0.4997 | 6 | 2.0423 | 0.0436 | 1.9432 | 0.0872 | 2.4469 |
| *FDC-TR - Cond B* | 0.4312 | 0.1239 | 7 | 0.7494 | 0.5616 | 6 | 1.3429 | 0.1139 | 1.9432 | 0.2279 | 2.4469 |
| *RC - Cond B* | 0.3441 | 0.1349 | 7 | 0.8151 | 0.6643 | 6 | 0.4114 | 0.3476 | 1.9432 | 0.6951 | 2.4469 |
| *Cond B* | 0.3110 | 0.0939 | | | | | | | | | |
| *FDC-SR - Cond C* | 0.5255 | 0.1004 | 7 | 0.5892 | 0.3472 | 6 | 1.9459 | 0.0498 | 1.9432 | 0.0996 | 2.4469 |
| *FDC-TR - Cond C* | 0.4542 | 0.1170 | 7 | 0.6370 | 0.4058 | 6 | 1.2930 | 0.1218 | 1.9432 | 0.2436 | 2.4469 |
| *RC - Cond C* | 0.3622 | 0.1317 | 7 | 0.7173 | 0.5145 | 6 | 0.4467 | 0.3354 | 1.9432 | 0.6708 | 2.4469 |
| *Cond C* | 0.3190 | 0.0914 | | | | | | | | | |
| *FDC-SR - Cond D* | 0.4907 | 0.1130 | 7 | 0.7726 | 0.5969 | 6 | 1.8987 | 0.0532 | 1.9432 | 0.1064 | 2.4469 |
| *FDC-TR - Cond D* | 0.4229 | 0.1262 | 7 | 0.8141 | 0.6628 | 6 | 1.1228 | 0.1522 | 1.9432 | 0.3044 | 2.4469 |
| *RC - Cond D* | 0.3377 | 0.1359 | 7 | 0.8752 | 0.7660 | 6 | 0.0353 | 0.4865 | 1.9432 | 0.9730 | 2.4469 |
| *Cond D* | 0.3353 | 0.0881 | | | | | | | | | |

## E.2 Ammonium Thiosulphate Leaching – SCM with Unshrinking Particles

**Table E-7: Estimated time for complete conversion *τ* – ATS leaching**

| *Conditions* | *τ (h)* |
|---|---|
| *Cu w/o AP* | 28.8 |
| *Cu with AP* | 20.9 |
| *Ni w/o AP* | 14.1 |
| *Ni with AP* | 11.2 |

**Table E-8: SCM-generated data and experimental data – Cu-ATS w/o AP**

| | | | | | | **1 - X** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Shrinking Core Model** | | | **Data** |
| **Time (min)** | **Time (h)** | **Extraction (%)** | **Conversion (X)** | **1-X** | **t/τ** | **FDC** | **ADC** | **RC** | **Cu w/o AP** |
| 0 | 0 | 0 | 0 | 1 | 0.000 | 1 | 1 | 1 | 1.0000 |
| 60 | 1 | 17.26 | 0.1726 | 0.8274 | 0.035 | 0.97 | 0.6995 | 0.8995 | 0.8274 |
| 120 | 2 | 16.50 | 0.1650 | 0.8350 | 0.069 | 0.93 | 0.5917 | 0.8059 | 0.8350 |
| 180 | 3 | 16.58 | 0.1658 | 0.8342 | 0.104 | 0.90 | 0.5120 | 0.7190 | 0.8342 |
| 240 | 4 | 17.38 | 0.1738 | 0.8262 | 0.139 | 0.86 | 0.4489 | 0.6387 | 0.8262 |
| 300 | 5 | 18.61 | 0.1861 | 0.8139 | 0.174 | 0.83 | 0.3963 | 0.5645 | 0.8139 |
| 360 | 6 | 20.82 | 0.2082 | 0.7918 | 0.208 | 0.79 | 0.3525 | 0.4964 | 0.7918 |

