Evaluating the efficiency of a metal recycling process by means of life cycle assessment and exergy analyses
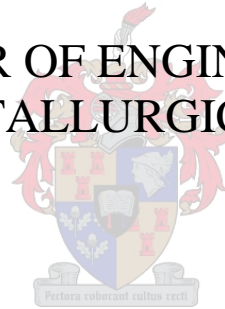
by

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ABSTRACT

Various recycling technologies for metal production from electronic waste (e- waste) have been proposed in literature. Traditionally, pyrometallurgical processes are employed to recover non-ferrous metals as well as precious metals from e-waste. Hydrometallurgical processes offer an alternative to metal recovery and present some advantages over pyrometallurgical processes such as lower capital cost, and being more predictable and easier to control. The aim of this project was to investigate the overall environmental impact and thermodynamic inefficiencies of a hydrometallurgical process proposed for copper and gold recovery. Exergy and life cycle assessment (LCA) analyses were used to determine the thermodynamic inefficiencies and the environmental impact of the overall process.

The process consists of a mechanical pre-treatment step for size reduction, chemical removal of solder in the form a nitric acid leaching system, and copper recovery via an (Leaching- Solvent Extraction and Electrowinning (L-SX-EW) process configuration with sulphuric acid as the lixiviant in the presence of hydrogen peroxide as the oxidising agent. The gold recovery process followed the traditional cyanidation and carbon-in-pulp (CIP) process route, with the final recovery with an EW-unit. A nitric acid washing circuit to remove the remaining base metals prior to the gold recovery processes were also considered. The overall copper and gold recovery is 81% and 97%, respectively.

The exergy analysis showed that the copper and gold recovery processes are the most inefficient processes in the overall process chain. This was established by determining the exergy destruction of each process unit as well as its relative contribution to the overall exergy destruction. Copper and gold recovery processes contributed 39% and 37% respectively to the overall exergy destruction. Unit process analysis showed that the copper leaching process and the gold elution process were the most inefficient process units within these two sections. Therefore, optimisation of these unit processes should be prioritised. The overall exergetic efficiency of the process was determined to be 0.85%. The sensitivity analysis showed that even though the process's exergy destruction values do vary with a change in electricity requirement and metal concentration, the relative contributions of the various sections remained the same.

The life cycle assessment (LCA) revealed that the gold elution, nitric acid washing stage and copper leach are the major contributors to the overall environmental impact. Their contribution respectively ranges from a minimum of 2.62% to 74.2%, 0.44% to 77.9% and 3.17% to 29.8% across the different impact categories. The main causes of impact are due to the use of sodium hydroxide and

coal-based electricity. Therefore, the reduction of these process inputs within the plant will reduce the overall environmental burden. The latter was confirmed by replacing sodium hydroxide with hydrated lime in the copper leach and reducing the electricity and sodium hydroxide requirement. Both LCA and exergy analysis highlighted the roles of gold elution and copper leach as the foremost contributors to the overall process inefficiencies.

OPSOMMING

Verskeie herwinningstegnologieë vir metaalproduksie van elektroniese afval (e-afval) is in die literatuur voorgestel. Tradisioneel word pirometallurgiese prosesse aangewend om nie-ysterhoudende metale sowel as edelmetale van e-afval te herwin. Hidrometallurgiese prosesse is 'n alternatief vir metaalherwinning en bied 'n paar voordele bo pirometallurgiese prosesse, soos laer kapitaalkoste en die feit dat dit meer voorspelbaar en makliker is om te beheer. Die doelwit van hierdie projek was om ondersoek in te stel oor die omgewingsimpak en termodinamiese ondoeltreffendheid van die hidrometallurgiese proses wat voorgestel was om koper en goud te herwin. Eksergie- en lewensiklus assessering (LSA) ontledings tegnieke was gebruik om die termodinamiese ondoeltreffendheid en die omgewingsimpak van die algehele proses te bepaal.

Die proses fokus op die produksie van koper en goud. Die proses maak gebruik van meganiese skeidingstegnieke, chemiese verwydering van die soldeer-werke in die vorm van 'n salpetersuurloging stap, koperherwinning deurmiddel van 'n loging-oplosmiddel ekstraksie en elektroherwinning (L-SE-EW) proses konfigurasie waar swaelsuur as die logingsmiddel in die teenwoordigheid van waterstofperoksied as die oksideermiddel dien. Die goudherwinningsproses volg 'n tradisionele sianied loging stap gevolg deur geaktiveerde koolstof adsorpsie en desorpsie prosesroete waarvan elektroherwinning as finale stap dien. Die goud seksie maak ook gebruik van 'n salpetersuur-was stap om die oorblywende basismetale te verwyder voordat die sianied loging stap uitgevoer word. Die ontwerp en prosesmodellering het algeheel 81% koper en 97% goud herwin.

Die eksergie analise het getoon dat die koper- en goudherwinningsprosesse die mees ondoeltreffende prosesse is. Dit is bepaal deur die eksergie vernietiging van die algehele proses te analiseer en die relatiewe bydrae van die algehele prosesaanlegte te analiseer. Die koper herwinning afdeling het 39% tot die eksergie vernietiging bygedra waarvan die bydra van die goud herwinnings prosesse 37% is. Eenheidsproses-analise het getoon dat die koper-logingsproses en die goud-elueringsproses die oneffektiefste proseseenhede is in die twee afdelings. Optimisering van hierdie seksies moet dus geprioritiseer word as enige prosesverbetering aangebring word. Die algehele eksergie doeltreffendheid van die proses is 0.85%. Sensitiwiteitsanalise het getoon dat alhoewel die proses se eksergie vernietiging wissel met elektrisiteit en metaalkonsentrasie, het die relatiewe bydraes van die verskillende afdelings stabiel gebly.

Die lewensiklus assessering het getoon dat die goud afstropings proses, salpetersuur-was en koper-loging die grootse bydraes tot die algehele omgewingsimpak het. Die afsonderlike bydrae wissel onderskeidelik van 'n minimum 2,62% tot 74,2%, 0.44% tot 77,9% en 3,17% tot 29,8%. Die hoofoorsaak van impak kan toegeskryf word aan die gebruik van natriumhidroksied en steenkool-gebaseerde elektrisiteit. Daarom sal die vermindering van hierdie kommoditeite binne die aanleg die omgewingslas verminder. Die laasgenoemde is bevestig deur natriumhidroksied met gehidreerde kalk in die koper logingsproses te vervang en die behoefte aan elektrisiteit en natriumhidroksied te verminder. Beide LSA- en eksergie-analise het die rolle van die goud afstropings proses en koper logings proses geïdentifiseer as die hoof bydraers tot die algehele proses-ondoeltreffendheid.

NOMENCLATURE

Name	Symbol	Unit
Activity coefficient	γ	Dimensionless
Bed volumes	BV	m^3
Chemical potential	μ	J/mol
Current Efficiency	CE	Dimensionless
Density	ρ	kg/m^3
Enthalpy	H	J
Entropy	S	kW
Exergy	E	kW
Exergy destruction	I	kW
Exergy efficiency	Ψ	%
Faraday's constant	F	C/mole
Flow rate	Q	kg/hr
Gibbs energy	G	J
Mole/mass fraction	x	Dimensionless
Number of chemical species	N	Dimensionless
Number of moles	n	mol
Number of phases	π	Dimensionless
Pressure	P	kPa
Relative atomic mass	A	g/mole
Temperature	T	K
Valence	Z	Dimensionless
Volume	V	m^3
Volumetric thermal expansion coefficient	α_p	K^{-1}
Voltage	V_1	Volt
Work- Energy	W	kW

Acronym & Abbreviations	Name
ADP	Abiotic Depletion
AP	Acidification Potential

CIL	Carbon in Leach
CIP	Carbon in Pulp
DCB	1,4 dichlorobenzene
EEE	Electric and Electronic Equipment
EOL	End of Life
EOU	End of Useful life
EP	Eutrophication Potential
EW	Electrowinning
E-waste	Electronic Waste
GWP	Global Warming Potential
HTP	Human Toxicity Potential
LCA	Life Cycle Analysis/Assessment
MAETP	Marine Aquatic Eco toxicity Potential
NCV	Net Calorific Value
ODP	Ozone Layer Depletion Potential
PCB	Printed Circuit Board
PLS	Pregnant Leach Solution
PM	Precious Metals
POCP	Photochemical Ozone Creation Potential
RIL	Resin in Leach
RIP	Resin in Pulp
ROM	Run-Of-Mine
SX	Solvent Extraction
TETP	Terrestric Eco toxicity Potential

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1. INTRODUCTION

1.1 Background

The global electric and electronic (EE) goods markets have been growing at exponential rates over the course of the last three decades. The rapid technological advancements in this field are reducing the useful lifespan of EE. This results in high volumes of the electronic waste (e-waste) reporting to landfill sites. Landfill sites, in its current state, have not been developed to process or store the waste-waste and this is thus having a negative environmental impact. This is caused by the metallic make-up of the waste which can potentially be leached in the environment from the landfill sites.

The printed circuit boards (PCBs) found in electronic products contain approximately 40 valuable metals, which on average are present in greater concentrations when compared with their respective geological ore bodies. Gold, copper, silver, platinum group metals (PGMs), and many other metals are found in commercially viable concentrations in the PCBs. The global gold demand for PCBs was an estimated to be 750 tonnes out of the total 3000 tonnes of gold produced globally in 2015. Global mining activity is not following the exponential growth of the electronic industry. This makes secondary recovery processes of the metals economically attractive and critical to the electronic industry's future growth.

1.2 Significance of the Problem

E-waste generation is increasing at an exponential rate globally and the current waste management facilities cannot manage this new form of waste effectively (A Tuncuk *et al.*, 2012). The toxic material from the PCBs leaches into the environment from the waste dumps and can potentially poison critical natural resources. The current recycling infrastructure and recycling technologies are not appropriate to create a true circular flow economy (Schluepa *et al.*, 2009).

The work done in this study will provide the quantitative environmental impact of hydrometallurgical metal recovery from e-waste. This will assist in the recycling technology selection and development, and will aid the efforts in creating a circular flow economy for the EE and metals industries.

1.3 Project Motivation

An exponential increase of waste EE devices are recognised annually, rendering metal recycling processes from such waste pivotal from both and economic and environmental management point of view. To date, various recycling technologies have been proposed in literature for metal recovery

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from waste PCBs (WPCBs). The focus are mainly shifted toward the operational and metallurgic technical aspects of electronic waste recycling and to a lesser extent on the analysis of the environmental burdens and resource efficiency of the proposed processing routes (Cui and Zhang, 2008). Quantitative analysis of the environmental consequences and resource consumption associated with each process route may influence and guide future studies with process selection.

This study therefore aims to quantitatively evaluate the sustainability of a potential metal recycling route to recover copper and gold, employing exergetic analysis and life cycle assessment (LCA) tools.

1.4   Research Questions and Hypothesis

In the last decade the focus of PCB waste treatment has shifted toward hydrometallurgical processing as it is easier to control, has a lower capital investment, can process lower throughputs and considered to be more environmentally benign when compared to its pyrometallurgical counterpart (Khaliq *et al.*, 2014). Owing to the heterogeneous nature of WPCBs, different processing steps have been suggested in literature for the recovery of copper and gold. These two metals respectively offer the greatest incentive for their recovery when the bulk and value thereof are considered (A Tuncuk *et al.*, 2012; Szalatkiewicz Jakub, 2014). Since different processing routes can be employed to recover copper and gold, an understanding of the environmental impact and resource consumption associated with these processes enables decision making with regards to the best route when environmental sustainability forms the basis of such a decision.

The objectives of this project are to:

1. Quantify the potential environmental impact associated with a hydrometallurgical process for the recovery of copper and gold by means of an LCA.
2. Quantify the resource intensity i.e. resource consumption associated with a process for the recovery of copper and gold by means of an exergy analysis.
3. Use results obtained from the aforementioned tools to critically identify weak areas (hot spots) in the system with regard to resource consumptions and impacts on the environment.

This project will therefore evaluate the sustainability of metal recovery from electronic waste from an environmental point of view. Previous studies investigated the process design parameters of various hydrometallurgical processing routes. This project will build on the previous studies, by

optimising unit operations and process integration by doing mass and energy balances as well as LCA and exergy analyses.

1.5   Thesis Outline

The work presented in this study will follow the following structure:

Chapter 2:   Literature Review

Developments in e-waste recycling are reviewed. This includes the current state of e-waste recycling, important legislation which is assisting the recycling process development and technologies employed to recover the target metals.

Chapter 3:   Process Description and Flowsheet Development

In this chapter the selected process technologies are discussed. This includes the motivation behind the various technology selections and calculated and simulated process in and outputs.

Chapter 4:   Process Modelling and Simulations

The process developed in Chapter 3 was modelled with HSC- Sim^{TM} and GaBi simulation packages. This chapter describes the modelling protocols followed and the data sources utilised to model the process.

Chapter 5:   Results and Discussion

The performance of the developed process will be discussed in this chapter. The general process performance are analysed and the process resource efficiency and environmental impact are described using the exergy analysis and LCA tools. The key process parameters are changed to test the process sensitivity in terms of resource efficiency.

Chapter 6:   Conclusion and Recommendations

The conclusions from the performance of the developed process are summarised. This chapter will also give recommendations for future studies and possible improvements on the analysis tools used in this study.

2. LITERATURE REVIEW

2.1 Historical Background

In recent decades the demand of electrical and electronic equipment (EEE) has substantially increased with the rapid advancement in technology. The rapid development of technology and the increasing market activity has decreased the useful lifespan of EEE. E-waste is defined as any piece of electronic equipment which has reached its end of useful life without the intent of re-used (Namias *et al.*, 2013). The end-of-life equipment is generally disposed in landfill sites. Landfill sites in its current state are not equipped to manage this material and this is creating environmental problems. The heavy metals content of the waste has the potential to leach into the environment which may negatively affect aquatic and soil based life (Khaliq *et al.*, 2014).

Printed Circuit boards (PCBs) are present in most of the e-waste and are a key component of electronic devices because it possess a high metal content (∼ 30 wt. %) (Mankhand *et al.*, 2012). PCBs contain relatively high contents of precious and base metals compared to their respective geological ores. The high contents of precious metals from e-waste are a major economic driver for recycling of EEE (A Tuncuk *et al.*, 2012).

2.2 E- Waste Composition and Classification

E-waste is the broad term that describes all electrical and electronic components that are at their end-of-useful life cycle. The PCB found in the EE-equipment acts as a mechanical support for the electric and electronic connections. They consist out of a range of layers, metals, ceramics and polymers and the configuration are dependent on the type of EE equipment. Typically PCBs contain 40% of metals, 30% of organics and 30% ceramics (Luda, 2011).

2.2.1 Metals

The potential to recover metals in particular precious metals from the PCBs is the main economic driver in the recycling process. On average a typical PCB has 40 different metals. Precious metals are used for their electrical conductance properties, as well as its chemical stability. Platinum group metals (PGMs) are used in most sensors and copper as an electrical conductor. Lead and tin constitutes 4-6% of the PCB weight and is used to connect/glue various metallic components to each other and to the PCB surface (Luda, 2011). The stripped (bare) PCB is on average 23% of the weight of the loaded PCB, but this is dependent on the age, manufacturer and the type of EE equipment. The typical compositions for the metallic fraction of PCBs are shown in Table 2-1.

Table 2-1: PCB material Composition

Metallic Element	(Birloaga *et al.*, 2013a)	(Yang *et al.*, 2009)	(Oishi *et al.*, 2007)	(Behnamfard, Salarirad and F, 2013)
Cu (wt. %)	30.57	25.06	26	19.19
Al (wt. %)	11.69	4.65	3.2	4.01
Fe (wt. %)	15.21	0.66	3.4	1.13
Sn (wt %)	7.36	1.86	4.9	0.69
Ni (wt. %)	1.58	0.0024	1.5	0.17
Zn (wt. %)	1.86	0.04	2.6	0.84
Pb (wt. %)	6.7	0.8	3	0.39
MN (wt. %)	-	-	0.11	0.04
Sb (wt. %)	-	-	0.16	0.37
Au (ppm)	238	-	-	130.25
Ag (ppm)	688	-	-	704.31

It is evident from Table 2-1 that the concentrations of the valuable metals are present in considerably higher concentrations when compared with the respective metallurgical ore bodies. When large scale industrial mining started a century ago, copper was mined at concentration of 7-9%; currently it is being mined at concentration below 1%. The lower concentrations have a significant effect on the operating cost of mining and the metallurgical processing operations. This is evident in the all mining and metal markets. The effect of the reducing concentration, the age and depth of the mines combined with legislative and other factors have increased the operating cost of gold production. The gold market is one of the most important metal markets globally and the production cost has increased from 280USD/oz to 850USD/oz over the course of the last decade (Hieronymi, Kahhat and Williams, 2013).

2.2.2 Polymer matrix and reinforcement

The PCB substrate generally is a thermosetting composite. This is predominantly epoxy and cyanate resins which are organised in multi-layered glass reinforced boards (Khaliq *et al.*, 2014). The substrates also contains bromine based fire-retardants and other reactive fire retarding material. The bromine is typically present as polybrominated diphenyl ethers (PBDPE) or tetrabromo-bisphenol (TBBA). These components create material end-of-life issues. It has been shown that

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polybrominated dibenzo-dioxins (PBBD) and polybrominated dibenzofurans (PBDF) are generated when the material is subjected to moderate heat (Luda, 2011). These substances are highly toxic compounds and are detrimental to environmental health. Typical compositions of the non-metallic fraction are reported in Khaliq *et al.*, (2014).

2.3   E-waste recycling in South Africa

E-waste has initially been seen to be only an issue in the developed world, but in recent decades it has become a global problem. Developing countries like South Africa is generating e-waste at significant rates and the current waste disposal infrastructures are not suitable to deal with the growing e-waste problems (Park *et al.*, 2017).

Currently South Africa generates approximately 322 000 tonnes of e-waste annually of which only 12% of all the waste generated is recycled (Greencape, 2017). The e-waste recycling market has grown significantly since 2009, from where there were only two companies recycling e-waste. Currently there are more than 20 companies recycling electronic waste in South Africa. The companies dismantle, refurbish and extract metal from the collected electronic waste. The recycled volumes increased from 9000 tonnes in 2009 tonnes to 45 000 tonnes in 2015 (Greencape, 2017). Even though the increase in the recycling rate can be seen as a positive there are still significant amounts of e-waste left on landfill sites. The current waste generated and recycled in South Africa is listed in Table 2-2.

Table 2-2: South African E-Waste (Greencape, 2017)

e-Waste Classification	Generated Waste Volumes (tonnes/year)	% Recycled
Large Appliances	125000	39%
Consumer Equipment	78000	24%
Information Technology Equipment	77000	24%
Small Household Appliances	40000	13%

Efforts have been made by the waste management industry in South Africa in order to increase the recycling capacity by 20% in the next 5 years. However this is still not enough to meet the rate at which the waste is being generated (STEP, 2015). If it can be proved that there is a sustainable and economically viable process available to recover pure metals from PCBs, it may improve the rate of electronic waste recycling significantly.

2.4   Policy and Regulation

E-waste recycling legislation is important in providing firm guidelines for individuals and industry on how to dispose of e-waste safely and effectively. Various policies and legislation have been established in the developing world to manage this waste effectively. Any process that will be developed will have to comply with aspects of the relative laws for a specific geographical area. Strong legislation can be seen as a catalyst to start developing feasible and sustainable e-waste recycling processes. This section gives a brief background of the current international and South African legislation which can be seen as driving forces behind the development of the recycling technology.

2.4.1   WEEE directive

The waste from electrical and electronic equipment (WEEE) directive is a European Union Directive with the aim of reducing and managing the e-waste more effectively. The directive was introduced in 2012 and is viewed as the first major and comprehensive legislative directive with the objective to reduce electrical and electronic waste which currently reports on landfill sites.

This legislation is closely related to the Restriction of the use of certain Hazardous Substances (RoHS) directive and the two documents complement each other. The RoHS directive has the objective of removing hazardous substances from the EE products during the construction phase. The WEEE directive was designed to evaluate the entire electrical and electronic equipment life cycle. This includes design, dismantling and eventually sustainable recycling of the products. This directive engages government, private sector and the consumer and creates the legislative framework in which recycling and e-waste management simpler and more economical (Parliament *et al.*, 2012).

2.4.2   Basel Convention

The Basel Convention on Hazardous waste is an international agreement which was adopted in 1989 and enforced globally in 1992 by all 160 countries who took part in the agreement. Amendments made in 2002 included e-waste in the agreement. This included the environmental management, illegal trafficking in developing countries and e-waste management strategies. The agreement manages and controls the trans-boundary movement of hazardous waste. The agreement was created as part of the United Nations Environment Programme's Montevideo Programme on environmental law. It was a response to reports in the 1980's which showed large scale dumping of toxic waste in Africa and other developing/third world countries (Secretariat of the Basel Convention, 2016).

2.4.3   South Africa

South Africa currently does not have clear legislation to manage e-waste effectively. The general South African waste management strategy has been to focus on the end-of-life management of waste. The key ministries currently responsible for the waste management frameworks for e-waste are the Department of Environmental Affairs and Tourism and the Department of Trade and Industry (Finlay and Liechti, 2008). Currently the governing legislation for e-waste recycling is National Environmental Management Act (No. 107 of1998) (NEMA) and National Environment Management: Waste Act (No. 59 of 2008). These constitutional acts aim to "to secure an environment that is not harmful to the health and well-being of the people of South Africa" and it creates a waste management hierarchy with the goal to minimise waste generation and to recycle (Greencape, 2017).

2.5   E- Waste Recycling Economic Opportunities

PCBs contain an array of valuable metals, from copper to gold and platinum (Table 2-1). The PCBs originates from mobile phones, computers, household appliance and all other electronic equipment. The useful/active lifespan of mobile phones and computers have decreased significantly over the course of the last decade (Khaliq *et al.*, 2014). Figure 2-1 shows the current average usable lifespan of EE equipment. Even though the usable life of mobile phones and computers are 4.5-5.5 years, it is currently being replaced every second year to keep up with technological trends (Ely, 2014).

Currently the electronic material reports to waste dumps after its useful life. The decrease in the
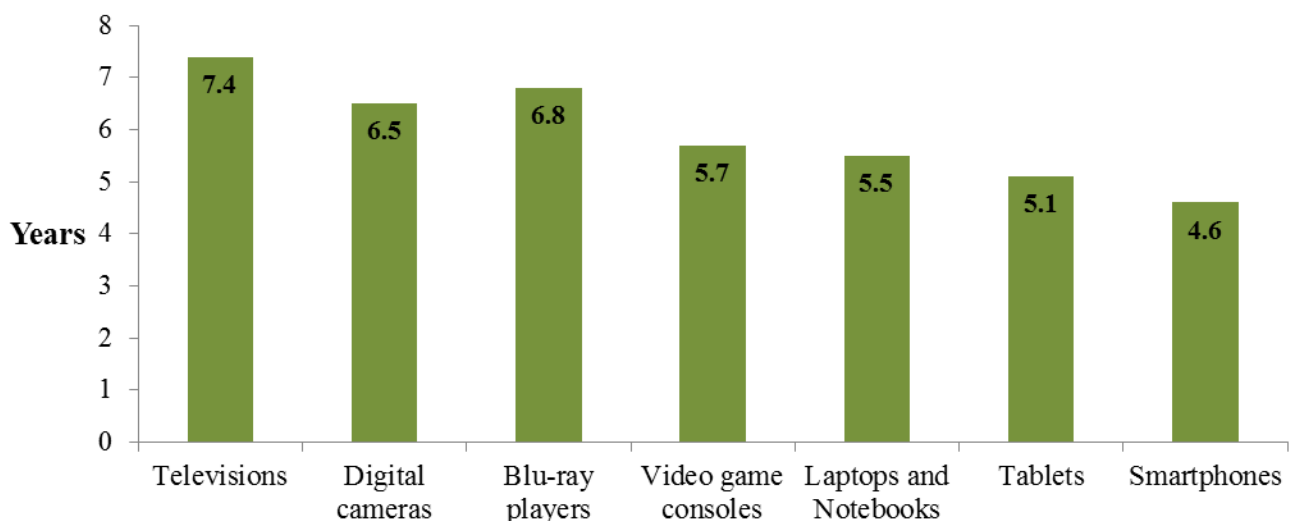
Figure 2-1: Life of EE equipment (Redrawn: (Taylor, 2015))

useful lifespan and the increase in EEE industry production are leading to a major environmental

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issue, because the waste dumps are not equipped to control the toxicology which is associated with the PCB's in the equipment.