**Table E-9: SCM-generated data and experimental data – Cu-ATS with AP**

| | | | | | | **1 - X** | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | **Shrinking Core Model** | | | **Data** |
| **Time (min)** | **Time (h)** | **Extraction (%)** | **Conversion (X)** | **1-X** | **t/τ** | **FDC** | **ADC** | **RC** | **Cu with AP** |
| 0 | 0 | 0 | 0.0000 | 1.0000 | 0.000 | 1 | 1 | 1 | 1.0000 |
| 60 | 1 | 21.92 | 0.2192 | 0.7808 | 0.048 | 0.95 | 0.6529 | 0.8629 | 0.7808 |
| 120 | 2 | 27.06 | 0.2706 | 0.7294 | 0.096 | 0.90 | 0.5284 | 0.7390 | 0.7294 |
| 180 | 3 | 31.42 | 0.3142 | 0.6858 | 0.144 | 0.86 | 0.4408 | 0.6275 | 0.6858 |
| 240 | 4 | 34.09 | 0.3409 | 0.6591 | 0.192 | 0.81 | 0.3723 | 0.5278 | 0.6591 |
| 300 | 5 | 36.02 | 0.3602 | 0.6398 | 0.240 | 0.76 | 0.3162 | 0.4393 | 0.6398 |
| 360 | 6 | 28.78 | 0.2878 | 0.7122 | 0.288 | 0.71 | 0.2689 | 0.3613 | 0.7122 |

**Table E-10: SCM-generated data and experimental data – Ni-ATS w/o AP**

| | | | | | | 1 - X | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Shrinking Core Model | | | Data |
| Time (min) | Time (h) | Extraction (%) | Conversion (X) | 1-X | t/τ | FDC | ADC | RC | Ni w/o AP |
| 0 | 0 | 0 | 0 | 1 | 0.000 | 1 | 1 | 1 | 1.0000 |
| 60 | 1 | 28.29 | 0.2829 | 0.7171 | 0.071 | 0.93 | 0.5865 | 0.8016 | 0.7171 |
| 120 | 2 | 27.05 | 0.2705 | 0.7295 | 0.142 | 0.86 | 0.4440 | 0.6314 | 0.7295 |
| 180 | 3 | 18.10 | 0.1810 | 0.8190 | 0.213 | 0.79 | 0.3465 | 0.4872 | 0.8190 |
| 240 | 4 | 23.59 | 0.2359 | 0.7641 | 0.284 | 0.72 | 0.2725 | 0.3667 | 0.7641 |
| 300 | 5 | 46.89 | 0.4689 | 0.5311 | 0.355 | 0.64 | 0.2138 | 0.2680 | 0.5311 |
| 360 | 6 | 42.63 | 0.4263 | 0.5737 | 0.426 | 0.57 | 0.1659 | 0.1888 | 0.5737 |

**Table E-11: SCM-generated data and experimental data – Ni-ATS with AP**

| | | | | | | 1 - X | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | | Shrinking Core Model | | | Data |
| Time (min) | Time (h) | Extraction (%) | Conversion (X) | 1-X | t/τ | FDC | ADC | RC | Ni with AP |
| 0 | 0 | 0 | 0 | 1 | 0.000 | 1 | 1 | 1 | 1.0000 |
| 60 | 1 | 37.50 | 0.3750 | 0.6250 | 0.089 | 0.91 | 0.5436 | 0.7551 | 0.6250 |
| 120 | 2 | 38.51 | 0.3851 | 0.6149 | 0.179 | 0.82 | 0.3895 | 0.5539 | 0.6149 |
| 180 | 3 | 31.75 | 0.3175 | 0.6825 | 0.268 | 0.73 | 0.2877 | 0.3920 | 0.6825 |
| 240 | 4 | 33.64 | 0.3364 | 0.6636 | 0.358 | 0.64 | 0.2115 | 0.2652 | 0.6636 |
| 300 | 5 | 65.41 | 0.6541 | 0.3459 | 0.447 | 0.55 | 0.1535 | 0.1692 | 0.3459 |
| 360 | 6 | 53.63 | 0.5363 | 0.4637 | 0.536 | 0.46 | 0.1078 | 0.0997 | 0.4637 |

**Table E-12: Goodness of model fit – t-est: two sample for means (ATS leaching)**

| *Pair* | *Mean* | *Variance* | *n* | *Pearson Correlation R* | Coeff. of Det. $R^2$ | *df* | *t Stat* | *P(T<=t) one-tail* | *t Critical one-tail* | *P(T<=t) two-tail* | *t Critical two-tail* |
|---|---|---|---|---|---|---|---|---|---|---|---|
| *FDC - Cu w/o AP* | 0.8959 | 0.0056 | 7 | 0.7370 | 0.5432 | 6 | 2.4661 | 0.0244 | 1.9432 | 0.0487 | 2.4469 |
| *ADC - Cu w/o AP* | 0.5716 | 0.0496 | 7 | 0.9093 | 0.8268 | 6 | -4.4853 | 0.0021 | 1.9432 | 0.0042 | 2.4469 |
| *RC - Cu w/o AP* | 0.7320 | 0.0330 | 7 | 0.7634 | 0.5828 | 6 | -2.2308 | 0.0336 | 1.9432 | 0.0672 | 2.4469 |
| *Cu w/o AP* | 0.8469 | 0.0048 | | | | | | | | | |
| *FDC - Cu with AP* | 0.8561 | 0.0107 | 7 | 0.7675 | 0.5891 | 6 | 3.7629 | 0.0047 | 1.9432 | 0.0094 | 2.4469 |
| *ADC - Cu with AP* | 0.5114 | 0.0634 | 7 | 0.9428 | 0.8888 | 6 | -4.3163 | 0.0025 | 1.9432 | 0.0050 | 2.4469 |
| *RC - Cu with AP* | 0.6511 | 0.0531 | 7 | 0.8221 | 0.6758 | 6 | -1.6631 | 0.0737 | 1.9432 | 0.1473 | 2.4469 |
| *Cu with AP* | 0.7439 | 0.0149 | | | | | | | | | |
| *FDC - Ni w/o AP* | 0.7868 | 0.0236 | 7 | 0.7992 | 0.6388 | 6 | 1.4390 | 0.1001 | 1.9432 | 0.2002 | 2.4469 |
| *ADC - Ni w/o AP* | 0.4327 | 0.0830 | 7 | 0.8281 | 0.6858 | 6 | -4.3883 | 0.0023 | 1.9432 | 0.0046 | 2.4469 |
| *RC - Ni w/o AP* | 0.5348 | 0.0864 | 7 | 0.7969 | 0.6351 | 6 | -2.7093 | 0.0176 | 1.9432 | 0.0351 | 2.4469 |
| *Ni w/o AP* | 0.7335 | 0.0243 | | | | | | | | | |
| *FDC - Ni with AP* | 0.7319 | 0.0373 | 7 | 0.8017 | 0.6427 | 6 | 2.1921 | 0.0354 | 1.9432 | 0.0709 | 2.4469 |
| *ADC - Ni with AP* | 0.3848 | 0.0956 | 7 | 0.8664 | 0.7507 | 6 | -3.8499 | 0.0042 | 1.9432 | 0.0085 | 2.4469 |
| *RC - Ni with AP* | 0.4621 | 0.1074 | 7 | 0.8216 | 0.6750 | 6 | -2.2160 | 0.0343 | 1.9432 | 0.0686 | 2.4469 |
| *Ni with AP* | 0.6279 | 0.0416 | | | | | | | | | |

# APPENDIX F

## PRELIMINARY ECONOMICS ANALYSIS

# APPENDIX F : Preliminary Economics Analysis

**Table F-1: Preliminary information for economics analysis**

| **Basis** | **1 metric ton PCBs** |
|---|---|
| Au Content | 524 g/t-PCB |
| Au Price* | 47.52 USD/g |
| USD/ZAR Exchange Rate* | 14.99 R/USD |

* date: 20-Nov-2019

**Table F-2: Chemical reagent prices**

| Reagent | Cost (R/kg) | Cost (USD/kg) | Source* |
|---|---:|---:|---|
| Sodium Cyanide | 1,809.00 | 120.68 | *Sigma-Aldrich* |
| Ammonium Thiosulphate | 738.00 | 49.23 | *Sigma-Aldrich* |
| Copper | 86.64 | 5.78 | *infomine.com* |
| Nickel | 221.40 | 14.77 | *infomine.com* |

* date: 20-Nov-2019

**Table F-3: Gross margin comparison – Part 1**

| Chemical Process | Gold Conversion (%) | Reagent Consumption (kg/t-PCB) | | Lixiviant Price (USD/kg) | Metal Oxidant Price (USD/kg) | Lixiviant Cost (USD) | Metal Oxidant Cost (USD) |
|---|---:|---:|---:|---:|---:|---:|---:|
| | | Lixiviant | Metal Oxidant | | | | |
| Cyanidation | 97.10 | 17.5 | - | 120.68 | - | 2,112 | - |
| Cu-ATS Leaching | 36.02 | 72.06 | 38.1 | 49.23 | 5.78 | 3,548 | 220 |
| Ni-ATS Leaching | 65.41 | 47.7 | 35.2 | 49.23 | 14.77 | 2,348 | 520 |