The material that is being dumped contains high value metals. The operating cost to produce the metals with primary extraction and mining methods are becoming more expensive due to age of current mining operations. The current global metal production cannot keep up with the EE industry growth, so it is important to evaluate the metal recovery potential.

It should be kept in mind that even though the operating cost has increased, the demand has also increased. This is evident when we look at trends like the waste trends illustrated in Figure 2-2.The increase in demand created an increase in metal prices. This in turn creates investment opportunities for exploration for primary mining and metals industries. The market will thus always be feasible as long as there remain unexplored areas on earth (Hieronymi, Kahhat and Williams, 2013). The concentrations of the metals available make it attractive for recovery, because it is assumed that the final product will be produced at a significantly smaller operating cost. The size of the potential revenue from e-waste recycling, assuming 100% recycling rate globally is shown in Figure 2-2. This shows that there is a significant market available.
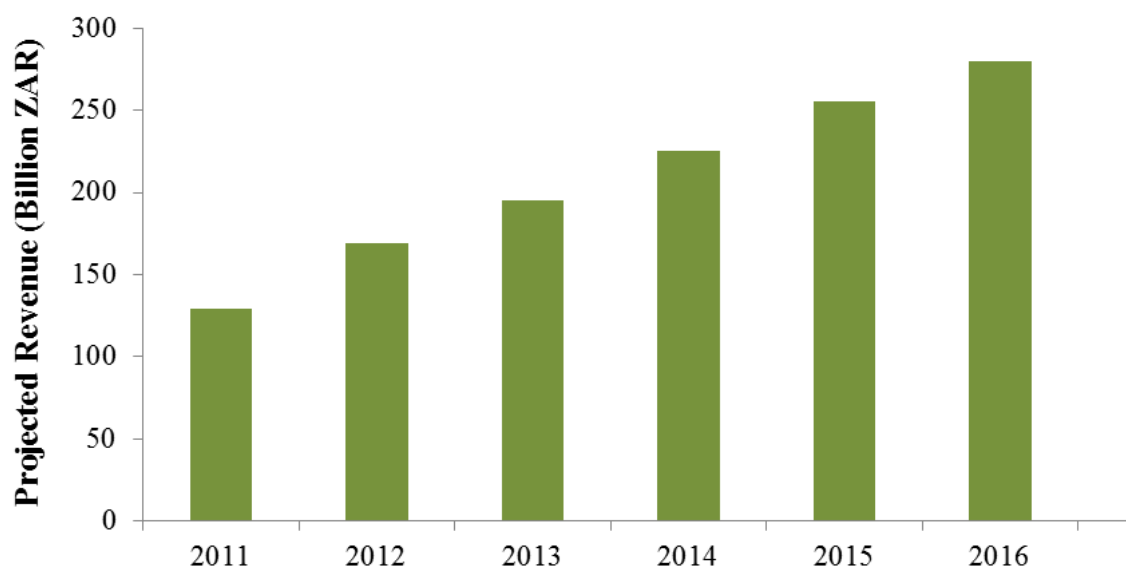
Figure 2-2: Projected Revenue from E-Waste Recycling (Data: (Markets, 2015))

The recycling of the waste is also more attractive because the industry has the potential to create jobs throughout the value chain. It was estimated that 30 jobs will be created for every 1000 tonnes of e-waste diverted from landfill sites (MAIA, et al., 2011).

2.6   Current E-Waste Recycling Processes

With the aim of highest metal recovery, WPCB recycling processes usually involve three stages namely disassembly, size reduction and purification/refining which includes mechanical treatment or chemical treatment processes. Chemical treatment involves techniques from pyro-, hydro- bio- and electrometallurgy (Birloaga et al., 2013b; Kaya, 2016). Owing to the heterogeneous nature of PCBs a combination of the aforementioned purification/refining are employed to produce high quality metals (Birloaga et al., 2013a). In literature the focus is mostly on pyrometallurgical and hydrometallurgical processes as treatment options for e-waste (A. Tuncuk *et al.*, 2012; Birloaga *et al.*, 2013b; Akcil *et al.*, 2014; Ghosh *et al.*, 2015; Ghodrat *et al.*, 2016). A brief overview of the advantages and shortfalls of the aforementioned technologies are discussed in sections 2.6.1 and 2.6.2w.

2.6.1   Hydrometallurgical Treatment

Hydrometallurgical processes compared to a pyrometallurgical process is generally perceived to be more environmentally benign, yields higher metal recoveries, low capital cost and are also suitable for relatively small- scale applications (A Tuncuk *et al.*, 2012; Jadhav and Hocheng, 2015; Ghodrat *et al.*, 2016). Hydrometallurgical processes are also more exact, has more flexibility during up scaling & control processing and are more predictable compared to pyrometallurgical processes (Oh *et al.*, 2003).

A hydrometallurgical process mainly consists of a series of selective acid or caustic leaching processes, followed by separation and purification to isolate and concentrate the metals. Electro-refining is used to treat the concentrated solution for metal recovery (Ghodrat *et al.*, 2016). A peculiar characteristic of PCBs is that the metals are present in their natural state and/or alloys which are of practical significance for the selection of a suitable leaching process. Generally, an oxidative leaching process is needed for effective extraction of precious and base metals that are of interest. Oxidation reaction of some elements is given in Equation 2-1 to Equation 2-4 (A Tuncuk *et al.*, 2012).

$$Cu^0 + 2H^+ \leftrightarrow Cu^{2+} + H_2(g) \qquad \Delta G^0 = 65.50 \quad \text{kJ/mol} \qquad \textbf{Equation 2-1}$$

$$Cu^0 + \frac{1}{2}O_2 + 2H^+ \leftrightarrow Cu^{2+} + H_2O \qquad \Delta G^0 = -171.63 \quad \text{kJ/mol} \qquad \textbf{Equation 2-2}$$

$$Au^0 + 3H^+ \leftrightarrow Au^{3+} + \frac{3}{2}H_2(g) \qquad \Delta G^0 = 439.97 \quad \text{kJ/mol} \qquad \textbf{Equation 2-3}$$

$$Au^0 + \frac{3}{2}O_2 + 6H^+ \leftrightarrow 2Au^{3+} + 3H_2O \qquad \Delta G^0 = -84.23 \quad \text{kJ/mol} \qquad \textbf{Equation 2-4}$$
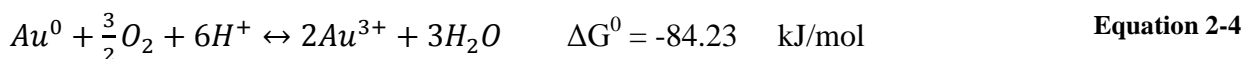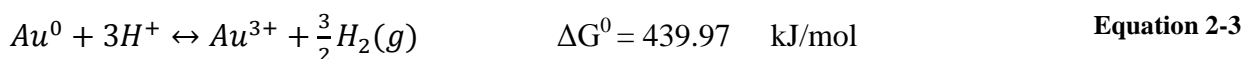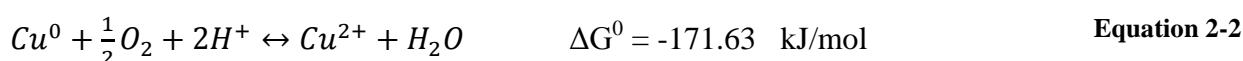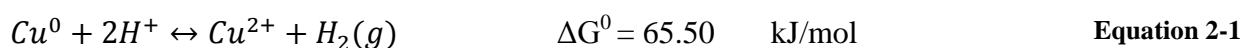
A two-stage process can be developed for the hydrometallurgical treatment of e-waste, which typically consists of an oxidative acid leaching process for the recovery of base metals, particularly copper in PCBs, followed by the leaching of precious metals using cyanide, thiosulfate, thiourea or halide as reagent(s). Alternatively, ammonia oxidative leaching can also be used to recover copper, however oxidative acid leaching is more often employed (Koyama, Tanaka and Lee, 2006).

2.6.1.1 Hydrometallurgy in Industry

Hydrometallurgical recovery of metals from e-waste does not deviate too much from the current industrial processes. The pre-treatment is the only major modification to a process. A summary of typical leaching agents and the investigated process conditions are summarised in Table 2-3.

Table 2-3: Hydrometallurgical Recovery of valuable Metals from e-waste

Leaching agent	Process conditions	Recovered metals	References
Aqua regia	Metals/Leachant = 1:20 g/mL	Au, Ag and Pd	(Park and Fray, 2009)
1st Stage- HNO$_3$ 2nd Stage- Epoxy Resin 3rd Stage- Aqua Regia	Self-agitated 3 stage Extraction	Au	(Sheng and Etsell, 2007)
H$_2$SO$_4$, Chloride, Thiourea Cyanide	Leaching and metals recovery by cementation, precipitation, ion exchange and carbon adsorption	Au, Ag, Pd and Cu	(Quinet, Proost and Van Lierde, 2005)
HNO$_3$ Aqua Regia	Roasting of e-waste in the presence of carbon; leaching with HNO3 and aqua regia; and solvent extraction with diethylemalonate	Au	(Chmielewski, Urbtiski and Migdal, 1997)
HCl, H$_2$SO$_4$ NaClO$_3$	Combustion of e-waste at 400–500 °C followed by leaching	Ag, Au and Pd	(Zhou, Zheng and Tie, 2005)
HCl, MgCl$_2$,	Dissolution of e-waste in different solvents and leaching conditions; and	1st Stage Al, Sn, Pb,	(Kogan, 2006)

H_2SO_4 H_2O_2	recovery of metals in stages	Zn 2nd Stage Cu and Ni 3rd Stage- Au, Ag, Pd, Pt	
Aqua Regia H_2SO_4	Mechanical processing followed by dissolution of e-waste in different solvents	Cu	(Veit *et al.*, 2006)
HNO_3	Electrochemical deposition of Cu at cathode from solution	Pb and Cu	(Mecucci and Scott, 2002)

2.6.1.2   Limitations of Hydrometallurgy

The hydrometallurgical processes are generally favoured above the pyrometallurgical processes due to its efficient and selective recovery of metals and because it is considered as a more environmentally friendly solution. In industrial application this might not always be the case, because during scale up the process has various limitations which impact the economics of the process as well as the sustainability. The current limitations found in previous studies are listed below (La Brooy, Linge and Walker, 1994; Hilson and Monhemius, 2006; Cui and Zhang, 2008).

- Cyanide is a dangerous material to handle. It might lead to environmental issues if the process is not managed properly.
- Halide leaching requires expensive corrosive resistant equipment, which increases the capital investment.
- The pre-treatment is more intensive and critical in hydrometallurgical applications.
- Thiourea leaching is currently not cost effective, because it has a high commodity cost when compared to other leaching agents and the consumption is high.
- Thiosulphate is a slow leaching agent and the consumption is high when compared to industrial leaching agents like cyanide

2.6.2   Pyrometallurgical Treatment

Pyrometallurgy is the branch of extractive metallurgy which utilises thermal energy to extract metals from the ore bodies. The high temperatures with the process reagents induce physical and

chemical transformations which makes the extraction of the metals or alloys possible. This branch of extractive metallurgy uses the calcination, roasting, smelting and refining to produce the final metal alloys.

The pyrometallurgical processes are commonly less selective than hydrometallurgical methods and the high energy requirements (high operating temperatures) and the gas emissions makes it a less attractive extraction technique (Liew, 2008). Pyrometallurgical processes are still widely used because it is seen as the most economically viable solution for the large scale production of metals. At high production volumes the fast reaction kinetics increase production significantly and the reduction of certain compounds such as plastics that are present in WPCBs makes it an attractive alternative when compared to hydrometallurgy (Thakur, 2014).

Pyrometallurgy is traditionally used for the recovery of iron, titanium and ferrochrome among many other bulk metals. In metal recovery from e-waste pyro metallurgy has successfully been used for the recovery of non-ferrous metals. The pre-processed PCBs are fed into a blast furnace where at a specific temperature the metal is separated from the waste and converted into a viable product. Depending on the metal to be recovered the plastic in the PCB can be used as reducing agents and the other metals present in the PCB's can be used as collector agents (Xakalashe, 2012).

Pyrometallurgical processes for e-waste recycling commonly utilises blast furnaces at operated at temperatures exceeding 500^0C. Incineration, smelting in furnaces (plasma arc or blast furnaces), sintering, melting, reactions in a gaseous phase at high temperatures are traditional employed pyrometallurgical processes (Cui and Zhang, 2008; Ghodrat *et al.*, 2016). In a smelting process, the crushed e-waste is fed into a high temperature furnace to remove the plastics and hydrocarbons, which in return also act as a reducing agents as well as an additional energy source due to exothermic reactions of these substances. During smelting, a slag phase is formed from elements that easily oxidises such as aluminium, silicon and iron, also an enriched valuable metal carrier (i.e. the base metals) and off gasses are produced. The metal oxides react with a reducing agent (coal/carbon) to the furnace which produces CO_2. The non-metallic waste is removed from the furnace with a fluxing agent. This process produces a clear separation of the metal and the waste by means of gravity separation, because the non-metallic compound will float on top of the metal and can be tapped off separately (Liew, 2008). The described smelting process is typically integrated into a base metal production process such as a copper (or lead) smelter where valuable metals (Ag, Au, Pt, Pd) are recovered and enriched in liquid copper. This concentrated solution is further treated

to recover high purity copper and valuable metals through electro-fining and various extraction processes (Cui and Zhang, 2008; Ghodrat *et al.*, 2016).

2.6.2.1   Pyrometallurgy in Industry

Pyrometallurgy has successfully been used to recover metals from e-waste at an industrial level. Table 2-4 below is a summary of current successful processes/plant (Gholamhossein and Ghaziaskar, 2015). An overview of the Noranda and Umicore processes are discussed in sections 2.6.2.1.1 and 2.6.2.1.2.

Table 2-4: Current Pyrometallurgical E-Waste Processing Systems

Techniques	Metals recovered	Main results
Noranda Process	Cu, Au, Pt, Pd, Se, Te, Zn	High recovery for Copper
Boliden Rönnskar	Cu, Au, Ag, Pd, Zn, Pb	High recovery of Precious metals
Umicore precious metal refining	Cu, Au, Ag, Pd, Pt,	Copper (Recovery >99%)
Dunns patent for gold refining	Au	Recovering metals: Sb, Bi, Sn, Se, Te, In
Days patent for refractory ceramic precious metals	Pt, Pd	Pt (Recovery =80.3%) Pd (Recovery ~94.2%)
Aleksandrovich's patent for Recovery of gold	Au	Au Recovery

2.6.2.1.1 Noranda Process

Studies have been done on the recovery of valuable metals from PCBs via a black copper smelting route. This secondary copper production process was chosen based on several reasons; Firstly, PCBs is rich in copper (~20 wt. %) due its high electrical conductivity property (Behnamfard, Salarirad and F, 2013) secondly, copper is an excellent metal carrier/solvent for a number of valuable metals particular those contained in PCBs such as Ag, Au, Pt, Pd etc. and lastly, the black copper smelting route has shown high flexibility in terms of process operation, different feed compositions and material types; it can process different types of secondary copper resources such as copper oxides and copper alloys.

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The Noranda Process in Canada is currently one of the biggest industrial pyrometallurgical processes where metal is produced from e-waste. The plant is currently processing an average of 100 000tons of e-waste per annum. This equates to 14% of the plants total annual production (Vidyadhar, 2015).

The process blends the pre-treated e-waste with the run-of-mine ore. The blend is fed into a furnace at 1250 °C where it reacts with ± 39% oxygen. Impurities are (Fe, Pb etc.) is converted to their oxide form which will report to the slag phase. The slag is cooled after the tapping process and the impurities can be recovered by other downstream processes. The matte, which contains the target element in the process, copper, is sent to a converter which produces the blister copper. The blister copper is sent to anode furnaces where the final copper product is produced with a purity of 99.1%. The balance, 0.9%, contains Au, Pd, Pt and other precious metals which are recovered through downstream electro winning processes (Vidyadhar, 2015). The precious metals recovered load (0.9% of total product) in this process is relatively low, due to the fact that the material is blended with run of mine copper ore.

The e-waste introduced in this process did not only increase the production volumes, but it also decreased the energy requirements for the process. This is due to the energy produced by the combustion of the residual plastics in the e-waste. Previous studies proved that the energy required to recover copper from e-waste is one-sixth of the energy required to recover copper from virgin ore (Xakalashe, 2012). The process is illustrated in Figure 2-3.

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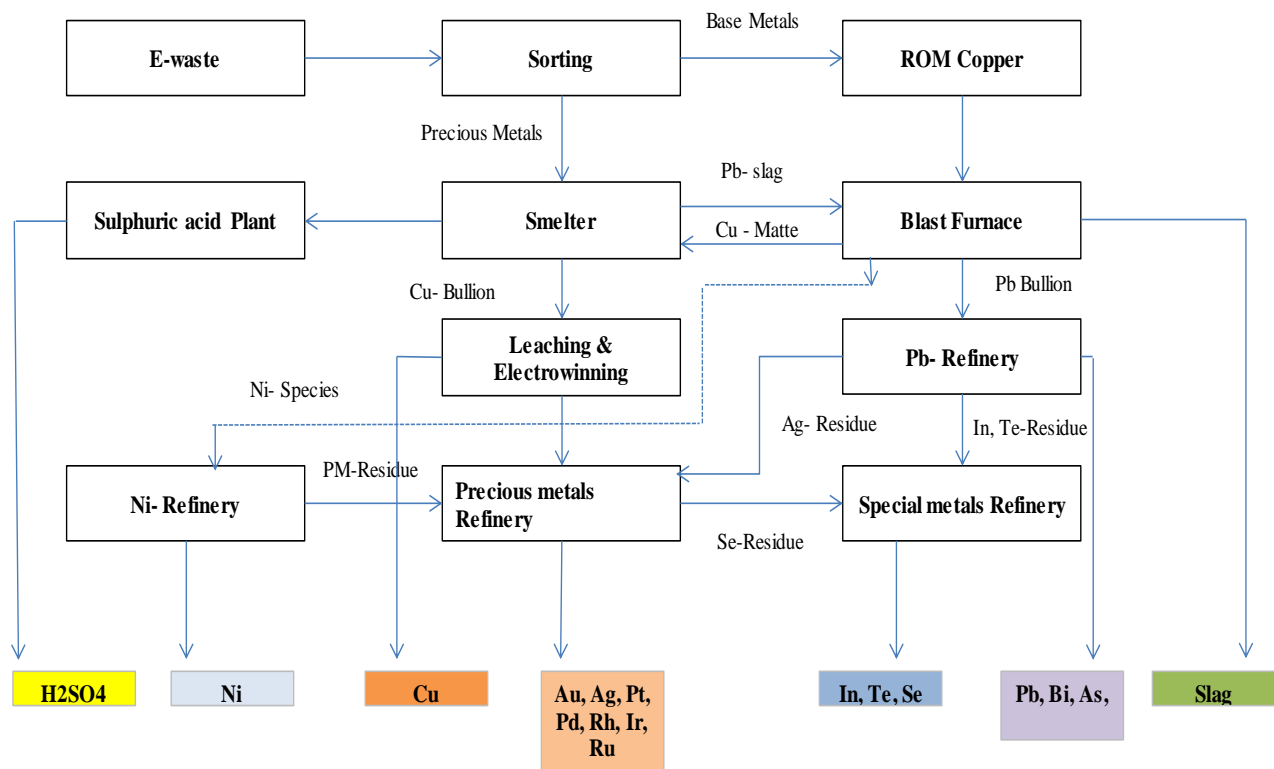
Figure 2-3: Noranda Process

2.6.2.1.2   Umicore Process

The Umicore process is currently the world's largest pyrometallurgical e-waste process. The plant process on average 250 000 tons of e-waste and is able to produce 50 tons of PGMs, 100 tons of gold and 2400 tons of silver from e-waste (Hagelüken, 2005, 2006; Hagelüken, C., 2006; Reuter, 2013). The Umicore process is an integrated smelting and refinery process, utilising both pyro metallurgy and hydrometallurgy principles for the production of the final products. The process also utilises the copper smelting route, but includes a range of other process to minimise the precious metal losses and to reduce the impact on the environment. Figure 2-4 depicts the main process inputs and outputs of the Umicore process.

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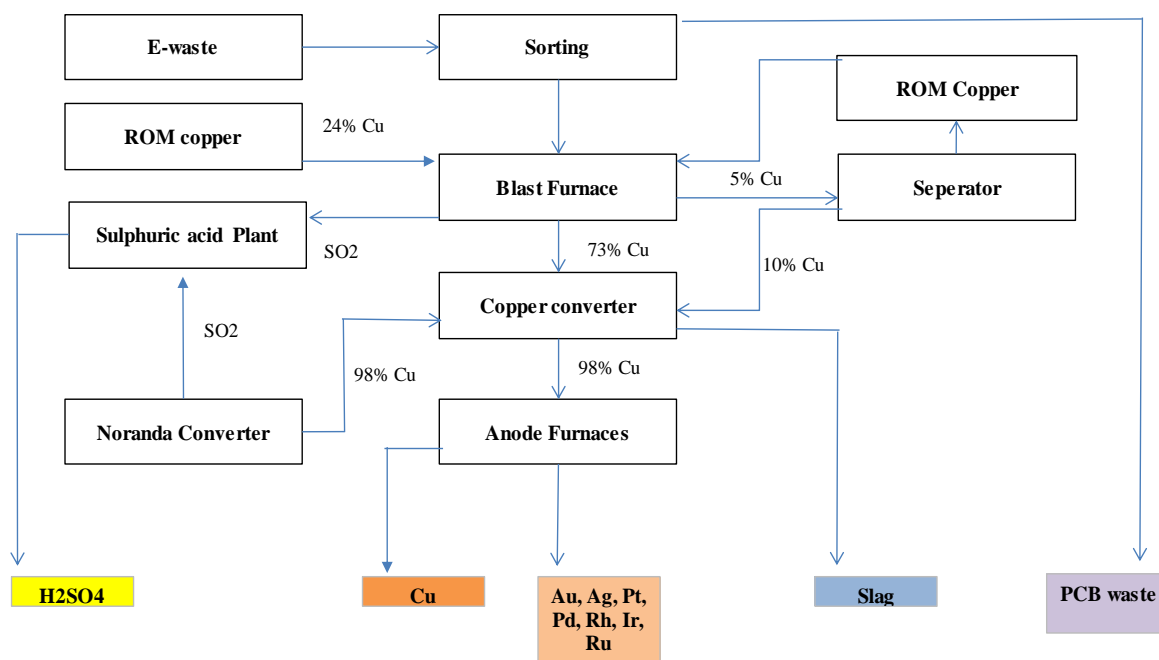
Figure 2-4: Umicore process

2.6.2.2 *Limitations of Pyrometallurgy*

The success of industrial applications of e-waste metal recovery is not without limitations. There are still various issues that require research and development. Some of the main issues are listed below (Xakalashe, 2012; Khaliq *et al.*, 2014).