**Table F-4: Gross margin comparison – Part 2**

| Chemical Process | **Raw Materials Costs (USD)** | Product (Au) Price (USD/g) | Revenue (USD) | **Gross Margin (USD)** |
|---|---:|---:|---:|---:|
| Cyanidation | **2,112** | 47.52 | 24,178 | **22,066** |
| Cu-ATS Leaching | **3,768** | 47.52 | 8,969 | **5,201** |
| Ni-ATS Leaching | **2,868** | 47.52 | 16,287 | **13,419** |

# APPENDIX G

## SAMPLE CALCULATIONS

# APPENDIX G : Sample Calculations

## G.1 PCB Characterization

The gold and copper content of PCBs were determined from the aqua regia leaching results in Table A-3 and Table A-4 from the metal concentrations of pregnant leach solutions obtained after 24h of leaching time in the five replicate runs. The minimum, maximum and average concentrations for gold and copper are shown in Table G-1.

**Table G-1: Average gold and copper concentrations of pregnant aqua regia solution**

| | **Metal Concentration (mg/L)** | | |
|---|---|---|---|
| **Metal** | Min | Max | Average |
| **Cu** | 21765 | 24035 | 23092 |
| **Au** | 22.82 | 30.35 | 26.19 |

$m_T = 5\ g = 5000\ mg\ \ (PCB\ mass)$

$Pulp\ density = 50\ g/L$

$$V_T = 5g\left(\frac{L}{50\ g}\right)\left(\frac{1000\ mL}{1\ L}\right) = 100\ mL$$

$C_{Au} = 26.19\ mg/L$ *(from Table G-1)*

$$m_{Au} = 26.19\ \frac{mg}{L}\left(\frac{1\ L}{1000\ mL}\right)(100\ mL) = \underline{2.619\ mg\ Au}$$

$$x_{Au} = \frac{m_{Au}}{m_T} = \frac{2.619\ mg\ Au}{5000\ mg\ Au} = \underline{0.000524}$$

$$\boxed{\boldsymbol{Au\ Content = 0.0524\ wt\%}}$$

$$Au\ Content = 0.000524\ \frac{ton\ Au}{ton\ PCB}\left(\frac{10^6\ g\ Au}{1\ ton\ Au}\right)$$

$$\boxed{\boldsymbol{Au\ Content = 524\ g/ton\ PCB}}$$

The same procedure was used to determine the copper content.

## G.2 Acid Pre-treatment

### G.2.1 Metal Extraction – Run 1 (150 min)

The metal extractions obtained in Table C-4 and Table C-5 were calculated as follows.

$$Pulp\ density = 50\ g/L$$

$$Reaction\ Volume = 700\ mL = 0.700\ L$$

$$PCB\ mass = Pulp\ density\ x\ Reaction\ Volume = \left(50\ \frac{g}{L}\right)(0.700\ L) = 35\ g$$

Based on the average metal content in Table 4-3 (46.18 wt% Cu and 0.0524 wt% Au), the mass of copper and gold in 35 g of PCB is:

$$m_{Cu\ initial} = \frac{46.18(35)}{100} = \underline{16.16\ g}$$

$$m_{Au\ initial} = \frac{0.0524(35)}{100} = \underline{0.0183\ g}$$

The copper and gold concentrations of the pregnant leach solution for run 1 after 150 min (Table C-2 and Table C-3) were 21570 mg/L and 2.276 mg/L, respectively. Thus:

$$m_{Cu\ dissolved} = 21570\ \frac{mg}{L}\left(\frac{1g}{1000\ mg}\right)(0.700\ L) = 15.10\ g$$

$$m_{Cu\ dissolved} = 2.276\ \frac{mg}{L}\left(\frac{1g}{1000\ mg}\right)(0.700\ L) = 0.00159\ g$$

$$Cu\ extraction = \frac{m_{Cu\ dissolved}}{m_{Cu\ initial}} \times 100 = \frac{15.10\ g}{16.16\ g} \times 100 = \boxed{\mathbf{93.41}\ \%}$$

$$Au\ extraction = \frac{m_{Au\ dissolved}}{m_{Au\ initial}} \times 100 = \frac{0.00159\ g}{0.0183\ g} \times 100 = \boxed{\mathbf{8.69}\ \%}$$

### G.2.2 Material Balance

The material balance in Table C-6 was based on the optimum leaching conditions (A) that gave the highest copper extraction (93.72 %) and lowest gold extraction (8.83 %). It was safely assumed that the total PCB mass removed during acid pre-treatment was entirely due to copper extraction. This assumption was supported by the results discussed in Chapter 4 (Figure 4-4).

Considering 35 g of PCBs with 93.72 % Cu extraction and 8.83 % Au extraction,

$$m_{Cu\,initial} = 16.16\ g$$
$$m_{Au\,initial} = 0.0183\ g$$

$$m_{Cu\,final} = (16.16\ g)(1 - 0.9372) = 1.015\ g$$
$$m_{Au\,final} = (0.0183\ g)(1 - 0.0883) = 0.0168\ g$$

$$m_{Cu\,removed} = m_{Cu\,initial} - m_{Cu\,final} = 16.16 - 1.015 = 15.15\ g$$
$$m_{Au\,removed} = m_{Au\,initial} - m_{Au\,final} = 0.0183 - 0.0168 = 0.0016\ g$$

The metal content of PCBs after acid pre-treatment was calculated as follows:

$$m_{T2} = 35 - 15.15 = 19.85\ g \quad (total\ PCB\ mass\ after\ acid\ leaching)$$
$$x_{Cu} = \frac{m_{Cu\,final}}{m_{T2}} = \frac{1.015\ g\ Cu}{19.85\ g\ PCB} = \underline{0.0511}$$
$$x_{Au} = \frac{m_{Au\,final}}{m_{T2}} = \frac{0.0168\ g\ Au}{19.85\ g\ PCB} = \underline{0.000842}$$

$$Cu\ Content = \boxed{\mathbf{5.11\ wt\%}}$$
$$Au\ Content = \boxed{\mathbf{0.0842\ wt\%}}$$

$$Cu\ Content = 0.0511\ \frac{ton\ Cu}{ton\ PCB}\left(\frac{10^3\ kg\ Cu}{1\ ton\ Cu}\right) = \boxed{\mathbf{51.1\ kg/ton\ PCB}}$$
$$Au\ Content = 0.000842\ \frac{ton\ Au}{ton\ PCB}\left(\frac{10^6\ g\ Au}{1\ ton\ Au}\right) = \boxed{\mathbf{842\ g/ton\ PCB}}$$

## G.3 Ammonium Thiosulphate Leaching

### G.3.1 Gold Extraction – Ni-ATS w/o AP (Run 1)

The metal extractions obtained in ammonium thiosulphate leaching processes without acid pre-treatment were calculated as follows.

$$Pulp\ density = 50\ g/L$$

$$Reaction\ Volume = 700\ mL = 0.700\ L$$

$$PCB\ mass = Pulp\ density\ x\ Reaction\ Volume = \left(50\ \frac{g}{L}\right)(0.700\ L) = 35\ g$$

Based on the average metal content in Table 4-3 (0.0524 wt% Au), the mass of copper and gold in 35 g of PCB is:

$$m_{Au\ initial} = \frac{0.0524(35)}{100} = \underline{0.0183\ g}$$

The gold concentration of the pregnant leach solution for run 1 after 300 min (Table D-2) was 12.87 mg/L. Thus:

$$m_{Au\ dissolved} = 12.87\ \frac{mg}{L}\left(\frac{1g}{1000\ mg}\right)(0.700\ L) = 0.0090\ g$$

$$Au\ extraction = \frac{m_{Au\ dissolved}}{m_{Au\ initial}} \times 100 = \frac{0.0090\ g}{0.0183\ g} \times 100 = \boxed{\mathbf{48.95}\ \%}$$

### G.3.2 Gold Extraction – Ni-ATS with AP (Run 3)

The metal extractions obtained in ammonium thiosulphate leaching processes with acid pre-treatment were calculated as follows.