- Large capital investment to include e-waste recycling in the current process
- Can be costly to control gas emissions caused by the burning of plastics
- Plastic is lost in the process. This is dependent on the pre-treatment and the pre-treatment efficiency.
- Ceramics report to slag. This increases the slag volume and might lead to the loss of precious metals, because they might be entrapped in a complex slag matrix.
- Only partial recovery of precious metals is possible with the current industrial Pyrometallurgical routes.
- The feed material to the furnace is complex and varies more than with standard ROM ore. This complicates the thermodynamics and the overall process control.
- Iron and aluminium are lost to the slag phase as oxides
- Dioxins are formed from e-waste flame retardants

2.7 Process

The process developed for this project follows traditional hydrometallurgical processing routes. The detailed design and simulations are presented in Chapters 3 and 4. The major process components are depicted in Figure 2-5.

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│ Copper Leach ├─────▶│Solvent Extraction├─────▶│ Electrowinning├─────────│    Cu    │
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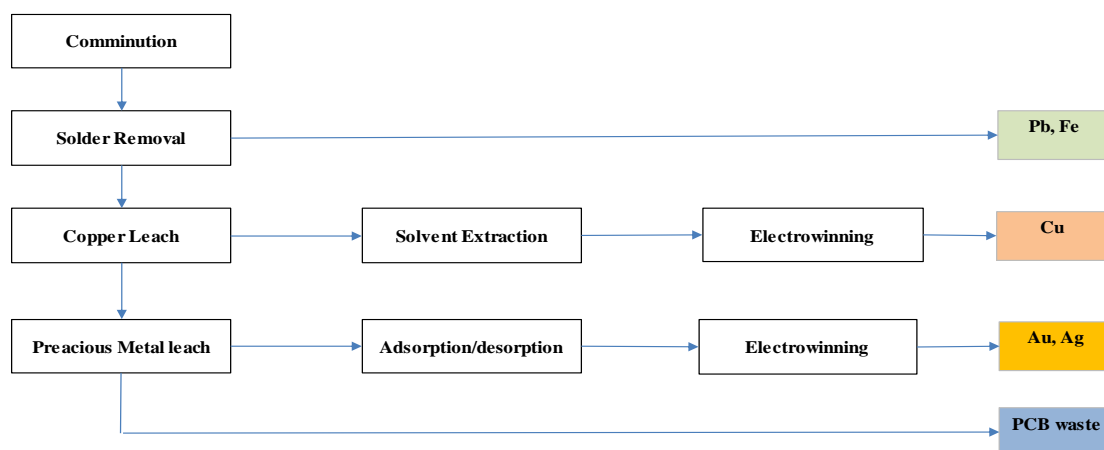
Figure 2-5: E-waste Metal Recovery Process

2.7.1 Mechanical Pre-Treatment

The complex structure of PCBs necessitates a mechanical pre-treatment step for the recovery of valuable metals via a hydrometallurgical treatment route. Effective leaching will only occur when the metal components are liberated from the non-metallic components such as plastics and ceramics to promote contact with the leaching solution. Subsequent steps in metal recovery such as purification will in addition be easier (Lee, Song and Yoo, 2007; Jadhav and Hocheng, 2015). Most of the reported processes have a pre-treatment step to pulverise waste PCBs to expose metals for efficient extraction in subsequent processes. Size reduction is necessary due to the complex structure of PCBs that inhibits effective contact between lixiviants and metallic elements. Table 2-5 shows the typical percentages for metals liberated at specific sizes (Das, Ari and Mehrotra, 2009).

As an alternative process, Jadhav and Hocheng (2015) investigated the recovery of precious metals from large PCBs pieces instead of using a grounded sample. The waste PCBs was first treated with sodium hydroxide (NaOH) prior to the hydrometallurgical treatment to remove the chemical coating in order to expose the metals to the leaching agent, hydrochloric acid (HCl). This suggested process offers to be a promising alternative owing to the possibility of high to total recovery of metals depending on the operating conditions. In this study, mechanical treatment will be considered as an integral pre-treatment process for the recovery of metal recovery.

Table 2-5: Liberation data of comminuted E-waste

Size (µm)	Liberated Metal (%)	Interlocked (%)	Liberated Gangue (%)
500-300	20.08	7.87	72.05
300-250	15.3	5.73	78.96
250-150	13.5	3.75	82.65
150-100	12.3	1.94	85.76
100-75	9.37	0	90.62
75-44	4.58	0	95.42
<44	-	-	-

2.7.2   Solder Removal

The solder material is predominantly a mixture of lead and tin is used to connect different electronic components on the surface of PCBs.

2.7.2.1   *Effect of different leaching agents*

Jha et al. (2012) compared different acidic leaching agents such as sulphuric acid, nitric acid and hydrochloric acid for effective lead dissolution using a pure lead sample. Complete (99.99%) dissolution was achieved in 30 minutes using a 0.5 M nitric acid solution at 90°C, while the percentage lead dissolution achieved after 75 minutes when using 0.5 M sulphuric acid and 0.5 M hydrochloric acid was 0.19% and 1.24%, respectively. Similar results were noticed for a fresh solder sample (47.36% lead and the remaining tin) at lower concentrations of leaching agents (0.2M). In terms of selectivity for lead dissolution, nitric acid is a suitable reagent. The lower dissolution noticed for sulphuric acid and hydrochloric acid may be attributed to the possible formation of lead precipitates. The mechanism of lead dissolution from HNO_3 is given in the reactions below. Lead is oxidised to lead oxide, which is subsequently converted to lead nitrate (Manis Kumar Jha *et al.*, 2012). Lead can be recovered through precipitation using a NaCl solution (Ranitović *et al.*, 2016).

$$Pb(s) + 2HNO_3(aq) \rightarrow PbO(s) + H_2O(aq) + 2NO_2(g) \qquad \text{Equation 2-5}$$

$$PbO(s) + 2HNO_3(aq) \rightarrow Pb(NO_3)_2 + H_2O(aq) \qquad \text{Equation 2-6}$$
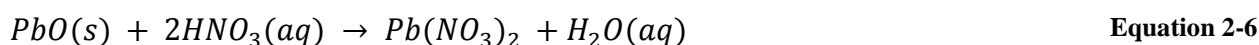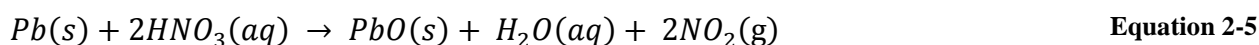
Unlike lead, the dissolution of tin in nitric acid solution decreases with increasing HNO_3 concentration. At low HNO_3 concentrations, it partially dissolves, but at higher concentrations it forms a protective layer, called metastannic acid (H_2SnO_3) which leads to the reduction in rate of dissolution. The reaction of tin and aqueous nitric acid is given in the following reaction:

$$Sn(s) \;+\; 4HNO_3(s)(aq) \rightarrow H_2SnO_3(s) \;+\; 4NO_2(g) \;+\; H_2O \qquad \text{Equation 2-7}$$
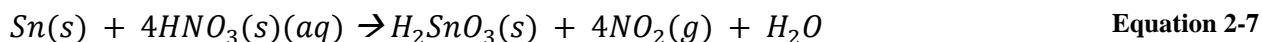
Chaurasia, Singh and Mankhand (2013) discussed the above phenomenon with a Pourbaix diagram (potential/pH) for a tin-nitrate-water system. The E-pH Diagram for tin-nitrate-water solution (298K, aNO3=1), tin exists as a dissolved species in very alkaline conditions (pH>12.6) or in the acidic region with pH< -0.42. Between these two pH spectrums, tin exists as solid stannous oxide. Tin may be recovered by dissolving the metastannic acid in low hydrochloric acid concentrations according to Equation 2-8 or applying heat metastannic oxide is converted to stannic oxide according to Equation 2-9 (Manis Kumar Jha *et al.*, 2012):

$$H_2SnO_3(s) \;+\; 6HCl \;\rightarrow\; H_2SnCl_6 \;+\; 3H_2O \qquad \text{Equation 2-8}$$
$$H_2SnO_3 \;+\; \text{Heat} \;\rightarrow\; SnO_2(s) \;+\; H_2O \qquad \text{Equation 2-9}$$

2.7.2.2 *Effect of different HNO_3 concentrations*
The effect of different HNO_3 concentration (0.1-0.4M) on lead dissolution was also investigated by Jha et al. (2012) at 90°C using the same solder sample. For 0.1M and 0.2M HNO_3 an increase from 65.95% to 99.99% was observed respectively in 120 minutes. However, a decrease in percentage lead dissolution was observed for further increases, 0.3 M (90.67%) and 0.4M HNO_3 (86.21%).

2.7.2.3 *Effect of temperature and pulp density variations*
A temperature increase from 60°C to 90°C resulted in a lead dissolution increase from 42.23% to 99.99% using 0.2M HNO_3 solution for a leaching time of 120 minutes. For the same experimental conditions the effect of variation in solid to liquid ratios; 10 g/l, 50 g/l, 100 g/l and 150 g/l on lead extraction was considered for 0.3M HNO_3 solution. Higher pulp densities resulted in the precipitation of $Pb(NO_3)_2$, thus resulting in overall reduction of lead dissolution. The highest pulp density lead to the extraction of 90.67% lead compared to 21.14% at the lower end of the pulp density spectrum.

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2.7.2.4   *Partial dissolution of Ag in a HNO₃ leaching system*

The effects of different HNO_3 concentrations, temperature and leaching time were also investigated by Ranitovic et al. (2015). After the recovery of lead with 4M NaCl solution, analysis of this precipitate showed co-extraction of Ag. At optimum conditions; 80°C, 2 M HNO_3 and leaching times of 1, 2 and 3 hours, the Ag content present in the precipitate was 8.3%, 8.5% and 14.2% respectively. Thus the recovery of lead with HNO_3 is associated with partial extraction of Ag even at low concentrations (1 M HNO_3, 6.7% Ag) (Ranitović *et al.*, 2016).

Considering that lead is a highly toxic metal and raises several environmental concerns, the use of alternative solders such as tin- copper and tin-silver-copper solders is gaining more importance (Chaurasia, Singh and Mankhand, 2013). The potential change in solder composition may result in the reconsideration of including solder removal step. The results obtained from various independent studies for solder (tin and lead) recovery are summarised in Table 2-6.

Table 2-6: Published Solder Removal Results

	(M. K. Jha *et al.*, 2012)	(Ranitović *et al.*, 2016)
Material	**Fresh solder**	**WPCBs**
Pb/Sn (%)	47.36/ 52,64	3.3/1.2
HNO_3 Conc. (M)	0.2	2
Temperature (°C)	90	80
Stirring speed (rpm)	400	300
S: L ratio (g/ℓ)	10	200
Particle size (mm)	50-70	2.5
Leaching time (min)	120	60,120,180
Pb recovery (%)	99.99	>98 (all above leaching times)
Sn recovery (%)	0.74	12.6 ; 10.4 ; 4.8

2.7.3   Copper Recovery

The copper recovery step is done before the precious metal recovery to increase the gold recovery, reduce the cyanide load and to produce the maximum amount of copper from the printed circuit boards. The high recovery of copper from this process block is important, because it has a significant influence on the process economics and efficiency of the downstream precious metal

processes. Even though the focus of e-waste recycling from an economic perspective has traditionally been focused on the recovery of precious metals, it should be noted that the precious metal concentration is continuously being decreased in products and that copper is a valuable economic prospects in the quantities that is present in PCBs (Seongjun and Cui, 2012; Khaliq *et al.*, 2014).

Eighty percent of the world's copper is produced using pyrometallurgical processes and the balance being treated with hydrometallurgical process routes. The general hydrometallurgical process utilises the following process steps (Davenport *et al.*, 2002):

- Sulphuric acid leaching from ore body pre-treated ore-body.
- The pregnant solution is upgraded using solvent extraction.
- High grade solid copper is produced by electrowinning techniques.

With referral to traditional copper treatment processes and successful hydrometallurgical recovery of e-waste utilising similar techniques, this project will follow a similar approach for metal recovery from PCBs (Xu, Li and Liu, 2016).

2.7.3.1   Copper Leach

Copper leaching can be done using various lixiviants. The selection of the lixiviant is based on process economics, downstream process considerations, ore type and process environmental impacts.

2.7.3.1.1 Nitric Acid Lixiviant

Nitric acid can be utilised as a leaching agent to oxidise the copper in the PCB. The process is effective because it can be manipulated to recycle copper, lead and tin. The disadvantage of using this leaching agent is that the pregnant leach cannot be pumped directly to the electrowinning circuit, because the acid used in this circuit is commonly sulphuric acid. This leads to a high NaOH demand for neutralisation which has the potential for sodium build-up in the circuit. The use of this process also reduces the current efficiency in the subsequent electrowinning step (Mecucci and Scott, 2002).

The primary leaching reactions are shown in Equation 2-10 and Equation 2-11:

$$3Cu + 8HNO_3(dilute) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O \qquad \textbf{Equation 2-10}$$

$$3Cu + 8HNO_3(concentrated) \rightarrow 3Cu(NO_3)_2 + 2NO + 4H_2O \qquad \textbf{Equation 2-11}$$
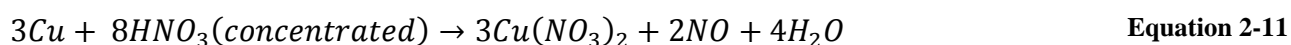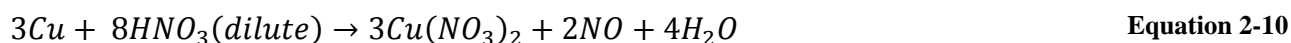
2.7.3.1.2 Sulphuric Acid Lixiviant

Sulphuric acid on its own is not able to dissolve copper from the PCB. It requires a strong oxidising agent to mobilise the copper from the ore body into the solution. The resulting leaching rate and recovery are high, 99%, but due to the nature of sulphuric acid the materials of constructive of the equipment can make the process un-economical. This also has the potential of introducing impurities into the system from the corrosion products (Xu, Li and Liu, 2016).

The mechanism for the dissolution of copper using sulphuric acid and hydrogen peroxide is shown in the reactions below (Kumar *et al.*, 2014):

$$2H_2O_2 \rightarrow 2H_2O + O_2 \qquad \text{Equation 2-12}$$

$$H_2SO_4 + H_2O_2 \rightarrow H_2SO_5 + H_2O \qquad \text{Equation 2-13}$$

$$Cu + H_2SO_5 \rightarrow Cu^{2+} + SO_4^{2-} + H_2O \qquad \text{Equation 2-14}$$

Empirical work done by Kumar et al. (2014) concluded that nitric acid leaching recovers more copper when compared with the sulphuric acid/hydrogen peroxide leach. The nitric acid leach recovered 96% copper compared to 75.7% with sulphuric acid/hydrogen peroxide. The sulphuric acid/peroxide blend is still preferred because lower concentrations are required and the kinetics are 20% faster and the sulphuric acid is complimentary for the downstream electrowinning circuit (Kumar *et al.*, 2014). Nitric acid leaching also has the potential to leach gold. Rossouw, (2015) reported that 12% of gold can be leached with nitric acid at 85 $^{\circ}$C, whereas no leaching of precious metals was observed with sulphuric acid in the presence of hydrogen peroxide.

2.7.3.2   Solvent Extraction (SX)

Solvent extraction (SX) is used in metallurgical processes to upgrade, purify and concentrate the target metal in pregnant leach solutions (PLSs). The technology has been utilised for over a century in analytical chemistry and was only used in metallurgy for uranium recovery. The technology was first proposed for commercial use in 1960 and the first commercial process was operational by 1968 (Kordosky, 2002).

In normal Run of Mine (ROM) ore processing operations, copper in the PLS is normally between 1 and 10g/ℓ. This low concentration together with high impurity loads is not conducive for the electrowinning process. To increase electrowinning efficiency the PLS concentration needs to be upgraded to 45-55 g/ℓ and the impurities should be reduced significantly (Schlesinger *et al.*, 2011b).

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2.7.3.2.1 SX Process Mechanism

The solvent extraction process consists of two sections; the extraction stage and stripping stage. The general process flow is depicted in Figure 2-6. The PLS is fed into an extraction phase where it is contacted with an organic extractant. This organic extractant selectively forms a complex with the copper ions present in the PLS according to the reaction as given by Equation 2-15.

$$2RH\ (org) +\ Cu^{2+}(aq) +\ SO_4^{2-}(aq) \rightarrow R_2Cu(org) + 2H^+(aq) +\ SO_4^{2-}(aq) \qquad \textbf{Equation 2-15}$$
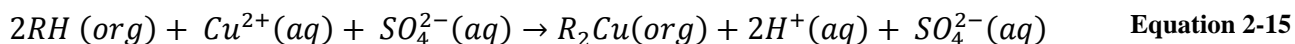
The acidic nature of the solution favours the extraction process. After extraction, the loaded organic solution is transferred to the stripping stage and the barren PLS also referred to as the raffinate, is recycled back to the copper leaching circuit. The acid present in the raffinate can be reused in the leaching circuit. The loaded organic solution is contacted with a strong acid (electrolyte) from the electrowinning circuit, allowing the removal of copper from the organic phase to the electrolyte. The barren organic stream is recycled back to the extraction step and the pregnant electrolyte enters the electrowinning circuit. The stripping reaction is explained in Equation 2-16.

$$2H^+(aq) + SO_4^{2-}(aq) +\ R_2Cu\ (org) \longrightarrow 2RH\ (org) +\ Cu^{2+}(aq) +\ SO_4^{2-}(aq) \qquad \textbf{Equation 2-16}$$
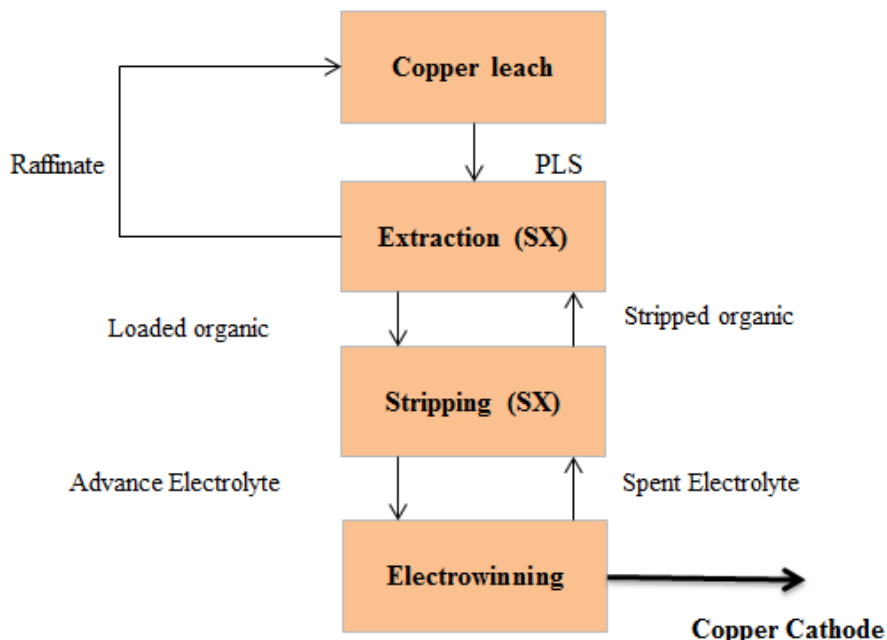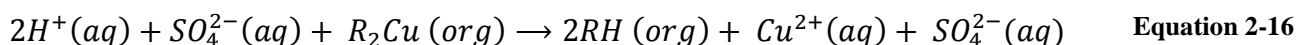
Figure 2-6: Conceptual Copper Leach/SX/EW Process flow (Adapted from: (Kordosky, 2002))

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2.7.3.2.2 Organic Phase

The organic solution in solvent extraction can selectively recover/extract copper from the PLS. Most of the modern copper extractants are oxime (aldoxime, ketoxime etc.) based. The extractant is selected based on the PLS copper concentration and downstream electrowinning circuit configuration/mode of operation. The extractant forms a complex with the copper ions in a chelating process. The characteristics of the ideal process extractant are enumerated below (Kordosky, 2002):

- Operate at the same pH as PLS.

- Extract copper selectively over other metals.

- Strip copper into an electrolyte at the concentrations required by the downstream electrowinning process.

- Favourable extracting and stripping kinetics.

- Does not form an emulsion with the aqueous phase.

- Must be stable i.e. does not break down during continuous recycling of extraction and stripping processes.

- Soluble in a suitable diluent.

- Does not absorb acid media.

- Adhere to general safe operational requirements- non-toxic, non-flammable, non-carcinogenic.

2.7.3.2.3 Diluents

Typical extractants used for copper recovery are viscous by nature; hence a suitable diluent to reduce the viscosity of the organic solution is required. Diluents are typically added to a 5-35 vol. % extractant concentration. This combination ensures that the organic solution can be easily pumped, mixed and separated from the PLS. The diluents used for copper recovery are commonly refined petrochemical by-products such as kerosene (Schlesinger *et al.*, 2011b).

2.7.3.2.4 Operation and Impurity Management

Various operational configurations and operating conditions should be monitored and controlled to optimise the operation of the solvent extraction circuit i.e. extract the maximum amount of copper and reduce the impurities in the electrowinning feed.

Owing to the complex nature of the PCB composition, the management of the impurity load is critical to the performance of the copper recovery step. Impurities can be transferred from the PLS

via physical and chemical mass transfer methods. The chemical transfer is predominantly managed by the correct selection of the extractant. Physical transfer, in the form of entrainment can be managed by the diluent selection and operating at a low density and viscosity (Tinkler, 2009). Entrainment can also be managed by operating the mixer-settler equipment at impeller tip-speeds of less than 350 m/min (Schlesinger *et al.*, 2011b).

If the PLS contains significant quantities of impurities (Fe, Mn, Co etc.) that can be entrained in the loaded organic phase then the circuit can contain a washi9ng step between the extraction and stripping phases. The washing media should be compatible with the PLS and electrowinning circuit. Sulphuric acid at a pH of 2 is typically used for this purpose (Hein, 2005). The loaded wash solution is normally circulated between the washing stage and the extraction block. The process is illustrated in Figure 2-7. Crud formation can be a risk when processing PCBs. Crud is a solid emulsion which forms from particulate waste that is found in the PLS. This is minimized by managing the solid load in the PLS and by periodical operational removal of the crud from the SX circuit.