$Pulp\ density = 50\ g/L$

$PCB\ mass = 19.54\ g$ (Mass recorded after acid pre-treatment as shown in Table D-1)

$$Reaction\ Volume = \frac{PCB\ mass}{Pulp\ density} = (19.54\ g)\left(\frac{L}{50\ g}\right) = 0.391\ L$$

Based on the metal content of the acid-treated (concentrated) PCBs in Table 4-3 (0.0842 wt% Au), the mass of gold in 19.54 g of PCB is:

$$m_{Au\ initial} = \frac{0.0842(19.54)}{100} = \underline{0.0165\ g}$$

The gold concentration of the pregnant leach solution for run 3 after 300 min (Table D-2) was 28.70 mg/L. Thus:

$$m_{Au\ dissolved} = 28.70\ \frac{mg}{L}\left(\frac{1g}{1000\ mg}\right)(0.391\ L) = 0.0112\ g$$

$$Au\ extraction = \frac{m_{Au\ dissolved}}{m_{Au\ initial}} \times 100 = \frac{0.0112\ g}{0.0165\ g} \times 100 = \boxed{\mathbf{68.16}\ \%}$$

### G.3.3 ATS Consumption – Ni-ATS with AP (Run 3)

The ATS concentration obtained in run 3 after 300 min of leaching time (Table D-17) was 0.079 mol.L$^{-1}$. The ATS consumption in kg/t-PCB was obtained as follows:

$C_{ATS\ initial} = 0.1\ mol.L^{-1}$

$C_{ATS} = 0.079\ mol.L^{-1}$

$M_w = 148.21\ g/mol$ (Molar mass of ATS)

$V_T = 0.391\ L$ (Reaction volume)

$m_T = 19.54\ g$ (PCB mass)

$$ATS\ consumption = \frac{(C_{ATS\ initial} - C_{ATS})V_T M_T}{m_T}$$

$$ATS\ consumption = (0.1 - 0.079)\frac{mol}{L}(0.391\ L)\left(148.21\frac{g\ ATS}{mol}\right)\left(\frac{1}{19.54\ g\ PCB}\right)$$

$$ATS\ consumption = 0.0619\ \frac{g}{g\ PCB} = 0.0619\ \frac{kg}{kg\ PCB}\left(\frac{1000\ kg\ PCB}{1\ ton\ PCB}\right)$$

$$ATS\ consumption = \boxed{\mathbf{61.9\ kg/ton\ PCB}}$$

## G.4 Shrinking-Core Model and Rate-Limiting Mechanism – Ni-ATS with AP

The mathematical procedure summarised in this section holds for both acid pre-treatment and ammonium thiosulphate leaching. The shrinking-core models used for acid pre-treatment and ATS leaching are discussed in Chapter 2 (section 2.7).

In the analysis of the experimental data in terms of rate-limiting mechanism, it was essential to incorporate the time for complete conversion $\tau$. However, a direct approach to determining $\tau$ was not achievable. Therefore, this variable was estimated from the total leaching time and corresponding gold conversion.

For Ni-ATS with AP (Table E-11), the gold extraction obtained after 360 min (total reaction time) was 53.63%. Thus,

$$t = 360\, min = 6\, h$$

$$X = \frac{53.63}{100} = 0.5363$$

$$\tau = \frac{Reaction\ time}{Gold\ Conversion} = \frac{t}{X} = \frac{6\, h}{0.5363} = 11.2\, h$$

$$\frac{t}{\tau} = \frac{6\, h}{11.2\, h} = \underline{0.536} \qquad (fraction\ of\ time\ for\ complete\ conversion)$$

$$1 - X = 1 - 0.5363 = \underline{0.4637} \qquad (shrinking\ of\ unreacted\ core)$$

The SCM-generated conversion data (FDC-SR, FDR-TR, RC for acid-pre-treatment, and FDC, ADC, RC for ATS leaching) were determined from the respective mathematical expressions of the reaction mechanisms, with the reaction time expressed as $t/\tau$, as shown in Table 2-7 in chapter 2. It is worth noting that the model-generated data points were calculated at the same time intervals as the experimental data, allowing for the use of statistical means (paired two-sample t-test) to determine the goodness of model fit to the experimental data and to estimate the corresponding coefficient of determination ($R^2$).

The SCM expressions (equations (33), (35) and (37) for acid leaching, and equations (29), (31) and (33) for ATS leaching) were rearranged in such a way to obtain (1 – X) as a function of t/τ, making (1 – X) as the subject of each expression. For instance, the mathematical expression for the RC mechanism was rearranged as:

$$\frac{t}{\tau} = 1 - (1 - X)^{1/3} \quad \Longrightarrow \quad (1 - X)^{1/3} = 1 - \frac{t}{\tau}$$

$$(1 - X)_{RC} = \left(1 - \frac{t}{\tau}\right)^3$$

Thus, at $t/\tau = 0.536$ ($t = 6\ h$):

$$(1 - X)_{RC} = (1 - 0.536)^3 = \underline{0.0997}$$

## G.5 Preliminary Economics Analysis – Gross Margin of Ni-ATS Leaching

$$\boldsymbol{Basis = 1\ ton\ PCBs}$$

$$Au\ Content = 524\ g/t\ PCB$$

$$Au\ Price = 47.52\ USD/g$$

$$NaCN\ Price = 120.68\ USD/kg$$

$$(NH_4)_2S_2O_3\ Price = 49.23\ USD/kg$$

$$Cu\ Price = 5.78\ USD/kg$$

$$Ni\ Price = 14.77\ USD/kg$$

$$Au\ Conversion = 65.41\ \%$$

$$Au\ Mass = \frac{65.41}{100}(524\ g) = 342.7\ g$$

$$Revenue = Au\ Mass \times Au\ Price = 342.7\ g\left(\frac{47.52\ USD}{g}\right) = \underline{\mathbf{16\ 287\ \boldsymbol{USD}}}$$

$$ATS\ Consumption = 47.7\ kg/t\ PCB$$

$$ATS\ Cost = ATS\ Consumption \times ATS\ Price = 47.7\ kg\left(\frac{49.23\ USD}{kg}\right) = \underline{2\ 348\ USD}$$

$$Ni\ used = 35.2\ kg/t\ PCB$$

$$Ni\ Cost = Ni\ used \times Ni\ Price = 35.2\ kg\left(\frac{14.77\ USD}{kg}\right) = \underline{520\ USD}$$

$$Raw\ Materials\ Cost = ATS\ Cost + Ni\ Cost = 2\ 348 + 520 = \underline{\mathbf{2\ 868\ \boldsymbol{USD}}}$$

$$Gross\ Margin = Revenue - Raw\ Materials\ Cost = 16\ 287 - 2\ 868$$

$$\boxed{\boldsymbol{Gross\ Margin = 13\ 419\ USD}}$$

### G.6 Mathematical Derivation of Shrinking-Core Model – Reaction Control

In this section, the derivation of the SCM in terms of reaction control is outlined. The remaining SCMs have been derived and discussed extensively by Levenspiel (1999).

Considering the following reaction between a solid A surrounded by a fluid B:

$$A(g) + bB(s) \;\longrightarrow\; products \tag{28}$$

When a solid-fluid reaction is chemically controlled, the interaction is independent of the presence of any ash or film layer surrounding the unreacted particle core. The rate of reaction is therefore proportional to the total surface of the unreacted core. The reaction rate for the stoichiometry of reaction (28) is:

$$-\frac{1}{4\pi r_c^2}\frac{dN_B}{dt} = -\frac{b}{4\pi r_c^2}\frac{dN_A}{dt} = bk"C_{Ag} \tag{G-1}$$

Where k” is the first-order rate constant for the surface reaction.

Writing $N_B$ as a function of the unreacted radius $r_c$ and substituting in equation (G-1) gives:

$$-\frac{1}{4\pi r_c^2}\rho_B 4\pi r_c^2\frac{dr_c}{dt} = -\rho_B\frac{dr_c}{dt} = bk"C_{Ag} \tag{G-2}$$

Integrating gives:

$$-\rho_B\int_R^{r_c} dr_c = bk"C_{Ag}\int_0^t dt \tag{G-3}$$

$$\boxed{t = \frac{\rho_b}{bk"C_{Ag}}(R - r_c)} \tag{G-4}$$

Complete conversion corresponds to the disappearance of the unreacted core. Thus, taking the time for total conversion as $\tau$ and corresponding unreacted core size $r_c = 0$ gives:

$$\boxed{\tau = \frac{\rho_b R}{bk"C_{Ag}}} \tag{34}$$

The size reduction of the unreacted core or increase in the fractional conversion can be expressed in terms of $\tau$ by combining equations (G-4) and (34), giving:

$$\boxed{\frac{t}{\tau} = 1 - \frac{r_c}{R} = 1 - (1 - X_B)^{1/3}} \tag{33}$$