2.7.3.1 Electrowinning (EW)

Electrowinning involves the application of a direct current (DC) voltage to an electrolytic solution which enables the reduction and deposition of metals onto the cathode. The electrolytic solution may be the leach solution or the purified PLS. The ionic composition of the electrolytic solution will have a significant impact on the operation of the circuit (Beukes and Badenhorst, 2009). The main chemical reactions involved in copper electrolysis are given by Equations 2-17 and Equations 2-18:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$ **Equation 2-17**

$$H_2O \rightarrow H^+ + OH^- \rightarrow \frac{1}{2}O_2 + 2H^+ + 2e^-$$ **Equation 2-18**
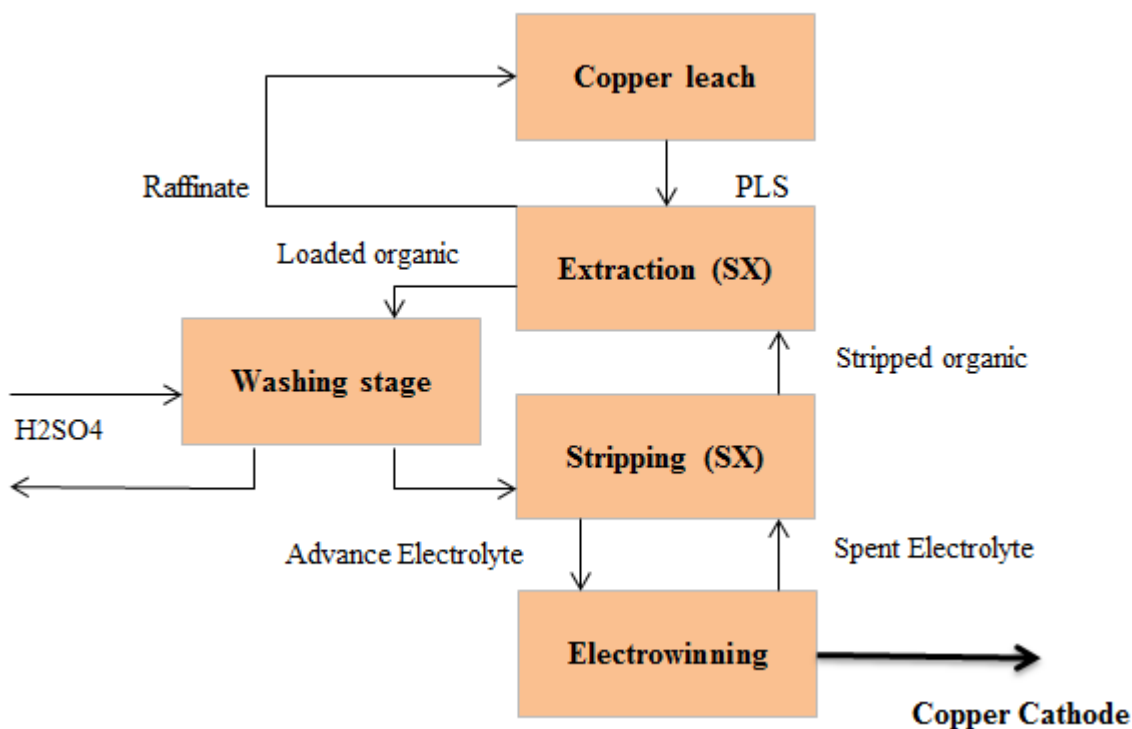
Figure 2-7: Copper SX-EW Circuit with Impurity Washing Stage

2.7.4 Gold Recovery

Gold has been used by mankind since 3400 BC for its aesthetic properties. Gold is still used for its cosmetic properties in the modern world, but its chemical properties made it a critical component in the medical and technological industries. Gold's electrical conductivity, corrosion resistance and low contact electrical resistance make it the ideal metal for the electric and electronic industries (Baba, 1987). The growth in industry and environmental pressures on current mining activities makes the recovery of gold an attractive prospect (Syed, 2012).

Gold can be recovered from PCBs via a range of processing technologies such as mechanical separation, pyrometallurgical, biological process and hydrometallurgical process technologies. All of these technologies have its advantages and challenges- this project will only focus on the hydro metallurgical process route for recovery. Pyrometallurgical recovery has become the standard treatment for gold recovery from electronic waste, but when compared with hydrometallurgical processing routes it is less selective and predictable. Hydrometallurgy is also the traditional recovery route for gold globally (Andrews, Raychaudhuri and Frias, 2000).

2.7.4.1 Base Metal Process Issues

Base metals are a major concern in the hydrometallurgical recovery of gold. When cyanide is the lixiviant of choice the base metals, more specifically copper are more reactive than gold. This

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reduces overall gold recovery, increases total cyanide consumption and complicate downstream processes due to impurities in PLS. Copper concentrations in excess of 1% in the gold feed are considered the maximum treatment load for a cyanide leaching circuit. Maintaining the copper concentration below this threshold ensures that the gold recovery process remains economically viable (Stewart and Kappes, 2012; Oraby and Eksteen, 2016a).

Copper cyanide can exist in various forms in an aqueous solution. The reactions below show the various copper cyanide species (Lu, Dreisinger and Cooper, 2002):

$$Cu^+ + \ Cu^- \leftrightarrow CuCN_{(solid)}$$ **Equation 2-19**

$$CuCN + \ CN^- \leftrightarrow CuCN_2^-$$ **Equation 2-20**

$$CuCN_2^- + \ CN^- \leftrightarrow CuCN_3^{2-}$$ **Equation 2-21**

$$CuCN_3^{2-} + CN^- \leftrightarrow CuCN_4^{3-}$$ **Equation 2-22**

$$H^+ + \ CN^- \leftrightarrow HCN_{(aq)} \leftrightarrow HCN_{(g)}$$ **Equation 2-23**

There is a range of technologies that can be employed to reduce the copper load or optimise the cyanide consumption. The most prominent technologies employed are:

- Material Segregation

The copper and gold ore are separated with physical or physio-chemical processes. Mining and secondary metal collection can be done with the separation of the ore/metal bodies in mind. The separation of the two ore bodies makes downstream recovery simpler and reduces the risk of contamination. This is not always practical and the collected metals are separated with a flotation circuit. This has been employed in industry at Tefler Gold Mine, Brown's Creek Mine, El Indio and various other mines globally (Dai, Simons and Breuer, 2012).

- Selective Leaching

This option utilises dilute acids, ferric iron, copper (II)/chloride and ammonia to strip the copper from the feed material. These processes are currently not employed in the industry because it is uneconomical when working with low grade copper ores. Treating low grade material requires a high leaching agent consumption followed by a neutralization step which makes the process uneconomical (Muir, La Brooy and Cao, 1989). This can also potentially increase the negative impact of the process on the environment (Dai, Simons and Breuer, 2012).

- Copper Cyanide Destruction

After the cyanidation process copper will be present as copper cyanide in the process. Various destruction technologies are currently being used in industry: electrochemical oxidation, Caro's acid (H_2SO_5) addition, hydrogen peroxide addition, phytolysis and alkaline chlorination. One of the more popular technologies for the destruction of the copper complex is the Inco process. Sulphite reacts with the copper cyanide complex in the presence of air and the cyanide is oxidised to cyanate. The reacted copper species is then precipitated as a copper hydroxide (Dai, Simons and Breuer, 2012).

- Copper Cyanide Recovery

The increase in cyanide consumption due to the side reactions makes the process uneconomical. The recovery of the cyanide in the process tailings and the recycling of it yield environmental and economic benefits. The processes employed to do this include direct electrowinning, activated carbon adsorption, ion exchange, solvent extraction, membrane technologies, SART (sulfidization, acidification, recycle and thickening) and AVR (acidification, volatilisation and re-neutralisation) (Dai, Simons and Breuer, 2012).

2.7.4.2   Lixiviant Selection

The leaching step is one of the most critical steps in the recovery of any metal. It dissolved the desired metal species for upgrading in the downstream processing units. The leaching agents that have been used in industry and in test work is cyanide, thiourea, thiosulphate and halides (Syed, 2012).

2.7.4.2.1 Cyanide Leaching

Cyanide is the most ubiquitously used lixiviant in the gold mining industry. It has been used for gold recovery for more than a century, with the first commercial use of the cyanidation processing being implemented at Crown Mine in New Zealand in 1889 and by 1904 the technology was well established and widely used in the major gold mining countries, South Africa and Australia (Logsdon, Hagelstein and Mudder, 1999).

Cost effectiveness and the efficiency of cyanide are the main reasons for the lixiviants popularity in the industry. Cyanide is most commonly used in sodium, potassium and calcium form, with the CN^- ions being the active participants in the dissolution of gold from the ore body/PCB. The cyanide salt dissolves in water to activate the free CN- ion as shown in the Equation 2-24:

$$NaCN \rightleftharpoons Na^+ + CN^-$$ **Equation 2-24**

The cyanide process is highly dependent on the pH of the solution. The ideal operating pH has been determined to be greater than 9.3. At this point there will be free cyanide and hydrogen cyanide in the system, when the solution pH exceeds 9.3 the amount of free cyanide in solution increases and the dissolution of gold can thus be more efficient (Srithammavut, 2008).

The dissolution reaction of gold in a cyanide solution is in essence a redox reaction. The gold in the presence of a strong complexing agent (CN^-) forms a stable gold cyanide complex, $Au(CN_2)^-$. The chemical reactions are explained in the following reactions:

$$2\ Au + \ 4CN^- + O_2 + \ 2H_2O \ \longrightarrow 2Au(CN)_2^- + H_2O_2 + 2OH^- \qquad \text{Equation 2-25}$$
$$2\ Au + \ 4CN^- + \ H_2O_2 \ \longrightarrow 2Au(CN)_2^- + 2OH^- \qquad \text{Equation 2-26}$$
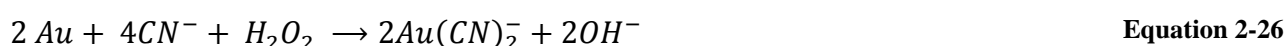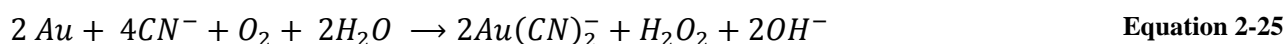
The summarised reaction is shown below. This reaction is known as Elsner's Equation.

$$4\ Au + \ 8CN^- + \ O_2 + 2H_2O \longrightarrow 4Au(CN)_2^- + 4OH^- \qquad \text{Equation 2-27}$$
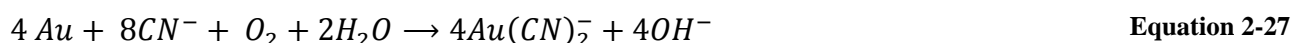
In recent years there has been pressure from environmental bodies to investigate the use of alternative more environmentally friendly lixiviants. This is a consequence of the high toxicity of cyanide and the negative impact the product has on the environment. In the mining environment cyanide is seen as a hazard for the following environmental sectors: aquatic life; avian life; mammals, reptiles and amphibians (Logsdon, Hagelstein and Mudder, 1999). It is thus important to evaluate other more environmentally friendly lixiviants.

2.7.4.2.2 Thiourea

Thiourea, NH_2CSNH_2, is a non-toxic, fast reacting gold leaching lixiviant alternative. Thiourea leaching is conducted at a pH of 1.5. The anodic reaction is expressed in Equation 2-28.

$$Au + 2CS(NH_2)_2 \rightarrow Au(S_2O_3)_2^- + e^- \qquad \text{Equation 2-28}$$

The rate of the reaction in Equation 2-30 is highly dependent on the lixiviant and oxidising agent concentration, the presence of ferric iron within the system and the pH of the solution (Pyper and Hendrix, 1981).

$$2Au + 4CS(NH_2)_2 + 2Fe^{3+} \leftrightarrow 2Au(CS(NH_2)_2)_2^+ + 2Fe^{2+} \qquad \text{Equation 2-29}$$
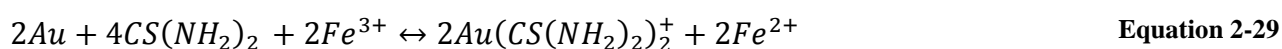
Studies have shown that thiourea can successfully be applied to the leaching of precious metals and when compared to cyanide the reaction is rapid with achievable gold recoveries of up to 99% (Yannopoulos, 1991). The performance is also not affected by the presence of base metals within the system. The lixiviant performs well compared to cyanide under the following conditions:

- When there is an acidic step prior to leaching. No neutralization is required because leaching is done under acidic process conditions.
- Feed contains base metals.
- Feed contains pyrite or chalcopyrite.

Even with the environmental benefits that thiourea possesses as an alternative to cyanide it is not being applied as the lixiviant of choice in the industry. This is because thiourea is an expensive lixiviant and the chemical consumption is high when compared with cyanide. The high consumption is largely due to the thermodynamic instability of the component in basic solution environments (Cui and Anderson, 2016). The gold recovery process also still requires industrial development (Syed, 2012).

2.7.4.2.3 Thiosulphate

Various studies have been done using thiosulphate in recent years. The studies showed that gold can effectively be recovered using both of the common thiosulphate compounds, sodium thiosulphate and ammonia thiosulphate. Thiosulphate is currently seen as the best alternative to cyanide leaching because it's viewed as an environmentally friendly and cost effective alternative when compared to cyanide. Residual cyanide in tailings streams requires potentially expensive treatment to reduce the environmental, where thiosulphate can be disposed into the environment without any treatment (Akcil *et al.*, 2015).

The main concern with the use of thiosulphate is the high chemical consumption. Studies have shown that the consumption is generally 25 kg/ton of ore and can exceed 165 kg/ton ore if the feed is contaminated with copper (Xu *et al.*, 2017). The reaction of thiosulphate with gold is shown in Equation 2-30. The gold forms a strong anionic complex in this reaction.

$$2Au + \frac{1}{2}O_2 + 4S_2O_2^{-3} + H_2O \rightarrow 2Au(S_2O_3)_2^{-3} + 2OH^-$$

Equation 2-30
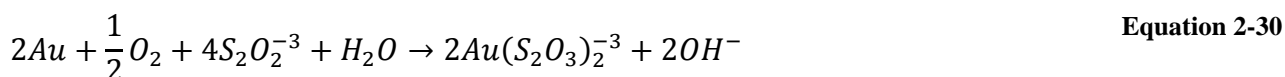
Studies have shown that the leaching performance with thiosulphate is favourable when compared to cyanide in high copper and carbonate based ore bodies.

2.7.4.2.4 Halides

Halides have been used for gold recovery since the 1800s. Chlorine was the first halide used in gold recovery and was later followed by bromine in 1846. Industrial halide leaching processes were replaced with cyanide, because of the superior performance of this lixiviant (Sadia and Jae-chun, 2018).

The stability of the halide/gold complexes is:

$I^- > Br^- > Cl^- > F^-$
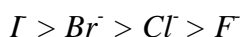
And the kinetics of the leaching reactions is:

$F^- > Cl^- > Br^- > I^-$
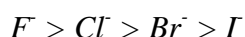
Chloride/Chlorine is the only halogen that is used in industry as a lixiviant for gold recovery. It is normally in the form of aqua regia, which is a combination of hydrochloric acid and nitric acid, which creates a strong oxidizing environment where a Cl^- - Au^{3+} bond can be formed (Sadia and Jae-chun, 2018). The reaction of gold in the halide medium is shown in Equation 2-31 and Equation 2-32 (Sheng and Etsell, 2007).

$$2HNO_3 + 6HCl \rightarrow 2NO + 4H_2O + 3Cl_2$$

Equation 2-31

$$2\,Au + 11HCl + 3HNO_3 \rightarrow 2HAuCl_4 + 3NOCl + 6H_2O$$

Equation 2-32
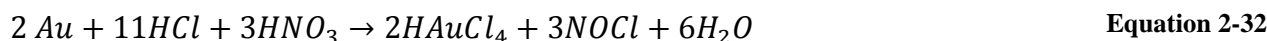
This reaction has better kinetics when compared with the cyanide leaching reactions. The problem with the halogen based leaching methods is the fact that low sulphide concentration and other reactive metals can potentially reduce the $AuCl_4^-$ to metallic gold (Syed, 2012).

The recovery of the gold after the halide leaching process is with activated carbon as metallic gold. The recovery from the activated carbon has significant volume of gold losses due to the small size of the gold particles on the carbon surface. Halide leaching process is expensive when compared with the capital equipment required for cyanide leaching. Equipment is required to be a high grade stainless steel with special liners because of the corrosive nature of the halides. The process also creates various health and environmental risk, because of the poisonous gas generated during the leaching processes (Syed, 2012).

2.7.4.3 *Gold Adsorption/Recovery*

Various technologies have been employed to recover gold from the pregnant leach solution. This project will utilise the carbon adsorption processes which are employed widely in the South African

metallurgical industry. In the process selected in this project a carbon in pulp (CIP) configuration was selected. It is however important to understand the other gold adsorption alternatives.

2.7.4.3.1 Merrill Crowe Process

The Merrill Crowe process was one of the first commercial gold adsorption processes. The process was developed and commercialised in 1890 and utilises zinc to precipitate gold from a pregnant cyanide leach solution. The process achieved high gold recoveries exceeding 98%. The process is still effective in processing ore with high silver content as well as a feed with extreme fluctuations in gold concentrations (Marsden and House, 2002).

The process works by employing traditional redox reaction principals to a pregnant cyanide leach solution. The process is highly dependent on the effectiveness of a post leach solid-liquid separation process step. This is one of the key factors that made carbon adsorption a more cost effective recovery step (Walton, 2005).

During the zinc cementation reaction the gold is reduced to its metallic state and the zinc is component is oxidised to form a zinc-cyanide complex. The reaction is shown in the following reaction:

$$2Au(CN)_2^- + Zn^0 \longrightarrow 2Au^0 + Zn(CN)_4^{2-}$$

Equation 2-33

Even with the introduction of the popular carbon adsorption process, the Merrill Crowe process is still used in 25-30% of the global gold metallurgical plants (Marsden and House, 2002). The Merrill Crowe process is utilised in the following modern gold recovery applications:

- **High silver to gold ratio:** If the ore has silver to gold ratio greater than 2, the Merrill Crowe process is preferred over the carbon adsorption process. The carbon adsorption process fails because the cyanide soluble silver reduces the adsorption efficiency of the gold onto the carbon. This thus leads to a greater carbon requirement which makes the Merrill Crowe process more economically favourable (Walton, 2005).

- **High Mercury Load:** Mercury can be dissolved by cyanide and will adsorb onto the carbon with the gold during carbon adsorption processes. The Mercury is also released from the carbon during the elution process and in addition has the potential to contaminate various process steps. During the Merrill Crowe process the contamination is more controlled. More than 95% of the mercury-cyanide complex is precipitated during the zinc precipitation process and removed with

the gold during the subsequent filtration steps. The management of the mercury content is thus more effective using this process (Walton, 2005).

- **Flotation Processes:** When upstream floatation processes are required for gold processing residual flotation chemicals normally present in the solution at the point of adsorption. These organic molecules adsorb onto the carbon surface and reduce the gold recovery. Depending on the ore grade and the size of the processing plant the Merrill Crowe process might be more economical (Walton, 2005).

2.7.4.3.2 Ion Exchange

The high selectivity of ion exchange resin technology makes it the ideal candidate for gold recovery processes. This technique has been popular within the Soviet Union, whereas in the western world carbon adsorption technology was the method of choice. New technological advancements in gold selective anion resins have led to the large scale commercial introduction of resin-in-pulp (RIP) and resin-in-leach (RIL) recovery systems in modern gold plants. Ion exchange technology might be selected over carbon adsorption because it has potentially higher loading capacities and higher loading rates. Resins are also less susceptible to organic poisoning and it does not require any regeneration (chemical or thermal). The main concern using resin technology is the high cost of the resin inventory when compared to carbon and the general durability and the robustness of the resin particles (Kotze *et al.*, 2005).

Even with the high selectivity of ion exchange resin the competing effect of base-metal cyanides are still being adsorbed onto the resin surface. In the high pH/alkaline cyanide solution the base metals like $Cu(CN)_3^{2-}$, $Ni(CN)_4^{2-}$ and $Fe(CN)_6^{4-}$ still creates similar problems as seen with carbon adsorption processes. Currently medium- and strong base anion are used to recover gold commercially. The strong base anion resin is not pH dependant and the medium base anion resin can be stripped with NaOH. The chemical mechanisms of protonation and adsorption of medium base anionic resins are shown in the following reactions:

Protonation: $P - NHR_2 + H^+ \rightarrow P - NR_2H^+$ **Equation 2-34**

Adsorption: $-NR_2H^+Cl^- + Au(CN)_2^- \rightarrow P - NR_2H^+Au(CN)_2^- + Cl^-$ **Equation 2-35**
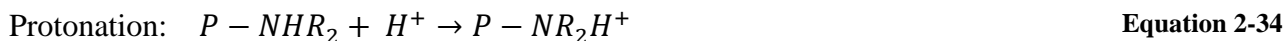
The strong-base anion resin utilised quaternary ammonium groups as the functional groups. This resin is independent of pH which makes it a highly attractive resin. The reactions are summarised in the reactions that follows (Kotze *et al.*, 2005):

Protonation: $P - CH_2Cl + NR_3 \rightarrow P - NR_3^+Cl^+$ **Equation 2-36**

Adsorption: $P - NR_3^+H^+Cl^- + Au(CN)_2^- \rightarrow P - NR_3^+Au(CN)_2^- + Cl^-$ **Equation 2-37**
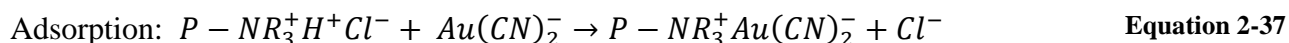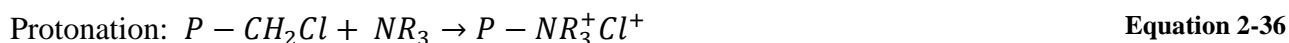
The main application of resin technology currently is recovery of gold from dilute solutions, refining of gold from chloride solutions and recovery from pregnant cyanide leach solutions (Sole, Mooiman and Hardwick, 2016).

2.7.4.3.3 Carbon Adsorption

Carbon adsorption was first used in 1894, where wood charcoal was used to recover gold from pregnant gold-cyanide solutions (Johnson, 1894). The first plant with the modern CIP configuration technology was introduced at the Homestake Mining Company in 1973. The plant operates with four carbon adsorption cells/stages followed by electrowinning. Carbon adsorption technology eliminates the need for expensive solid/liquid filtration processes which is required by the Merrill Crowe process. Also, capital cost is reduced and higher gold recoveries are achievable when compared to the Merrill Crowe Zinc Cementation process (McDougall and Hancock, 1981). The technology was first introduced to the South African gold mining market and is today the most ubiquitously used technique (Staunton, 2005).

The selection of the carbon source is important to achieve the desired recovery of gold. Activated carbon is a highly porous carbon based compounds. Activated carbon with a high surface area, greater than $1000m^2/g$, is normally preferred in the gold recovery process (Rogans, 2012). The material can be produced from a range of organic sources, but commonly peat and coconut shells. These material yields the desired qualities (kinetics, loading capacity and abrasion resistance) required for gold recovery (Staunton, 2005).

The mechanism of gold adsorption onto the surface of carbon is still being debated, but the following general steps have been accepted by industry.

- Electrostatic forces are responsible for the adsorption of the gold-cyanide complex.
- The gold cyanide complex is reduced and precipitates on the carbon surface.

The gold cyanide ion that is present after the leaching step is negative ($Au(CN)_2^-$ and is attracted to the cation that is present. The bond formed here has a significant effect on the adsorption capacity of the gold formed (Rogans, 2012).

$$H^+ > Ca^{2+} > Mg^{2+} > K^+ > Na^+$$

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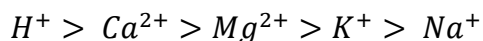
The cation and gold-cyanide forms a neutral ionic bond which adsorbs onto the carbon surface. The efficiency and the extent of the adsorption is dependent on various factors that should be controlled be considered during the process selection and design. The most important factors to consider are:

- Temperature
- Carbon particle size
- Pulp density
- Mixing configuration and efficiency
- Cyanide concentration
- Residence time
- pH
- Contaminants- organic and inorganic

Depending on the feed characteristics, one of three carbon adsorption models will be selected. Carbon in Pulp (CIP), Carbon in Column (CIC) or Carbon in Leach (CIL). Each one depends on the feed/type of the ore body. CIP and CIL circuits are used in high density pulp applications (up to 55% solids) where the gold is recovered directly from the pulp. CIC is commonly applied in heap leach applications where the pregnant cyanide is pumped into carbon packed columns (Mular, Halbe and Barratt, 2002).

2.7.4.3.4 Elution

In the elution (carbon desorption) stage, the neutral calcium-gold-cyanide ionic compound is placed under chemical conditions where the carbon will reject the compounds. The following steps were described by Rogan to illustrate the chemistry of the elution steps.

- Excess sodium ions are introduced to the system in the form of NaOH. The excess sodium creates an environment where the calcium from the calcium-gold-cyanide compound is exchanged with sodium.
- A hot acid wash (commonly hydrochloric acid), is used to break down the gold cyanide complex on the metal surface.
- The newly formed sodium-gold-cyanide ionic compound is unstable. By operating at elevated temperatures ($+90^{o}C$) the unstable bond is broken and released from the carbon surface.
- In most cases gold might be present in other chemical forms during the process. Additional cyanide is thus added to form gold, which will be transformed into a form that can be extracted during the adsorption step.

There are two main elution circuit configurations employed in industry, namely Zadra and Anglo American Research Laboratory (AARL) techniques. The major difference between the two configurations is the connection with the electrowinning processes. With the Zadra process the eluate is continuously circulated through the electrowinning cells and the elution column. The AARL circuit is a batch operation where the elution circuit and the electrowinning circuit is not directly connected in series, but separated by a break-system which enables the circulation of the eluate through the electrowinning circuit (Rogans, 2012). Figure 2-12 shows the key steps involved in gold recovery.

The de-adsorption steps is a critical step in the gold recovery process, therefore it is important to understand the main parameters that influence the performance of this circuit as noted by Rogans, (2012):

- Temperature- the elution efficiency is increased at elevated temperatures.
- Flow rates- the system requires flow rates in between (2-2.5 bed volumes/hr) to release the gold cyanide compounds
- Cation concentrations- even though NaOH is essential in releasing the gold from the carbon surface excessive sodium ions will reduce the elution efficiency. The same comment is valid for other cations that can be introduced to the system.

33
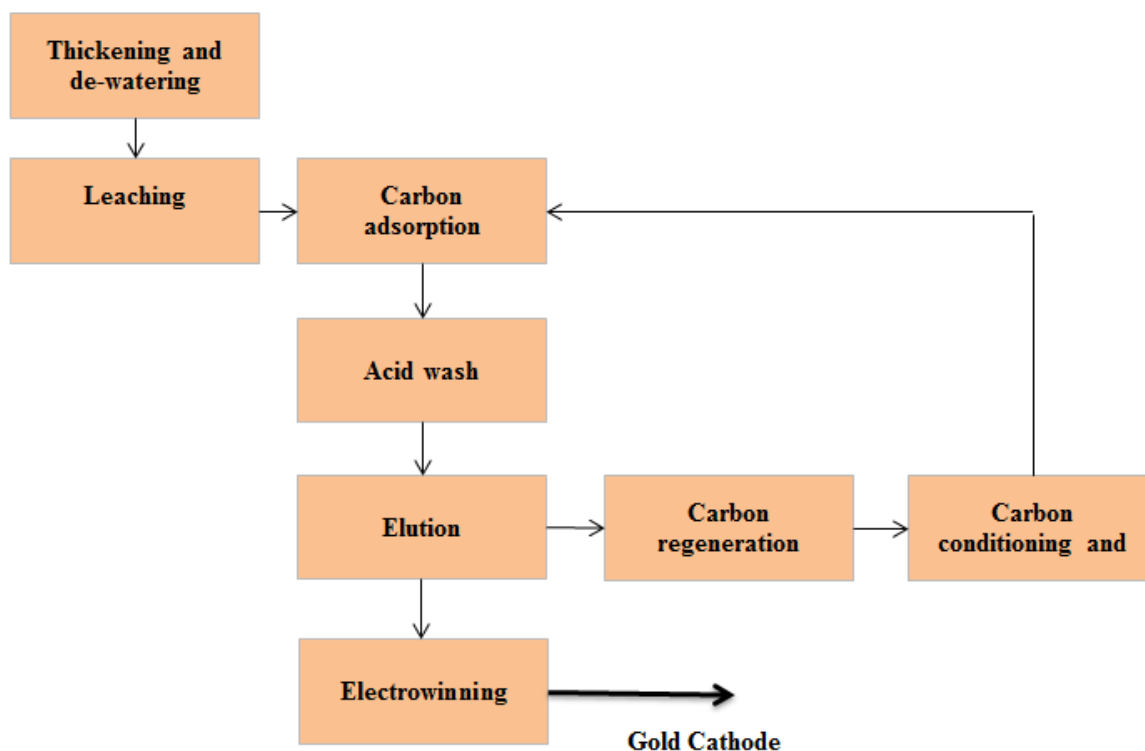
Figure 2-8: CIP Circuit (Adapted from: (Stange, 1999))

2.8 Analytical tools

The preservation of natural resources such as energy and primary materials and also the reduced environmental footprint depends significantly on the recycling of waste materials (Ignatenko, van Schaik and Reuter, 2007). However, due to the complexity in design of recyclates in this instance PCBs, the recovery of valuable metals through physical and metallurgical processes will require the use of natural resources and produce emissions which will have different impacts and effects on the environment. The need for non-renewable resources for recycling processes adds to the depletion thereof thus the sustainability of recycling technologies for metal recovery from PCBs needs to be assessed to prevent exhaustion of these natural resources (Ignatenko, van Schaik and Reuter, 2007).

The evaluation of environmental impacts and resource efficiency of metal recovery technologies an early stage of research, will lead technologies to a better environmental profile. The environmental tool, life cycle assessment (LCA) is an established method that is used to generate and evaluate potential environmental impacts of a product system. In order to determine the resource efficiency i.e. the optimal balance between minimum natural resource requirements and maximum recovery rates for the entire recycling system, exergy analysis can be used as a tool to determine this efficiency (Ignatenko, van Schaik and Reuter, 2007). Exergy losses and exergy efficiencies are

indicative of the performance of the entire recycling system (Ignatenko, van Schaik and Reuter, 2007).

This section provides a description of the analytical methods used to quantify the resource efficiency and potential environmental impacts, applied to a metal recovery technology from waste printed circuit boards.

2.8.1   Exergy

2.8.1.1   Exergy Concept

Thermodynamics plays an important role in the analysis of processes, systems and devices in which energy transfers and energy transformations occur. The first law of thermodynamics is the law of conservation, which states that energy cannot be created nor be destroyed. Thus, the first law describes the *quantity* of energy, but provides no information about the direction in which processes will spontaneously occur. The second law of thermodynamics states that for a thermodynamically defined process to actually occur, the sum of the entropies of the participating systems must increase or stay unchanged in a reversible process. In essence the second law deals with the *quality* of energy; specifically energy degradation during a process, lost opportunities to do work and entropy generation. The second law has proved to be useful in optimizing thermodynamic systems (Cornelissen, 1997). A simplified application of the second law of thermodynamics in the actual system analysis is using the exergy method. It can be used to compare, improve and optimize process designs by quantifying and identifying the sources of thermodynamic efficiencies (Tsatsaronis, 2008; Laukkanen, Järvinen and Fogelholm, 2011).

The term exergy was first introduced by Rant in 1953 and was generally referred to as work capacity or available work (Ahern, 1980; Ignatenko, van Schaik and Reuter, 2007). Currently, exergy is defined as the maximum work that can be produced from a system or a flow that is brought into thermodynamic equilibrium with a reference environment (Rosen, 2002; Ignatenko, van Schaik and Reuter, 2007). Thus, the exergy of a system or a flow is zero when it is in equilibrium with the environment and increases as state of the system increasingly deviates from the environment. Exergy at a specified state is a function of both the conditions of the environment as well as the system's properties (Rosen, 2002).

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2.8.1.2   Exergy balance

The exergy balance for any system can be derived by combining the energy and entropy balances that are given by the thermodynamic laws. Assuming steady-state conditions the overall exergy balance expressed in units of energy is given by Equation 2-38:

$$E_{Input} = E_{Output} + E_{Destruction}$$
Equation 2-38

Where E $_{destruction}$ denotes irreversibility, E $_{input}$ and E $_{output}$ denotes mass and energy streams. The different mass and energy forms of exergy are discussed in section 2.8.1.5. The exergy balance is a statement of the law of degradation of energy which is opposite of the conservation of energy as given by the first law. Degradation of energy occurs due to the irreversibilities that exist in real processes (Ignatenko, van Schaik and Reuter, 2007). Thermodynamic inefficiencies can be attributed to waste emissions or waste streams that are discarded into the environment (external losses) and the entropy changes within the system (internal losses) (Ignatenko, van Schaik and Reuter, 2007).

2.8.1.3   Exergy destruction

The exergy destruction, calculated from the exergy balance is the difference between the total input and output exergies. The exergy destruction or also known as the Gouy–Stodola relation is directly related to entropy generation as expressed by Equation 2-39:

$$E_{destruction} = T^0 S_{gen}$$
Equation 2-39

The entropy production and hence the exergy destruction associated with a process are a direct measure for the resource consumption of that process (Goßling-Reisemann, 2008). Therefore, is desirable to minimize the exergy destruction of a process to ensure a more sustainable process.

2.8.1.4   Reference Environment

The exergy is expressed relative to a reference environment, at which the system under consideration has no capability to do any further work once it reaches the same conditions of the environment. The conditions of the reference environment are often modelled as the actual surrounding environment in which the system under consideration exists. This choice of reference environment can be problematic because perfect thermodynamic equilibrium does not exist

(Szargut, 1980; Kotas, 1985). Szargut *et al.* (1986) proposed that each chemical element must have a reference substance (lowest chemical potential) that correspond to common components that occur in the environment i.e. the atmosphere, oceans and seas and a layer of the earth's crust (Kotas, 1985; Szargut and Morris, 1986). The temperature and pressure are taken to be the ambient conditions of the environment (Szargut, 1980; Szargut and Morris, 1986). Therefore, the reference environment has to be large enough so that its parameters are not affected by the interactions with the system under consideration (Reuter *et al.*, 2007).

2.8.1.5   *Exergy forms*

2.8.1.5.1   Exergy of thermal energy

The exergy associated with the heat transfer Q from and to the system can be expressed as:

$$E_Q = Q\left(1 - \frac{T^0}{T}\right)$$

Equation 2-40

Where E_Q denotes the thermal exergy, T^o and T are the reference and system temperatures respectively. The thermal exergy is represents the maximum work that can be obtained from the heat source.

2.8.1.5.2   Exergy of work

The exergy associated with shaft work, electricity etc. can be fully converted to useful work. Therefore, the exergy content of such streams is equal to the energy content of that stream both in magnitude and direction and can be expressed as:

$$E_w = W$$

Equation 2-41

Where E_W denotes the exergy of a work stream and *W* is the energy amount that is supplied to or produced by the system.

2.8.1.6   *Exergy of mass streams*

The exergy of a mass stream can be divided into four parts: physical exergy, chemical exergy, potential exergy and kinetic exergy as defined by Equation 2-38 (Ignatenko, van Schaik and Reuter, 2007; Laukkanen, Järvinen and Fogelholm, 2011). In practice the kinetic and potential exergies are negligible compared to the two other forms of exergy and are therefore not further explored

(Lehtonen, 2013). The calculation of chemical and physical exergy is discussed in the following sections.

$$E_{system} = E_{Physical} + E_{Kinetic} + E_{Potential} + E_{Chemical} \qquad \textbf{Equation 2-42}$$

2.8.1.6.1 Physical Exergy

The physical exergy is the maximum available work obtainable due to pressure and temperature differences between the system under consideration and the reference environment (Ahern, 1980; Kotas, 1985; Reuter *et al.*, 2007). The physical exergy of a substance at a temperature and pressure T and P is given by Equation 2-43.

$$E_{Physical} = (H - H^0) - T^0(S - S^0) \qquad \textbf{Equation 2-43}$$

Where H and S, is the system's extensive enthalpy and entropy at a given state; H^o and S^o is the system's enthalpy and entropy at equilibrium at the reference environment and T^o is the temperature of reference environment.

For an ideal gas with constant heat capacity C_p the above equation can be simplified to:

$$E_{Physical} = \sum_{i} n_i \left(c_{p.i} \cdot (T - T^0) - T^0 \left(c_{p.i} ln\left(\frac{T}{T^0}\right) - R \cdot ln\left(\frac{P}{P^0}\right)\right)\right) \qquad \textbf{Equation 2-44}$$

Where R is the universal gas constant.

For solids and liquids with average specific volume v_m and constant heat c capacity Equation 2-44 can be simplified to:

$$E_{Physical} = c\left((T - T^0) - T^0 ln\left(\frac{T}{T^0}\right) + v_m \cdot (P - P^0)\right) \qquad \textbf{Equation 2-45}$$

Where T^o, T and P^o, P are the reference and system temperatures and pressures respectively.

2.8.1.6.2 Chemical Exergy

The chemical exergy is the maximum available work obtainable due to a difference in composition between the system under consideration and the reference environment (Ahern, 1980; Kotas, 1985;

Reuter *et al.*, 2007). The chemical exergy of a substance at a temperature and pressure T^o and P^o is given by Equation 2-46:

$$E_{chemical} = \sum n_i \, (\mu - \mu^0)_i$$

Equation 2-46

Where μ is the intensive molar Gibbs function or chemical potential of component *i* of the substance and **μ^o** is the intensive molar Gibbs function or chemical potential of component *i* in the environment; **n** is the molar concentrations of component *i*.

After substituting each chemical potential in the above equation with Equation 2-47 and Equation 2-48 the chemical exergy of a substance can are given by Equation 2-49.

$$\mu = \mu^0 + RT^0 \ln a_i$$

Equation 2-47

$$\mu^0 = \mu_o + RT^0 \ln a_i^o$$

Equation 2-48

$$E_{chemical} = RT^0 \sum n_i \cdot \ln\left(\frac{a_i}{a_i^o}\right)$$

Equation 2-49

Where a_i and a_i^o are the activity coefficients of component *i* at similar conditions as the respective chemical potential; μ_o is the chemical potential of the pure substance at temperature T^o and pressure P^o. Szargut (1989) calculated and tabulated the chemical exergies of different elemental species at standard conditions. The reason was to create a table of chemical exergies of reference species which enables the calculation of non-reference species according to the following equation (Kotas, 1985; Reuter *et al.*, 2007):

$$E_{chemical, \ non-reference \ species} = \Delta G_i + \sum v_k * E_k{}^0$$

Equation 2-50

Where ΔG_i is the standard Gibbs energy of the non-reference substance *i*; E_k is the standard chemical exergy of the elemental reference species *k* in substance *i* and v_k is the stoichiometric coefficient of the elemental reference species.

The chemical exergy of mixtures are expressed by Equation 2-51 (Kotas, 1985; Reuter *et al.*, 2007).

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$$E_{chemical\,.mixture} = \sum_i x_i E_{chemical.i}{}^0 + RT^0 \sum_i x_i ln a_i \qquad \textbf{Equation 2-51}$$

Where $E_{chemical,i}{}^0$ is the standard chemical exergy of component i, R is the universal gas constant and a_i is the activity of component i in the mixture with mole fraction x_i. The chemical exergy of the mixture is always less than the sum of chemical exergies of the individual components at the conditions of the mixture. The second term of Equation 2-51 expresses the entropy increase due to mixing (Reuter *et al.*, 2007).

In cases where the Gibbs energy of a substance is unknown e.g. activated carbon, kerosene etc. the chemical exergy can be calculated using the following equation (Hader, Darabseh and Alothman, 2011):

$$E_{chemical} = LHV\left(1.0401 + 0.1728\left(\frac{x_H}{x_C}\right) + 0.0432\left(\frac{x_O}{x_C}\right) + 0.2169\left(\frac{x_S}{x_C}\right)\left(1 - 2.0628\frac{x_H}{x_C}\right)\right)$$

Equation 2-52

Where LHV is the lower heating value of the substance and x_C, x_H, x_S, and x_O are the mass fraction of the elements C, H, S and O in the substance.

2.8.1.7 *Exergy efficiency*

The exergy or exergetic efficiency of a process is ratio between the exergies of the products and the inputs (

Equation 2-53). The exergy efficiency is dimensionless and range from zero to a maximum of 1.The exergetic efficiency is indicative of how effectively the input exergy is converted to valuable products (Laukkanen, Järvinen and Fogelholm, 2011).

$$\Psi = \frac{\sum E_{products}}{\sum E_{inputs}} \qquad \textbf{Equation 2-53}$$

where, Ψ is the exergetic efficiency; $E_{products}$ is the exergy of the recovered or valuable products; and E_{inputs} is the total input exergy, which include the input of the recycled materials, raw materials, energy input such as electricity etc. (Ignatenko, van Schaik and Reuter, 2007).

In this study the exergetic efficiency and the exergy destruction are used as the performance indicators of the thermodynamic efficiency of the metal recycling chain. A summary of the performance indicators of an exergy analysis are summarised in Figure 2-9.
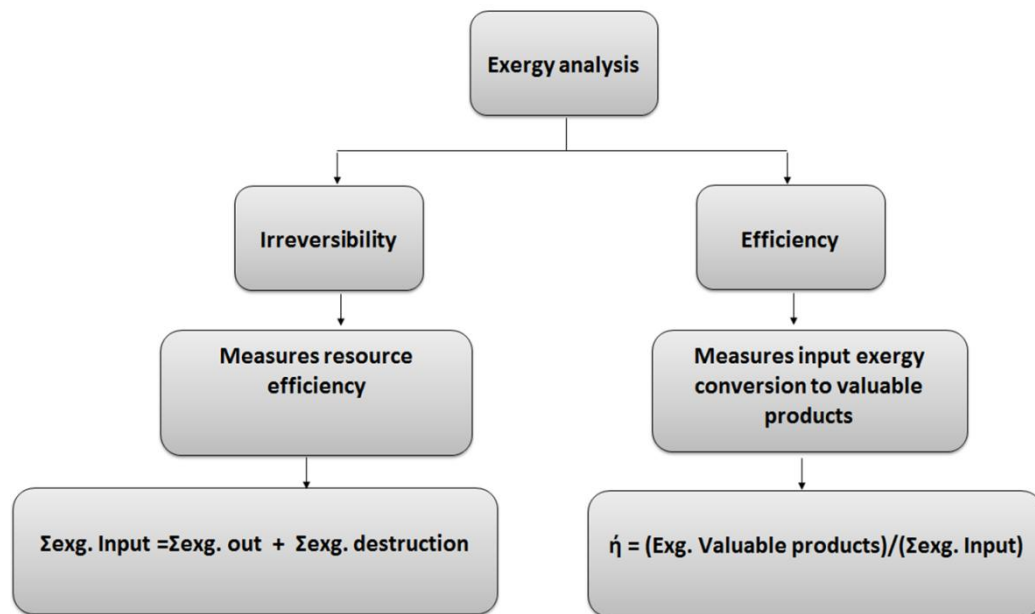
Figure 2-9: Performance Indicators for an Exergy analysis

2.8.2   Limitations of Exergy Analysis

The purpose of an exergy analysis is to identify and quantify the exergy destruction that occurs due to irreversibilities in process units (Laukkanen, Järvinen and Fogelholm, 2011). This information sheds light on possible causes of irreversibilities as well as which process units within the recycling chain have the greatest contribution to the overall exergy destruction. Based on the causes of these irreversibilities, possible process changes can be suggested to minimise the exergy destruction in the process units but the changes can only be justified through an economic analysis. Also, the possible improvement in one process unit may affect the thermodynamic performance of the other process components (Morosuk, Tsatsaronis and Schult, 2013). Therefore, only by gaining understanding of the mutual interdependencies of the process components can provide insight about true thermodynamic improvement potential. An advance exergetic analysis provides such insights by splitting the exergetic destruction into exogenous, endogenous, avoidable and unavoidable parts (Morosuk, Tsatsaronis and Schult, 2013; Penkuhn and Tsatsaronis, 2017). The exogenous and endogenous exergy destruction parts of a process component provide information whether the focus should be on the component under consideration or the other process components (Morosuk, Tsatsaronis and Schult, 2013). The avoidable and unavoidable exergy destruction parts of a process component describe the irreversibilities due to techno-economic limitations such as availability and

cost of materials and best available technology (BAT) (Penkuhn and Tsatsaronis, 2017). The scope of this study only extends to identifying and quantifying the irreversibilities and provides possible suggestions for improvement.

2.9   Life cycle Assessment

Life cycle assessment (LCA) is an established method to evaluate the environmental performance associated with products, services and processes over its complete life cycle (cradle-to-grave) by systematically accounting all resources used i.e. energy and raw materials as well as the emissions to water, air and soil. This tool highlights the potential environmental hotspots which can assist in decision making at an early stage of potential future systems such as the process presented in this thesis for recycling waste PCBs through a hydrometallurgical route.

2.9.1   Overview of the LCA Methodology

The framework to conduct a LCA study is detailed in the ISO 14040 series of standard (14040, 14041, 14042 and 14043). The four main steps: Definition of goal and scope, Inventory analysis, Impact assessment and Interpretation are demonstrated in Figure 2-10. The double arrows indicate the iterative nature of a LCA. This section gives an overview of each phase to be undertaken in a LCA study.
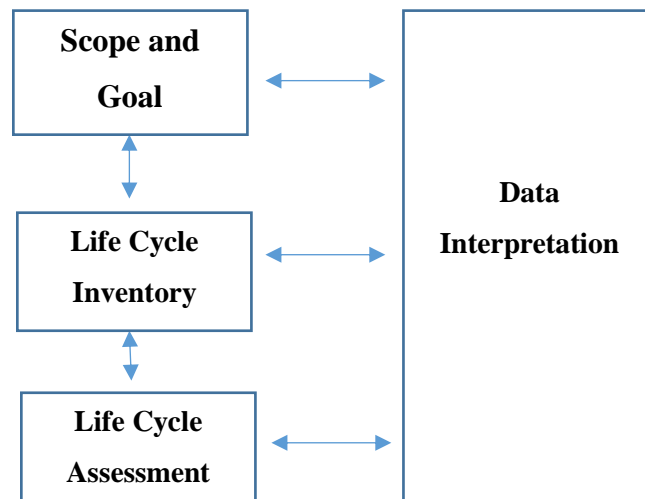
Figure 2-10: Life Cycle Analysis Methodology

2.9.1.1   Goal and Scope of the study

The first phase is establishing the goal and scope of the study. Defining the goal of the study should state the intended applications, the intended audience and reasons for doing the study (Heijungs *et*

al., 1992). The scope of the study must clearly define the boundaries of the product system, the function of the product system, the functional unit, assumptions made, limitations, allocation procedures, data requirements and the selected impact categories. All of the aforementioned issues should be sufficiently defined to ensure that the goal of the study is addressed. From the issues that are mentioned, defining the functional unit and system boundaries are of particular importance in any LCA study. The functional unit provides reference to which all the elementary data in the inventory phase will be related to which also sets the scale for comparative LCA studies (Jensen *et al.*, 1997). The definition of the system boundaries is subjective and therefore the assumptions and limitations should be clearly stated (Jensen *et al.*, 1997).

2.9.1.2   Life cycle Inventory Analysis (LCI)

The LCI phase involves collection, compilation and quantification of inputs and outputs relevant to the process and relates all data to the functional unit (ISO International Standard 14040, 2006). This normalised data form the inventory list for the system under study and is also the input to the next phase of the LCA. All the process flows are distinguished as either elementary or non-elementary flows. Elementary flows are inputs or outputs that are directly from or to the environment in the forms as resources and emissions. The non-elementary flows stay within the technosphere and therefore have no direct impact on the environment (Friedrich, 2001).

2.9.1.3   Life cycle Impact Assessment (LCIA)

The purpose of the LCIA phase is to evaluate the magnitude and significance of the potential environmental impacts using the LCI of the product system (ISO International Standard 14042, 2000). The LCIA phase consists of both mandatory and optional elements. The following elements are considered mandatory: selection of impact categories, assignment of inventory results to the impact category (classification), selection of characterisation models and characterisation. The optional steps are normalisation and weighting (ISO International Standard 14042, 2000). An overview of each step is discussed below.

2.9.1.3.1 Selection of impact categories and classification

This step involves the identification and selection of the impact categories which is in accordance with the goal of the study (ISO International Standard 14042, 2000). These categories will describe the impacts caused by the consumption of natural resources and emissions induced by the process. Each impact category is attributable to the three areas of protection (AoP): Human health, natural resources and eco system quality. Classification is the process by which the elementary input and

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output flows form the LCI are assigned to the selected impact categories according to the substances' ability to contribute to different categories.

2.9.1.3.2 Selection of characterisation methods and characterisation

This step involves the translation of inventory data into a profile of environmental impact scores. The elementary flows that are assigned to the different impact categories are converted to environmental indicators using characterisation factors. This is done by multiplying the results from the classification phase by the characterisation factors of each substance within each impact category (Menoufi, 2011). The characterisation factors for each substance are indicative of the potential impact of that substance in terms of the common unit of the impact category. For example, the impact category climate change expressed as kg CO_2-equivalents, the characterisation factors for 1 kg carbon dioxide and 1kg nitrous oxide is 1 and 310 respectively. Therefore the effect of I kg nitrous oxide on the environment is 310 times more than the effect of 1 kg carbon dioxide (Menoufi, 2011). Once all the substances are expressed in equivalent units for each impact category, all contributions are summed as a single impact score.

2.9.1.3.3 Normalisation & Weighting

Normalisation involves relating the impact scores from the characterisation phase to reference values and expressing the relative magnitude of the impact scores on a common scale. Weighting is the process of converting the normalised impact scores using weighting factors in order to express its relative significance (Menoufi, 2011). Both normalisation and weighting steps are subjective and optional according to the ISO 14040 standards but may facilitate the interpretation of the results (ISO International Standard 14040, 2006).

2.9.1.4   Interpretation

Interpretation is the final stage in the life cycle assessment. The results from the previous phases are evaluated in relation to the objective and scope of the study. The critical environmental impacts and the significance of the relative contributions of process units are highlighted. The results are verified by doing a completeness check; sensitivity analysis and performing a consistency check (Menoufi, 2011). Lastly, conclusions are drawn and recommendations are made. Depending on the results of the previous stage, iteration between the interpretation phase and the other LCA phases may occur to match the goal and scope of the study (ISO International Standard 14043, 2000).

2.9.2 Applications of LCA in WPCB recycling

Several LCAs have been conducted to shed some light on the environmental load that are associated with different end-of- life scenarios regarding valuable metal recovery from electronic waste (e-waste). An overview of the studies that focused on printed circuit board recycling via a hydrometallurgical route are summarised in Table 2-7. The results highlight the metal leaching stages as the main contributors to the overall environmental impact. The impacts of other recycling options are discussed by Xue and Xu (2017). It is worth noting that most of LCA studies reviewed by Xue and Xu (2017) were conducted in developed regions such as Europe whereas little to none LCA studies were performed in developing countries. Africa is an example where no LCA studies were performed on the recycling of electronic waste (Xue and Xu, 2017). An understanding of the potential environmental impacts of electronic waste treatment must therefore be prioritised in developing countries since these countries are often targeted countries as dumping sites for electronic wastes (Xue and Xu, 2017).

Table 2-7: Hydrometallurgical PCB Recycling LCA Studies Review

Title	Functional unit	Impact categories	Main findings	Ref.
Environmental impacts of a hydrometallurgical process for electronic waste treatment: A life cycle assessment case study	100 kg WPCBs	CML-IA: ADP, GWP, ODP, HTP,FAETP, MAETP, TETP, POP,AP, EP	The nitric acid leaching stage engendered the most impact on the environment, followed by adsorption stages.	(Iannicelli-zubiani *et al.*, 2017)
Waste Management of Printed Wiring Boards: A Life Cycle Assessment of the Metals Recycling Chain from Liberation through Refining	1000 kg WPCBs	CML-2001: ADP (fossil), GWP,HTP,FAETP, MAETP, TETP, POCP,AP, EP	The aqua regia leaching in the refining stage posed most of the environmental impact.	(Xue *et al.*, 2014)
Environmental Impact Assessment of Hydrometallurgical Processes for Metal Recovery from WEEE Residues Using a Portable	100 ton WPCBs	CML-2001: ADP, GWP, ODP, POCP,AP, EP	The copper leaching stage with sulphuric acid and hydrogen peroxide had the greatest impact on the environment. .	(Laura Rocchetti, Francesco Vegliò, Bernd Kopacek, 2013)

Prototype Plant				
Applying a life cycle perspective to research on metal recovery from electronic waste using bioleaching	1kg of cathode copper from PCB	CML-2001: ADP, GWP, ODP, HTP,FAETP, MAETP, TETP, POCP,AP, EP	The copper bioleaching stage the greatest impact on the environment.	(Villares, 2015)
Biological versus chemical leaching of electronic waste for copper and gold recovery	1kg WPCBs	CML-2001:ADP, GWP, ODP, HTP,FAETP, MAETP, TETP, POCP,AP, EP	Bioleaching is more environmentally benign than chemical leaching. Copper leaching with sulphuric acid and hydrogen peroxide and gold leaching with ammoniacal thiosulfate had the greatest impact on the environment.	(Isildar, 2018)

2.9.3   Limitations of LCA

Goßling-Reisemann (2008) stated that one of the drawbacks of the LCA methodology is that the focus is only on inputs and outputs and not on how these streams are treated within the technosphere. Reuter et al (2007) made a similar observation, indicating that the losses due to irreversibilities that occur during recycling processes are not effectively explained by a LCA. While it is true that most of the environmental impacts of a process can be explained by the inputs and outputs of a system, most often the environmental solution lies in the understanding of the irreversibilities within the system (Goßling-Reisemann, 2008). Based on this observation, Reuter et al (2007) suggested to evaluate the sustainability of a process from an environmental point of view, is to use both LCA and exergy analysis. Therefore, this study aims to use both analytical tools to gain understanding of the sustainability of a possible metal recycling process.

3. PROCESS DESCRIPTION AND FLOWSHEET DEVELOPMENT

This chapter describes the design considerations and basis used for the development of the final process solution. The technologies employed in the process are described in Chapter 2 and were continuously adapted during the study by taking the simulation outputs into consideration. The flow sheets developed for each process section were used for the process modelling and simulations in HSC-Sim and GaBi as discussed in Chapter 4.

3.1 Process Feed

The PCB feed composition varies significantly depending on the source material as explained in section 2.2. The metal content of PCBs is commonly reported as 40 wt.% of the total board which includes mounted electronic components such as capacitors (Akcil *et al.*, 2015). When these electronic components are removed from the PCB, the material distribution has been reported to be 28 wt.% metals, 23 wt.% plastic and 49 wt.% ceramics (Su *et al.*, 2017). The breakdown of the metallic fraction of the PCBs fed into the system was taken from Rossouw (2015) and the non-metallic composition was taken from Duan *et al.*, (2011). The combined analysis was normalised to the respective metal and non-metal distributions as reported by Su *et al.*, (2017). Ghodrat *et al.*, (2016) conducted an economic analysis on a traditional pyrometallurgical plant for e-waste recycling and found that the minimum plant capacity for an e-waste recycling should to be 30 000 tonnes/annum in order to be economic viable. Based on this finding, this project assumed a processing capacity of 30 000 tonnes PCBs/annum. Table 3-1 presents the mass fractions and mass flow rates of the PCBs considered in this study.

Table 3-1: Feed Analysis

PCB substrate	Mass fraction	Mass [kg/hr]
Metal	28%	
Cu	15.94%	729,81
Al	2.60%	118,84
Fe	2.25%	102,86
Sn	1.76%	80,60
Ni	0.39%	17,93
Zn	2.15%	98,48
Pb	2.86%	131,14
Au	0.01%	0,58

Ag	0.04%	1,82
Ceramics	**23%**	
SiO$_2$	12.78%	585,06
Al$_2$O$_3$	5.11%	234,03
CaO	5.11%	234,03
Plastics	**49%**	
C$_2$H$_4$	18.17%	831,89
C$_3$H$_6$	8.81%	403,34
C$_{10}$H$_8$O$_4$	8.81%	403,34
C$_{15}$H$_{12}$Br$_4$O$_2$	8.81%	403,34
C$_2$H$_3$Cl	4.40%	201,67
Total	**100%**	**4578.75**

3.1.1   Assumptions

The following assumptions have been made with regards to the feed composition:

- The feed material is disassembled and stripped from all relevant components such as capacitors, casing etc. before it enters the plant boundaries.

- There is no significant variation in the feed concentration or metal component ratios, i.e. copper/gold, will remain stable.

- Total processing capacity was taken to be 30 000 tonnes PCBs/annum.

- Plant availability is 92%.

- Total plant operating days are 312 days.

- Plant operating hours/day is 21 hours.

3.2   Pre-Treatment

The pre-treatment section of the plant employs traditional mechanical comminution techniques. This includes shredding and pulverisation techniques, which is used to transform the bare PCBs into a form suitable for subsequent recovery processes.

3.2.1   Process Section Motivation

Mechanical size reduction is an important step in liberating the metals from the PCB body. The reduction in size makes the material more manageable within the automated material transport structure within a process plant and it increases the overall downstream recovery of the metals in

the respective downstream circuits. The leaching circuits' metal recovery is increased when the metal fraction of the PCB is more exposed to the lixiviants (Luda, 2011; Rossouw, 2015).

3.2.2   Process

Industrial material crushers depend on the material characteristics: strength, hardness and the material make-up matrix. PCBs has a complex multi-layered material make-up. The reinforced layers and the wide range of bonding agents give the PCB great material strength in terms of impact toughness. Impact toughness levels have been reported as **96.85 kJ/m^2** (Chen, Li and Duan, 2010). These properties make the size reduction process more complex when compared to traditional ore comminution processes. The properties of the PCB do not allow for processing with a traditional crusher which only utilises extrusion forces.

Previous studies proved that metals can only be liberated successfully from PCB's in a two-step crushing circuit. The first stage consists out of a high speed shredder. This utilises shearing forces which can reduce the particles to the required sizes. The final step is a grinding with the aid of a hammer mill. The final product produced is less than 2mm (based on the recommendation of Rossouw, 2015) and liberates all of the enclosed metals (Li *et al.*, 2007).

Feed

30mm x30mm

Crushing

10mm x10mm

Grinding

2mm x2mm
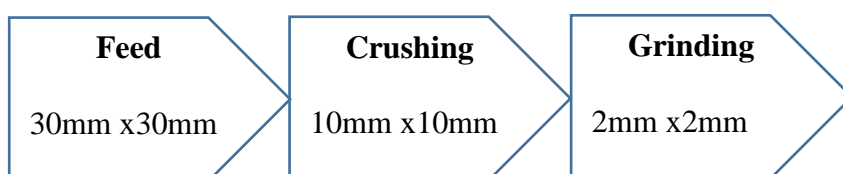
Figure 3-1: Particle Size Reduction

The process developed for the comminution of PCBs therefore consists of a two-step size reduction process. The first stage of size reduction is done with a shredder unit followed by a hammer mill for fine grinding to the required size. The basic block flow is shown in Figure 3-2.
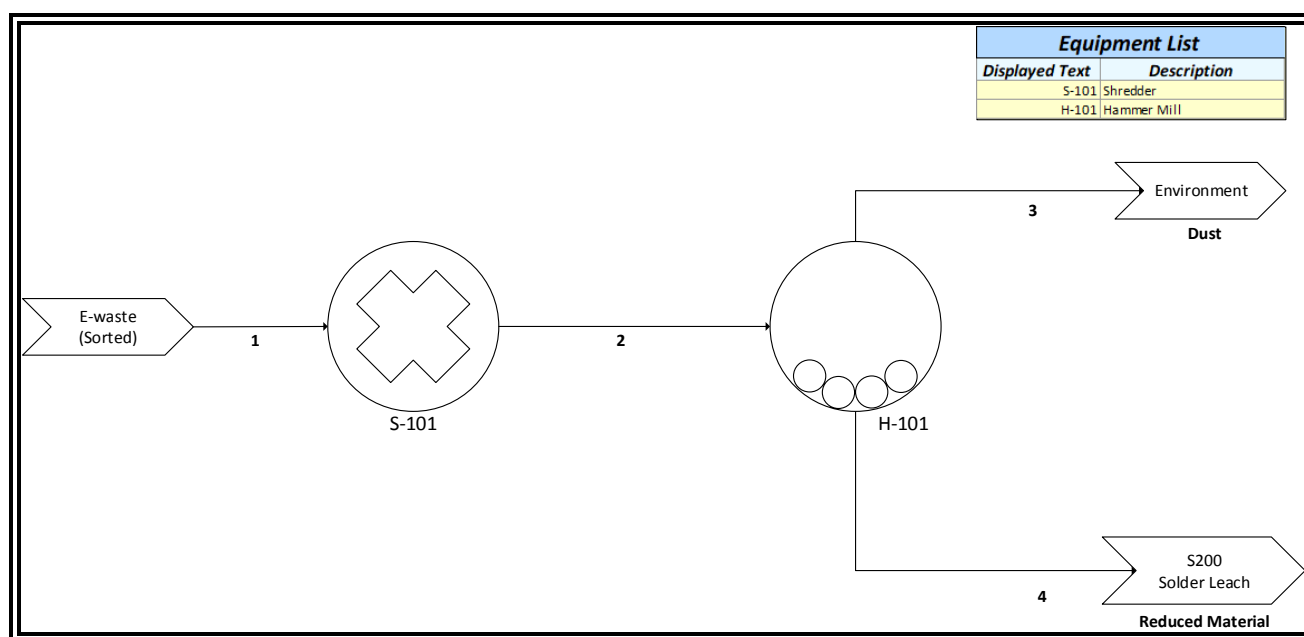
Figure 3-2:Pre-Treatment Process Flow

3.2.3   Material Balances

The comminution process does not have any additional material feed inputs into the process. When examining the process as shown in Figure 3-2 the process only has two process outputs- the reduced material that is fed into the downstream processes and the dust fraction that is lost to the environment. Generating dust during the comminution process is inevitable and it should thus be accounted for in the process design. E-waste recycling focused studies has shown that dust and various gasses are produced during the physical separation processes. Due to the fact that only crushing and milling will be employed in the physical separation process and that the assumption that no material will be oxidised the gas formation is ignored. The dust generated in the process was determined to be **3.7 wt%** of the total feed material. This is based on analysis done on recycling processes in China, America, Brazil, Canada and Pakistan (Wang *et al.*, 2015). All dust generated in the comminution process is then captured in a bag house and with a **73% efficiency**- the dust lost to the atmosphere is this **1%** of the total feed. The concentration of the dust is also assumed to be the same as the feed material composition.

3.2.4   Energy Requirements

Comminution processes are commonly the most energy intensive processes in a processing plant. This is due to the intensive forces required to liberate the metal from the PCB matrix. The energy required in this circuit utilised specific energy requirements obtained from literature and empirical

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comminution formulas from industry. The following energy calculation was used to determine the energy input for the mill.

$$W = \frac{10W_i}{\sqrt{P}} - \frac{10W_i}{\sqrt{F}}$$

Equation 3-1

W is the specific energy required per ton of material, W_i is the material work index, P is the d_{80} of the final product and F is the d_{80} of the feed material. P was assumed to be 30mm and F, 2mm. The Bond work index used was 21.2 kWh/ton. This was obtained from a study done on the liberation of metals from a furnace lining of a non-ferrous metal process plant (Krishna and Raghavendra, 2008). This was done because the characteristics of the material are similar to that of a PCB.

3.2.5   Assumptions

The following design assumptions were made for the comminution:

- All energy associated with ancillary equipment, i.e. conveyers and pumps were negligible when compared to the major equipment and are therefore ignored.
- All electrical work inputs are lost in the form of heat.
- During crushing the local temperature of the PCBs can increase to over 250°C due to impacting, resulting in pyrolytic cleavage of chemical bonds in the matrix that produces brominated and non-brominated phenols and aromatic/aliphatic ethers (Luda, 2011). This phenomenon was not considered.
- Oxidisation of metals during the comminution process was not considered.
- 3.7% of the feed to the circuit was considered to be lost as dust. The dust generated are assumed tol be collected by a bag-house system where 1% was assumed to be lost from this system to the environment (Wang *et al.*, 2015).
- The material is completely liberated at the size fraction smaller than 2mm.
- Bond work index was assumed to be 21.2 kWh/ton. This value was determined for metals entrapped in spent furnace linings used in the non-ferrous metal industry (Krishna and Raghavendra, 2008).
- Specific energy requirement for the shredder is 40 kWh/ton PCBs; values of 38.05 kWh/ton PCBs and 28 - 36 kWh/ton have been reported for a shredder of hammer mill type (Commission, 2001; Johansson and Björklund, 2010).

3.3   Solder Removal

The nitric acid leaching process step has both environmental and process objectives. The majority of electronic and electric components utilise a lead/tin alloy as solder. This keeps the various components connected to the circuit board. Removal of the solder from the board liberates the valuable metals for simpler/more efficient downstream recovery (Mecucci and Scott, 2002). The lead component in the solder is also highly toxic when discharged into the environment or via traditional waste management systems (Chaurasia, Singh and Mankhand, 2013).

3.3.1   Process

The solder process was based on the results and process development done by previous studies (Mecucci and Scott, 2002; Rossouw, 2015). The reduced feed from the comminution circuit is fed into a leach tank reactor. The solid residue is brought into intimate contact with a 1.5 M nitric acid (HNO_3) solution. The mixture is mechanically agitated and has a reaction time of 8 hours. Two output streams are produced from the reactions; gas and slurry streams. The gas stream consists of hydrogen and nitrous oxides (NO_x) components. This project did not consider the downstream waste management process design, but the NO_x and hydrogen gas streams were assumed to be released to the environment. The waste management options are discussed in Appendix D. The reactions for this process are shown in Table 3-2. The extents of reactions were calculated from the work done by Rossouw (2015).

Table 3-2: Nitric Acid Leach Reactions

Progress %	Reactants		Products	H kJ
97,9	Pb+4HNO3(aq)	=	Pb(NO3)2(aq) +2H2O +2NO2(g)	-161,92
33,6	Ni+4HNO3(aq)	=	Ni(NO3)2(aq)+2H2O +2NO2(g)	-214,22
1,7	3Zn+8HNO3(aq)	=	3Zn(NO3)2(aq) + 4H2O +2NO(g)	-1148,84
1,3	3Ag+4HNO3(aq)	=	3AgNO3(aq) + 2H2O(g)+NO(g)	73,93
15,3	Al+4HNO3(aq)	=	Al(NO3)3(aq)+2H2O+NO(g)	-876,51
76,2	Fe+4HNO3(aq)	=	Fe(NO3)3(aq)+2H2O+NO(g)	-392,17
0,2	3Cu+8HNO3(aq)	=	3Cu(NO3)2(aq)+4H2O+2NO(g)	-492,75
7	3Sn+8HNO3(aq)	=	3Sn(NO3)2(aq)+2NO(g)+4H2O	-718,56

The slurry is sent to a filter press unit, which has 100% solid/liquid separation efficiency. The filtrate contains the leached metals and the solid phase contains the remaining metals in the solid phase. Previous studies proved that the dissolution of lead is dependent on the HNO_3 concentration and temperature. Lead dissolution is directly proportional to the increase in the lixiviant concentration and the operating temperature (Kumari *et al.*, 2010; Rossouw, 2015). The dissolution of copper in this leaching circuit is also possible and should thus be controlled. A lead recovery study from PCBs showed that at 23 $^{\circ}$C, a nitric acid concentration of 1M and 6 hour retention time yielded 99% lead recovery and minimal copper dissolution (Mecucci and Scott, 2002). The effect of the solid concentration in the leaching circuit and the copper dissolution rate was also shown to influence to copper dissolution rate; it was seen that the copper concentration is inversely proportional to the solid concentration in the leach tank. The study showed that that at the same operating temperature and lixiviant concentration the copper dissolution increased from 43.2% to 82.4% with the decrease in solid concentration of 10% to 2% (Bas, Deveci and Yazici, 2014). Taking all of the studies into consideration and operating the system at a 35% solid concentration, retention time 8hours, the nitric acid concentration was taken as 1.5M and the operating temperature is 25 ^{0}C.

No additional cementation and recovery steps are included in the process design because the recovery of lead and tin is not part of the process objectives. Chloride cementation can be done to recover the lead from the PLS generated in this process. The process can be executed at room temperature with 4M NaCl and yields a +99% of $PbCl_2$ and other metal salts. The salts formed in this process are stable and can be sold as a secondary product for further processing (Quinet, Proost and Van Lierde, 2005; Ranitović *et al.*, 2016). In addition to this approach, lead can also be precipitated as lead sulphate.
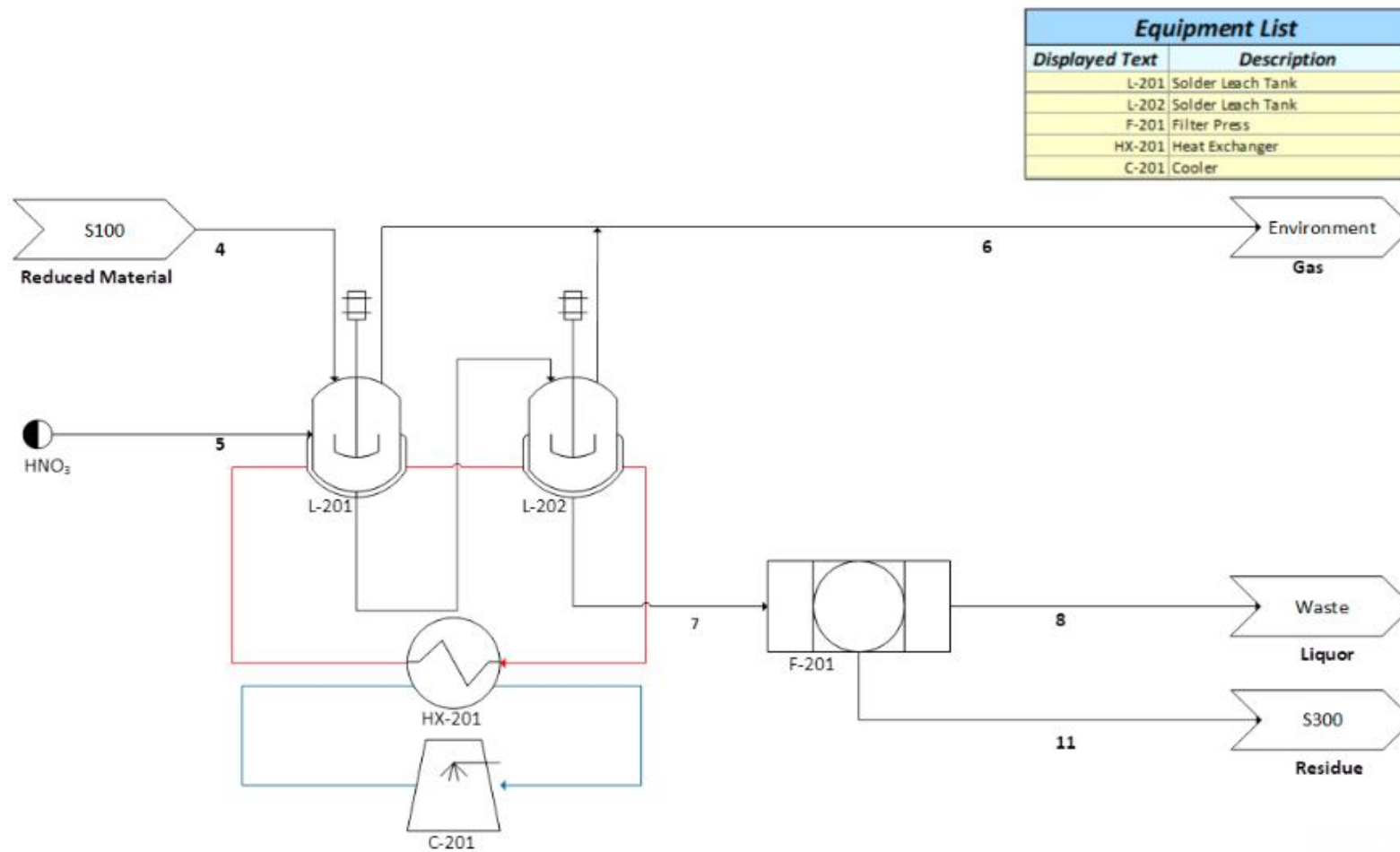
Figure 3-3: Nitric Acid Leach Process

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3.3.2   Energy

There are two major energy inputs in the solder removal process; leach tank agitation and circuit cooling. The leach tank agitation energy requirements were based on standard agitation equations as given by Hall, (2012). The formulas used are shown from Equation 3-2 to Equation 3-8:

Batch Volume $= \dfrac{3\pi T_{eq}}{4}$ **Equation 3-2**

Agitator Diameter (D) $= 0.4 \times T_{eq}$ **Equation 3-3**

Bulk Velocity (Vc) $= Scale\ of\ Agitation \times 6$ **Equation 3-4**

Pumping Rate (Q) $= \dfrac{V_c \pi T_{eq}2}{4}$ **Equation 3-5**

Pumping Number (N_q) $= \dfrac{Q}{ND^3}$ **Equation 3-6**

Reynolds Numbers (Re) $= \dfrac{D^2 N \rho}{\mu}$ **Equation 3-7**

Power (P) $= N_p \rho N^3 D^5$ **Equation 3-8**

The power number (N_p) is obtained from the Reynolds Agitator graphs (Perry, Green and Maloney, 1997). The impeller selected in all the leaching tanks is a square pitch 3 blade impeller, because it will create the ideal mixing, solid suspension and lowest energy consumption of the selected material under the selected operating conditions. The laminar regime is generally taken to occur when the Reynolds number is smaller than ten, and viscosity dominates in this regime. At high Reynolds number of turbulent operation (i.e., $Re > 10^4$), viscosity has little effect and the process is mainly controlled by inertial forces. In transitional regime, both viscous and inertial forces affect the process. The results obtained for the mixing energy requirements are shown in Table 3-3.

The reactions that occur in the leaching process in this circuit are highly exothermic, if left uncontrolled the increased operating temperature may affect the performance of the circuit. Therefore, the circuit's temperature is controlled at 25 $^{\circ}$C. This is done by employing evaporative

cooling towers and circulating the chilled water through a cooling jacket. The energy required for this section is can be estimated by the following equation:

$$Q = mc_p(T_{final} - T_{initial})$$

<div align="right">**Equation 3-9**</div>

HSC-Sim also provides the option to calculate the required cooling water with the use of controls. This is done by setting the initial and final temperatures for the leach tank and the temperature increase of the cooling water. The required cooling water is then calculated based on the total heat lost in the leach tank. The same approach can be used for heating. Controls were used to calculate all the cooling requirements and heating requirements for the entire recycling chain.

<div align="center">**Table 3-3: Nitric Acid Leach Mixing Energy Requirement Calculations**</div>

Parameter	Value	Units
Agitator Speed	2	rps
	120	rpm
Re	53823,62	
N_p	0,32	
T_{eq}	100	m^3
$D_{(tank)}$	4,00	m
D_{imp}	1,60	m
Motor Efficiency	68,00	%
Impeller Power	17,68	kWh/hr
Number of Tanks	3	
Total Power	53,04	kWh/hr

3.3.3 Assumptions

A summary of the assumptions made for the solder removal process are enumerated below:

- The solid liquid separation step is 100% i.e. no moisture is trapped in solid phase and no solid slippage to the liquid phase was assumed.
- 10% of the total heat energy is lost to the atmosphere.

<div align="center">56</div>

- All energy associated with ancillary equipment, i.e. pumps was ignored.

- Similar extent of reactions are assumed as reported by Rossouw, (2015).

- Operating conditions: 1.5M HNO_3, 25ºC and 1atm.

- Cooling water outlet temperature was taken to be 60ºC.

3.4   Copper Recovery

The sulphuric acid leaching process was employed to recover high purity copper for commercial value and to improve the performance of the downstream precious metal recovery circuit. The process designed in this section follows the general hydrometallurgical copper recovery processing routes as discussed in Davenport *et al.*, (2002). The major steps are enumerated below:

- Sulphuric acid leaching from pre-treated metal bearing body (traditionally ore body, in this case it is the PCB) for copper recovery.

- The pregnant solution is upgraded using solvent extraction.

- High grade solid copper is produced with electrowinning techniques.

3.4.1   Process

The copper recovery processes were developed by considering traditional copper hydrometallurgy recovery techniques, and previous studies that focused on copper recovery from PCB. The completed process flow sheet is shown in Figure 3-4.

3.4.1.1   *Copper Leaching*

The solid material from the solder removal circuit is fed into a leach reactor and reacted with sulphuric acid and hydrogen peroxide. Comparative studies showed that only 2% of copper is leached when the reaction is performed in the absence of an oxidising agent. The presence of an oxidising agent is thus critical for the extraction process (Deveci and Yazici, 2010). Following the experimental findings of Rossouw (2015), hydrogen peroxide is fed to the system continuously with sulphuric acid to leach the copper selectively from the PCB body. This is done to mitigate the reduction in concentration of hydrogen peroxide due to decomposition. The sulphuric acid was fed at 2.5M and the hydrogen peroxide at 30 wt%. The leaching process occurs at 25 ^{0}C and a retention time of 480min. No gold/precious metal dissolution occurs under these operating conditions. The reactions and the extent of reactions are summarised in Table 3-4 (Rossouw, 2015).

Equipment List

Displayed Text	L-301	L302	V-301	F-301	HX-301	C-301	V-302
Description	Copper Leach Tank	Copperr Leach Tank	pH Correction tank	Filter Press	Heat Exchanger	Cooler	Bleed/Raffinate Splitter Vessel
Displayed Text	SX-301	SX-301	HX-302	C-302	EW-301		
Description	Solvent Extraction System	Solvent Extraction System	Heat Exchanger	Cooler	Electrowinning System		

Figure 3-4: Copper Recovery Process

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Table 3-4: Sulphuric Acid Leach Reactions

Progress %	Reactants		Products	H kJ
0	$Pb+H_2SO_4(aq)$	=	$PbSO_4+H_2(g)$	-10,59
96,5	$Cu+H_2SO_4(aq) +H_2O_2(aq)$	=	$CuSO_4(aq) +2H_2O$	-315,68
18,4	$2Al+3H_2SO_4(aq) +3H_2O_2(aq)$	=	$Al_2(SO_4)_3(aq) +6H_2O$	-2204,76
16,3	$Fe+H_2SO_4(aq) +H_2O_2(aq)$	=	$FeSO_4(aq) +2H_2O$	-469,53
57,8	$Ni+H_2SO_4(aq) +H_2O_2(aq)$	=	$NiSO_4(aq) +2H_2O$	-429,78
93,4	$Zn+H_2SO_4(aq) +H_2O_2(aq)$	=	$ZnSO_4(aq) +2H_2O$	-518,82
8,5	$2Ag+H_2SO_4(aq) +H_2O_2(aq)$	=	$Ag_2SO_4(aq) +2H_2O$	-169,28
0,8	$Sn+H_2SO_4(aq) +H_2O_2(aq)$	=	$SnSO_4(aq) +2H_2O$	-392,54

3.4.1.2 pH Correction and Solid-Liquid Separation

The slurry from the leaching circuit is filtered and fed to a pH adjustment system. pH adjustment is controlled and managed with sodium hydroxide to produce a pH of 1.8 for the solvent extraction process. pH control of the PLS prior to SX circuit is imperative, since a variation of 0.5 in the pH can significantly influence the stripping efficiencies (Littlejohn and Dreisinger, 2007). When operating within a pH range of 1-2 copper is more soluble in the organic phase as shown in Equation 3-10. HX is the extractant and CuX_2 represents the copper-organic compound.

$$CuSO_4(aq) + 2HX(org) \rightarrow CuX_2(org) + H_2SO_4 (aq)$$ **Equation 3-10**
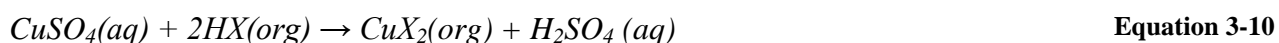
If the pH of the solution is below 1 the copper is more soluble in the aqueous phase as shown in Equation 3-11.

$$CuX_2(org) + H_2SO_4 (aq) \rightarrow CuSO_4(aq) + 2HX(org)$$ **Equation 3-11**
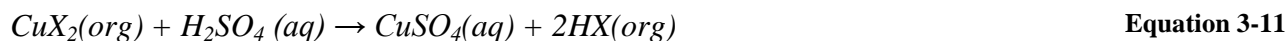
 The optimum pH was determined experimentally to be 2, but iron co-extracting is observed (Beukes and Badenhorst, 2009). The selection of the pH at 1.8 was done by considering the effect of pH of a high copper load PLS study. This pH yielded the best copper recovery in a solvent extraction process (Kafumbila, 2017). Solid and liquid phases are separated with filter press unit. The solids are fed into the subsequent precious metal recovery process.

3.4.1.3 Solvent Extraction

There are various factors that influence the efficiency of the solvent extraction process, with the PLS composition being the most important. This has an influence on the organic and aqueous (O/A) ratio selection, process kinetics and loading capacities. The entire solvent extraction process was modelled as a single process unit (black box) and not individual extraction and stripping units. The modelled area is shown in Figure 3-5.

Industrial SX extractant LIX 984N® was used for the copper extraction process. This extractant is a popular extractant in copper extraction processes. LIX984N® is a hydroxime derivative and is a 1:1 (v) blend of 2-hydroxy-5-nonyl-acetophenoneoxim and 5-dodecylsalicylaldoxime. This extractant has strong copper extraction properties and yields a good physical operational performance. The preferential extraction order under the correct operating conditions are (Asghari *et al.*, 2009):

Cu (II) > Fe (III) > Ga (III) > Ni (II) >In(III) > Co(II) > Zn(II) > Pb(II)
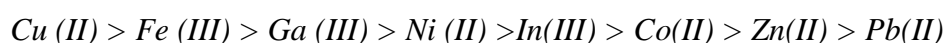
The selection was made considering all of the above mentioned factors and the stability of this extractant at various operating conditions as well the ubiquitous industrial applications with kerosene as the diluent.

The solvent extraction process was designed to operate in an organic continuous operation. This will assist in minimising the entrainment within the continuous phase. This mode of operation is selected because the nature of the PLS makes the control of the organic phase more critical, and it will minimise the organic contamination of the raffinate and the advanced electrolyte solutions. Organic continuous operation is also the most common mode for copper recovery, because the phase separation kinetics are faster (Schlesinger *et al.*, 2011b).

Copper extraction from the PLS with solvent extraction followed the common solvent extraction modelling equations. The performance of the organic phase is traditionally described by the net transfer rate of the copper per unit of extractant. This is calculated with Equation 3-12 (du Preez and Taute, 2015):

$$NT_{organic} = 100 \times \frac{Cu(organic)_{LO} - Cu(organic)_{SO}}{V_{extract}}$$

Equation 3-12

Where,

$NT_{organic}$ = organic net transfer rate

$V_{extract}$ = extractant concentration

The net transfer rate in typical copper operations is generally 0.25 g/ℓ. This value was only used as a guideline because the PLS copper concentration is significantly higher at 74.29 g/ℓ when compared to typical PLS copper concentrations which are typically less than 10 g/ℓ. At these concentrations direct electrowinning is an option, but due to the potential presence of unwanted metals in the PLS, the SX is required to act as a purification process as well as a metal upgrading process. The extractant concentration was assumed to be a maximum value of 32 vol% due to the high copper concentration in PLS. The theoretical rule of thumb is 4 vol% of extractant for 1 g/ℓ in the PLS. (Schlesinger *et al.*, 2011b). Utilising this information and the known parameters the O/A ratio is calculated with (Kafumbila, 2017).

$$OA = \frac{Cu(aq)_{PLS} - Cu(aq)_{raffinate}}{Cu(organic)_{LO} - Cu(organic)_{SO}}$$

Equation 3-13

This was calculated to be 4.64 with the assumption that the percentage copper extracted is 70%. The copper extraction might be higher, but this will have to be confirmed with experimental test work and the development of a McCabe-Thiele diagram.

The advance electrolyte (AE) and the spent electrolyte (SE) copper concentrations were assumed to be 35 g/ℓ and 45 g/ℓ respectively. Also, the sulphuric acid concentration in the SE is assumed to be 180 g/ℓ. This was based on typical industrial values. The advanced electrolyte is typically 45-50 g/ℓ and the spent electrolyte is 30-35 g/ℓ (Schlesinger *et al.*, 2011a).

In processes where copper is extracted from a PLS with a high copper concentration the acidity of the process becomes a concern. The recovery of copper with SX-EW technology is in essence a sulphuric acid production process. The solvent extraction reaction displayed in Equation 2-15 shows that the extraction of 1 g/ℓ of copper increases the sulphuric acid load in the raffinate by 1.55 g/ℓ. The increase in the system acidity inhibits the extraction process. In this scenario the extractant concentration can be increased, but this will yield a highly viscous organic phase which will lead to poor phase separation performance. The most economically feasible process flow sheets showed that in a process where the PLS copper concentration is high, a portion of the raffinate has to be bled to maintain the required water and pH balance of the circuit. The raffinate that is fed back to

the system reduces the leach circuit's acid (H_2SO_4) requirements. Copper present in the bleed stream can be recovered by smaller downstream SX process units. This has been done in various industrial processes in Pasminco Metals and Western Metals' Mt. Gordon Operation (Molnar and Verbaan, 2003). For this process design a similar approach was taken and the bleed raffinate split was simulated to yield a **57/43** split. 57% of the raffinate is returns to the leaching circuit and the remainder is treated in waste water treatment processes.
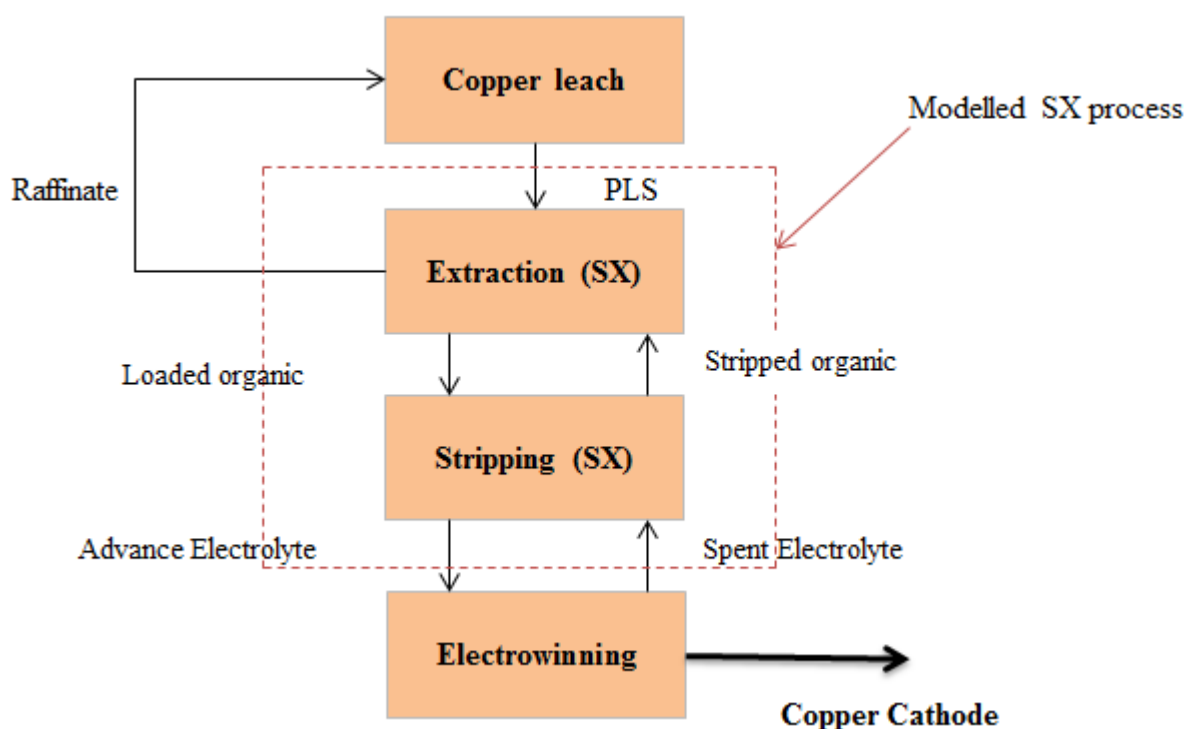
Figure 3-5: Modelled Solvent Extraction Block Flow

3.4.1.4   Copper Electrowinning

With the assumption of perfect stripping (no impurities), no washing stage is required before the AEi s fed into the EW process unit. The advance electrolyte from the SX circuit is pre-heated by a heat exchanging unit to 45^0C before entering the EW process. This is done because the temperature affects the physio-chemical properties of the electrolyte and the mass transfer dynamics of the copper within the process. The current efficiency of the process increases when the AE has a high copper concentration and a low metal impurity concentration (Ehsani, Yazıcı and Deveci, 2016). The operational temperature of 45^0C was based on industrial operational temperature which yielded a lower current density (Kafumbila, 2017).

The cathodes are generally made from conductive stainless steel (inert) blank material and the anodes are lead based alloys. The AE is subjected to a direct current (DC) which transmits through the AE between the cathode and anodes. During this process acid mist formation may occur on the surface of the cell. It was assumed that the process designed will utilise surfactants or mechanical tools to prevent this from occurring in the process. Mechanical tools are normally in the form of floating inert material on the cell liquid surface or covering the cell in a hood (Liow *et al.*, 2007).

The morphology of the cathodes was not considered for the process. Standard industrial operating procedures were assumed in terms of cathode smoothing agents. This is done in the form of glue and guar-additives to ensure smooth copper plating and to prevent any entrapment of electrolyte on the cathode surface during the electroplating process. Cobalt sulphate is also added to prevent anodic corrosion (Robinson *et al.*, 2012).

The process design utilised typical EW circuit extent of reaction of 30%. The overall process for copper ion reduction to metal is given by Equation 3-14 (Osman *et al.*, 2013):

$$[Cu^{2+} SO_4^{2-}] + H_2O \rightarrow Cu + [2H^{1+} SO_4^{2-}] + 0.5O_2 \qquad \textbf{Equation 3-14}$$
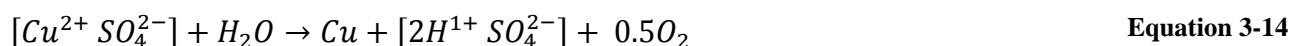
3.4.2   Energy

Energy inputs are required for the mechanically agitated leach tanks, stage pumping and agitation for the extraction stage as well as the electrowinning process. The same agitator design philosophy as discussed in section 3.3.2 was applied for the sulphuric leach agitator design. The results are summarised in Table 3-5.

Effective agitation between the aqueous and liquid phase is critical for effective solvent extraction design. Ineffective mixing can lead to poor extraction and valuable metal losses. A well designed mixer creates thorough organic and aqueous phase dispersion which assists in the metal mass transfer between the two phases. The physical design should allow for a narrow drop size to prevent air entrainment within the mixing chambers. Operating the system at a low mixer impeller tip speeds of less than 350 m/min also assist with the reduction in entrainment. At these operating conditions and a contact time of 2-3min the system is operated at a specific energy of 0.01 kWh/m^3. This was assumed to be appropriate for the copper extraction from PCBs process (Schlesinger *et al.*, 2011b).

Table 3-5: Sulphuric Acid Leach Mixing Energy Requirements

Parameter	Value	Units
Agitator	2	rps
	120	rpm
Re	28399,08	
N_p	0,32	
T_{eq}	100	m^3
$D_{(tank)}$	4	m
D_{imp}	1,6	m
Motor Efficiency	68	%
Impeller Power	21,90	kWh/hr
Number of Tanks	3	
Total Power	**65,69**	**kWh/hr**

In solvent extraction viscous material is pumped between the chambers. The pumping cost associated with these activities may contribute significantly to the overall unit process's power consumption. The specific energy based on published data of 0.02 kWh/m³ was used for the total pump power consumption (Kordosky, Sudderth, & & Virnig, 1999).

The energy related to the electrowinning input is predominantly related to the direct current applied to the electrolytic solution to drive the electroplating reaction for the production of copper on the cathodes.

$$Energy\ Consumption = \frac{V_l \times F}{\left(\frac{A}{Z}\right) \times 3600\ \times CE}$$

Equation 3-15

Where,

Energy Consumption in kWh/kg

V_l	=	Applied voltage (V)
A	=	Relative atomic mass (g/mole)
F	=	Faraday's constant (96485 C/mole)
CE	=	Current Efficiency (Dimensionless)
Z	=	Valence (dimensionless)

The current efficiency (CE) was assumed as 90% for the design. Typical copper EW unit processes achieve current efficiencies of 85-95% (Robinson *et al.*, 2013). The actual CE for the process designed may be higher and more aligned with the higher ranges seen in industry. The theoretical electrical potential required by an EW process is typically 2.0 V. In industrial applications the required electrical potential is 2.1 V. This value was used for the process design (Ehsani, Yazıcı and Deveci, 2016). Based on thus the total energy input required for the EW process was thus determined.

Similar to the solder leaching process, the reactions in the copper leach are highly exothermic. The same methodology as disused in section 3.3.3 was applied to determine the energy required for cooling.

3.4.3 Assumptions

The following assumptions were made in the copper recovery process:

- The solid liquid separation step yields perfect separation- no moisture is trapped in the solid phase and no solid slippage occurs to the liquid phase.
- 10% of the heat energy is lost to the atmosphere.
- All reagents are supplied to the system in excess of 25% of the stoichiometric requirements.
- The neutralisation process i.e. pH adjustment step, loses all of the heat generated in the exothermic reaction to the atmosphere.
- No crud formation in solvent extraction process unit.
- No physical entrainment in solvent extraction process unit.
- Operating conditions: 2.5M H_2SO_4, 30wt. % H_2O_2, 25ºC and 1atm.
- Reaction time is 8hrs.
- 50wt. % NaOH is used for neutralisations.
- pH of PLS is adjusted to 1.8.
- Cooling water outlet temperature was taken to be 60ºC
- 70% extraction efficiency and 100% efficiency for stripping in SX.
- Net transfer rate = 0.35 g/ℓ
- Extractant concentration is 32 vol. % and kerosene as diluent.
- The AE and SE copper concentrations were assumed to be 35 g/ℓ and 45 g/ℓ respectively.
- Sulphuric acid in SE is 180 g/ℓ.
- Electrowinning temperature is 45ºC and extent of reaction is 30%.

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- No acid mist formation.

- Operating conditions for EW: CE was assumed as 90%, overall potential is 2V, 45ºC and extent of reaction is 30%.

3.5   Gold Recovery

The following section focuses on the recovery of precious metals (PMs). The recovery of PMs has the highest revenue potential, but is also the most complex section of the process plant.

3.5.1   Process

The process developed for the gold recovery process deviates from the typical gold recovery flow sheet. This is because of the nature and mineralogical composition of the feed into the circuit. The process is displayed in Figure 3-6.

3.5.1.1   Nitric acid wash

The solid material from the copper recovery circuit is fed into an acid washing circuit. This is done because of the base and ferrous metal load that is still present in the feed to the PM recovery circuit. The feed analysis is shown in Table 3-6.

Table 3-6: Precious Metals Section Feed Concentration

Metal	Load (kg/h)	Metal Concentration (wt %)
Cu	25,33	11,87%
Al	78,89	36,96%
Fe	18,89	8,85%
Sn	74,13	34,73%
Ni	4,99	2,34%
Zn	6,30	2,95%
Pb	2,71	1,27%
Au	0,58	0,27%
Ag	1,63	0,76%
Total	**213,45**	**100,00%**

The presence of base metals reduces the free cyanide concentration in the leaching process, hence cyanide lixiviant consumption increases and gold recovery decreases. The following complexes can potentially form when the feed in its current form is fed to the leaching circuit: $Fe(CN)_6^{4-}$, $Ni(CN)_4^{2-}$, $Zn(CN)_4^{2-}$, $Ag(CN)_2^{-}$, $Cu(CN)_2^{-}$, $Cu(CN)_3^{2-}$ and $Cu(CN)_4^{3-}$. The detail of these side potential side reactions are shown in section 2.7.4.1 (Rees and Van Deventer, 1999).

Copper is notorious for creating the most problems associated with gold recovery process. When cyanide is used as the lixiviant the maximum copper load is 1 wt.% (Oraby and Eksteen, 2016b). From Table 3-6 it is evident that the copper concentration of 11.87 wt. % exceeds the allowable limit. It is thus important to include an additional base metal removal step. This will protect the PM circuit from base metal contamination, improve the gold recovery and reduce the lixiviant chemical consumption. It was assumed that this section removes 100% of the base metals and that no precious metals will be co-extracted in the circuit. Nitric acid was selected as the extraction medium and was employed at a concentration of 55wt. %. The reactions in the process are exothermic and the temperature will be managed at 25 ^{0}C with cooling systems. The reactions are shown in Table 3-7.

Table 3-7: Base Metal Washing Circuit Reactions

Progress %	Reactants		Products	H kJ
100	$Pb+4HNO_3(aq)$	=	$Pb(NO_3)_2(aq) +2H_2O+2NO_2(g)$	-161,92
100	$Ni+4HNO_3(aq)$	=	$Ni(NO_3)_2(aq) +2H_2O+2NO_2(g)$	-214,22
100	$Zn+4HNO_3(aq)$	=	$Zn(NO_3)_2(aq) +2H_2O+2NO_2(g)$	-314,22
100	$Ag+2HNO_3(aq)$	=	$Ag NO_3(aq) +H_2O+NO_2(g)$	29,71
100	$Al+6HNO_3(aq)$	=	$Al(NO_3)_3(aq) +3H_2O+3NO_2(g)$	-773,62
100	$Fe+6HNO_3(aq)$	=	$Fe(NO_3)_3(aq) +3H_2O+3NO_2(g)$	-289,11
100	$Cu+4HNO_3(aq)$	=	$Cu(NO_3)_2(aq) +2H_2O+2NO_2(g)$	-95,40
100	$Sn+4HNO_3(aq)$	=	$SnO_2 \cdot H_2O+4NO_2(g)+H_2O$	606,26

3.5.1.2 Cyanidation

After solid-liquid separation, the pH of slurry is adjusted to 11 prior to cyanidation with hydrated lime $Ca(OH)_2$ and sodium hydroxide (NaOH). In the base metal washing process metastannic acid

($SnO_2 \cdot H_2O$) was formed. Metastannic acid is an amphoteric molecule and can thus be dissolved by acids or base mediums. It was assumed that it will first react with the caustic from the adsorption circuit and then with the hydrated lime as shown Table 3-8 . Hydrated lime was selected for the pH correction step in favour of sodium hydroxide, because calcium ions are more favourable cations to have available for gold adsorption according to the relation given below (Snyders, 2015).

$$Ca^{2+} > Mg^{2+} > K^+ > Na^+ > H^+.$$

Table 3-8: Gold Leaching- pH correction reactions

Progress %	Reactants		Products
100	$Ca(OH)_2$	=	$Ca(OH)_2$(aq)
100	$2NaOH(aq) + SnO_2 \cdot H_2O(s)$	=	$Na_2SnO_3(aq) + 2H_2O$
100	$SnO_2 \cdot H_2O + Ca(OH)_2(aq)$	=	$CaSnO_3(s) + 2H_2O$

Sodium cyanide, NaCN is added at 120 mg/ℓ and at an excess of 25% to the pH corrected slurry before cyanidation. In literature it has been reported that the gold dissolution rate is mass transport controlled (Marsden, 1987; Nicol and Mbatha, 1998). Therefore, the reactants (oxygen and cyanide ions) through a fluid film around the solid PCB residue become the controlling factors in cyanidation. In practice it is easier to maintain high concentrations of cyanide ions but not high concentrations of dissolved oxygen (Jara and Bustos, 1992). At the selected cyanide concentration of 120 mg/ℓ and oxygen in air which has oxygen concentration 8 mg/ℓ in water, the dissolved oxygen in the reaction environment becomes the rate limiting element. This operational method yields a CN^-/O_2 molar concentration ratio of 7.96 which is higher than the limiting ratio of 6 in order to achieve optimum gold dissolution rates (Jara and Bustos, 1992). The reaction of the solid gold in the PCB matrix with sodium cyanide and oxygen is shown by Elsner's equation in Table 3-9.

Table 3-9: Gold Leaching Reactions

Progress %	Reactants		Products	H kJ
98	$4Au + 8NaCN(aq) + O_2(g) + 2H_2O$	=	$4NaAu(CN)_2(aq) + 4NaOH(aq)$	-583,25
100	$2NaAu(CN)_2(aq) + Ca(OH)_2(aq)$	=	$Ca(Au(CN)_2)_2(aq) + 2NaOH(aq)$	59,04

Equipment List							
Displayed Text	L-401	L-402	F-401	F-402	V-401	V-402	V-403
Description	PM Leach Tank	PM Leach Tank	se Metal Wash Filter Pr	Leach Filter Press	Base Metal Wash	Adjustme	Adsorption
Displayed Text	V-404	V-405	V-406	V-407	EW-401	K-401	A-401
Description	Cyanide Recycle Tank	Acid Wash	Elution Column	EW Conditioning	Electrowinning System	Kiln	Air Cooler
Displayed Text	HX-401	HX-402	HX-403	HX-404	B-401		
Description	Acid Heater	Rinse Water Heater	NaCN/NaOH Heater	Eluant Heater	Boiler		

Figure 3-6: Precious metal recovery process (a)

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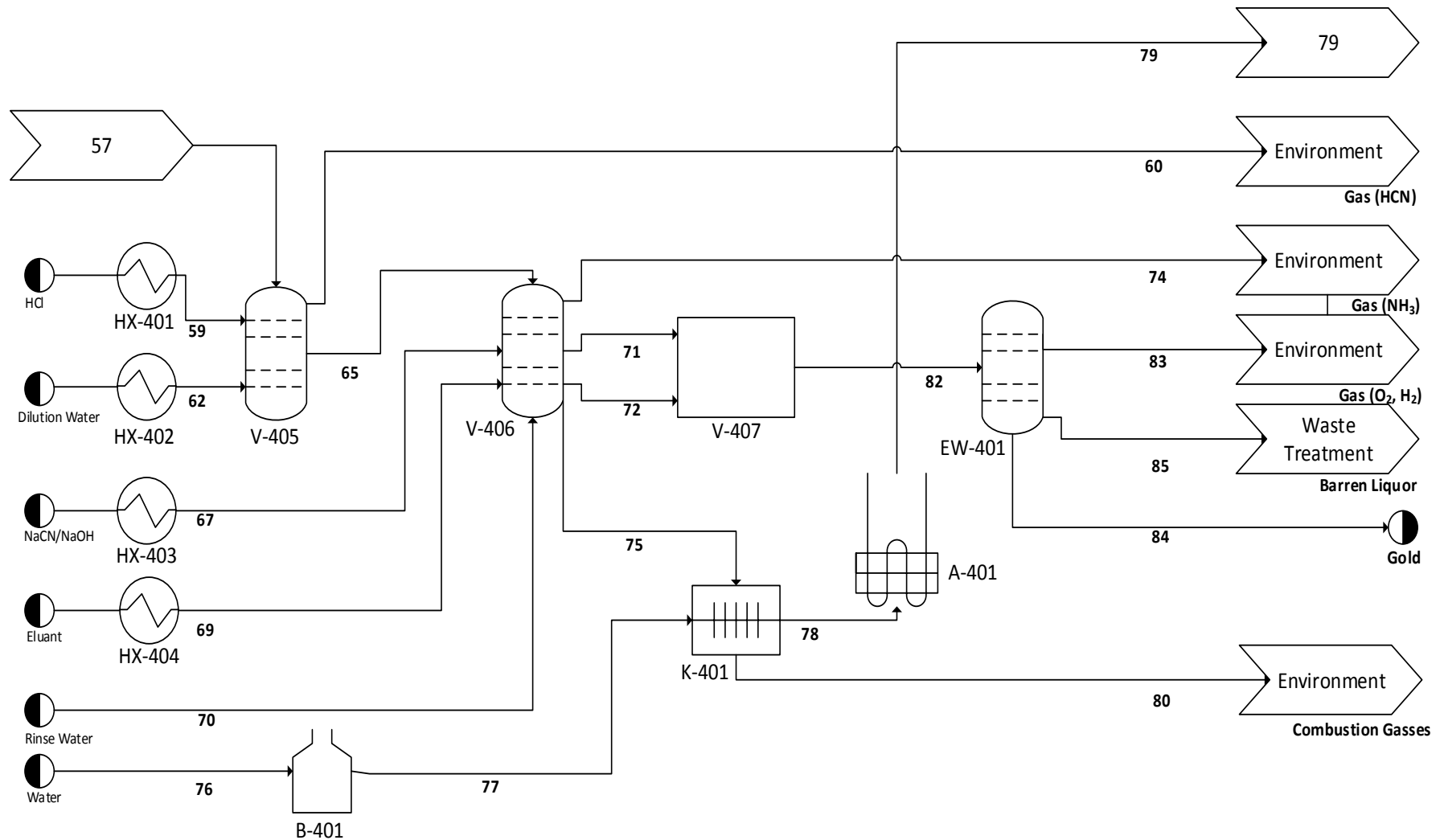
Figure 3-7: Precious metal recovery process (b)

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3.5.1.3   Carbon adsorption

The product stream from the gold leaching reactors contains 13.57 mg/ℓ free cyanide in the solution. The slurry from the leach tank is sent to a solid-liquid separation process where perfect separation was assumed. From this process the liquor is pumped to the carbon adsorption process. The adsorption process selected is the Anglo American Research Laboratories (AARL) CIP process. Activated carbon with a high surface area and the gold complex and cation, Ca^{2+}, is adsorbed as a neutral ionic bond to the carbon surface via electrostatic forces the reduction of the gold cyanide complex on the carbon surface. Cyanide losses within the adsorption process are a possibility; hence the losses attributed to the following were ignored in the process design:

- Leaching of gold may occur during adsorption. However this rate is slower than the adsorption rate and is thus considered negligible.

- Ammonia   production according to the following reaction, which is catalysed by activated carbon is not considered:

$$CN^- + \frac{1}{2}O_2 \rightarrow CNO^- + 2H_2O \rightarrow NH_4^+ + CO_3^{2-} \qquad \textbf{Equation 3-16}$$
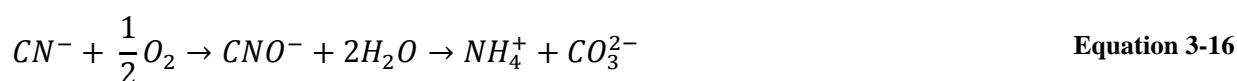
- Cyanide decomposes on contact with activated carbon at elevated temperatures, considering that the adsorption process is exothermic, increase in system temperature was assumed to have a negligible effect on cyanide decomposition.

Carbon losses due to attrition within the process were assumed to be negligible. Each carbon tank/reaction vessel is operated with a residence time of 60min and the carbon concentration is 25 g carbon/ℓ pulp which is industry standard. Each carbon tank was calculated to have a 25m^3 system volume. All aurocyanide is assumed to be adsorbed within the system and the system is operated under continuous flow operational mode. The following carbon composition was used in the modelling and process simulations (Mohd Iqbaldin *et al.*, 2013).

Table 3-10: Activated carbon composition

Element	Composition (wt. %)
Carbon	80,13
Hydrogen	2,36
Oxygen	16,35
Sulphur	0,06
Nitrogen	1,1

3.5.1.4 Hydrochloric Acid Wash

Following the carbon adsorption process the carbon is subjected to a hot acid wash. Hydrochloric acid can be applied as a hot or cold stream. Dilute hydrochloric acid soak, followed by rinse water, will remove impurities like zinc and calcium when cold and additional nickel, iron and silica when hot (60°C -90°C), but will not elute gold, copper and silver from the activated carbon (Snyders, 2015). The designed process utilised a hot hydrochloric acid stream at 90℃. The use of hot acid also makes it possible to use water with a higher salt load (worse quality water) during carbon de-adsorption (Snyders, 2015). This enables operating the plant with a close water balance. The key reaction considered in the acid wash process is described in Table 3-11.

Table 3-11: Acid Wash Reactions

Progress %	Reactants		Products	H kJ
100	$Ca(Au(CN)_2)_2(aq) +2HCl(aq)$	=	$2HCN(g)+2AuCN+CaCl_2(aq)$	-267,17

3.5.1.5 Elution

The gold elution is a desorption process and is a complete reversal of the carbon adsorption process. In this process step the adsorbed gold cyanide ions is released from the carbon surface. This is achieved by introducing excess sodium ions in the reaction environment. The excess sodium ions exchanges with the calcium in the system and the gold on carbon surface is transformed to $Na(Au(CN)2)$. The sodium bond with the carbon surface is weaker compared to the calcium gold complex bond. The instability is increased by operating the system at an elevated temperature of 110C. At the elevated temperature the bond breaks into the Na+ and Au(CN)2- ions. This is

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released by the carbon. If gold is still present in the calcium complex form additional cyanide is required to transform it into a complex that can be eluted. Additional cyanide is added in the designed process to meet this possible demand. The key operating parameters and operating schedule that were used in the process design are shown in Table 3-12 and Table 3-13 .

Table 3-12: Gold Elution Key Design Parameters

Parameter	Value	Units
NaOH	2%	mass%
NaCN	3%	mass%
Temp of elution	110	C
Pressure	2,01	bar
Temp of pre-soak	110	C
flow rate H2O	2	BV/hr

Table 3-13: Elution Operating Schedule

Operation	Stream/Process	Cycle Time(min)
Load Column	Carbon	90
HCl Wash	3% HCl	20
Rinse	Potable Water	90
Pre-Heat	Potable water	30
Pre-Soak	3%NaCN & 1% NaOH	30
Elution	Potable Water	180
Cooling	Potable Water	30
Carbon Transfer	Transfer Water	30

During the elution process the formation of ammonia is produced in one of the side reactions. This is driven largely by the elevated operating temperature and in the presence of activated carbon (Adams, 1990). Adams, (1990) reported that the cyanide consumed in the elution stage is approximately 10 to 20 per cent of the cyanide consumed during cyanide leaching. The extent of the conversion of sodium cyanide to ammonia was taken to be 10% of the cyanide consumed in the cyanidation stage. The main reactions considered for the elution is summarised in Table 3-14. The product stream for the process is sent to a pH conditioning vessel prior to electrowinning.

Table 3-14: Gold Elution Reactions

Progress %	Reactants		Products	H kJ
0,017	NaCN(aq) +3H$_2$O	=	NH$_3$(g)+CO$_2$(g)+H$_2$(g)+NaOH(aq)	37,68
100	AuCN+NaCN(aq)	=	NaAu(CN)$_2$(aq)	91,59

3.5.1.6 Carbon Regeneration

The spent solution from the elution process was assumed to be treated in a waste treatment plant and the carbon is sent to the carbon regeneration unit. The regeneration process occurs in a rotatory kiln where the adsorbed organics is removed from the carbon by applying thermal energy. During the process steam is produced within the boiler and sent to the kiln. At elevated temperatures, the Van Der Waals forces are broken which enables the decomposition of organics and the removal of volatile components as vapour. The kiln is operated 600 ^{0}C. The reactivated carbon is air cooled before it is re-used in the adsorption process. It is assumed that 6% of the carbon will be lost as carbon dioxide (Van Wyk, 2014) . The key reactions within this unit process is summarised in Table 3-15.

Table 3-15: Carbon Regeneration Unit Reactions

Progress %	Reactants		Products	H kJ
0	H$_2$O	=	H$_2$O(g)	44,00
6	C+2H$_2$O(g)	=	CO$_2$(g)+2H$_2$(g)	90,15

3.5.1.7 Gold Electrowinning

The electrowinning process unit is similar to the operation of the unit explained in 3.4. The pH of the gold cyanide solution is first corrected to 12 with sodium hydroxide before it sent to the electrowinning circuit. In the gold electrowinning process a current is applied to the bath and 99% of the gold in solution is assumed to deposit onto the surface of the steel wool cathodes. High gold recoveries in the electrowinning stage are reported by Norgate and Haque, (2012). The reaction is shown in Table 3-16. The solution from this unit process is sent to waste.

Table 3-16: Gold Electrowinning Reactions

Progress %	Reactants		Products	H kJ
99	$2NaAu(CN)_2(aq) + 2NaOH(aq)$	=	$2Au + H_2(g) + O_2(g) + 4NaCN(aq)$	577,56

3.5.1 Energy

Electricity is required for the mechanically agitated leach tanks, CIP process, cooling, steam generation in the boiler and the electrowinning process. The same agitator design philosophy as discussed in section 3.3.2 was used for the gold leach agitator design. The results are summarised in Table 3-17. The energy related to the adsorption and elution circuit involves mixing and inter-stage pumping of the pulp and solution. A specific energy of **5.8 kWh/ton** was assumed for this section of the gold adsorption process (Norgate and Haque, 2012). The energy requirements for the gold electrowinning was calculated using Equation 3-17.

Table 3-17: Gold Leach Agitator Design

Parameter	Value	Units
Agitator	2	rps
	120	rpm
Re	51189,76	Re
N_p	0,32	
T_{eq}	100	m^3
$D_{(tank)}$	4	m
D_{imp}	1,6	m
Motor Efficiency	68	%
Impeller Power	39,47	kWh/hr
Number of Tanks	6	
Total Power	**236,81**	**kWh/hr**

3.5.2   Assumptions

The following assumptions were made for the gold recovery process:

- Solid- liquid separation is 100% efficient -no moisture trapped in solid phase and no solid slippage to the liquid phase.

- 10% of the heat energy is lost to the atmosphere.

- All energy associated with ancillary equipment, i.e. pumps were ignored.

- It was assumed that nitric acid wash removes 100% of the base metals and that no precious metals will be co-extracted in the circuit.

- NaCN concentration is 120 mg/ℓ and fed in excess of 25%.

- The gold complex is adsorbed as a neutral component as $Ca(Au(CN)_2)_2$.

- Leaching of gold may occur during adsorption is considered negligible.

- Ammonia production catalysed by activated carbon is not considered.

- Cyanide decomposes on contact with activated carbon at elevated temperatures, (adsorption process is exothermic). The increase in system temperature was assumed to have a negligible effect on cyanide decomposition.

- Carbon losses due to attrition within the process were assumed to be negligible.

- 6% of the carbon will be lost as carbon dioxide during carbon regeneration.

- 99% of the gold in solution is assumed to deposit on cathodes.

- Specific energy of 5.8 kWh/ton was assumed for the adsorption unit.

A summary of all the assumption made for the process design are given in Appendix C.

4. PROCESS MODELLING AND SIMULATIONS

The tools that were used in this study to evaluate the thermodynamic and environmental performance of the hydrometallurgical process were the HSC-Sim^{TM} and GaBi software packages. In this section the purpose of each tool are describe as well as how it was used to meet the project objectives.

4.1   HSC-Sim ^{TM}

4.1.1   Process simulation

HSC is a thermodynamic calculation program developed by Outotec. Traditionally it was first named HSC Chemistry which is designed to only model and simulate independent chemical reactions and process units. HSC-Sim^{TM}, an extension to HSC uses the basis of HSC Chemistry to model and simulate a complete flowsheet made up of several process units and streams. The flowsheet(s) can be constructed from three unit operation modes: Reactions (Hydro), Distribution (Pyro) and Particle (Mineral processing) (HSC 8$^{®}$, Manual).

The Reactions (Hydro) mode calculates outputs based on the chemical reactions that occur in process units, whereas in the Distribution (Pyro) mode output species are produced based on the elemental distributions. The distribution can either be manually defined or wizards can be used. The Particle (Mineral processing) mode is mainly used to model processes such as grinding, crushing, flotation etc. where the main focus is the mechanical and statistical properties of the process flows (HSC 8$^{®}$, Manual).

Considering that all the process units except for the comminution stage are principally driven by chemical reactions, the Hydro mode was used to construct the recycling process chain. Due to a lack of information of the size distribution and mass distribution after each size reduction step and also how these size fraction change after each leaching step, complete separation of the WPCBs was assumed. The liberation results that were reported in of Table 2-5 was not used because the distrubution of each metal for each size fraction are not clear. The uncertainty of the metal distribution of the size fraction will increase the uncertainty of the exergy values after each leaching step, due to diffiulty in determing the % distrubution of which liberated or non-linerated metals are attacked during leaching. The dust fraction was calculated from literature as discussed in section 3.2. The assumptions that were presented in Chapter 3 in the process considerations were used to simulate the complete process flow diagram as presented in Figure 4-1 to

Figure   4-55.
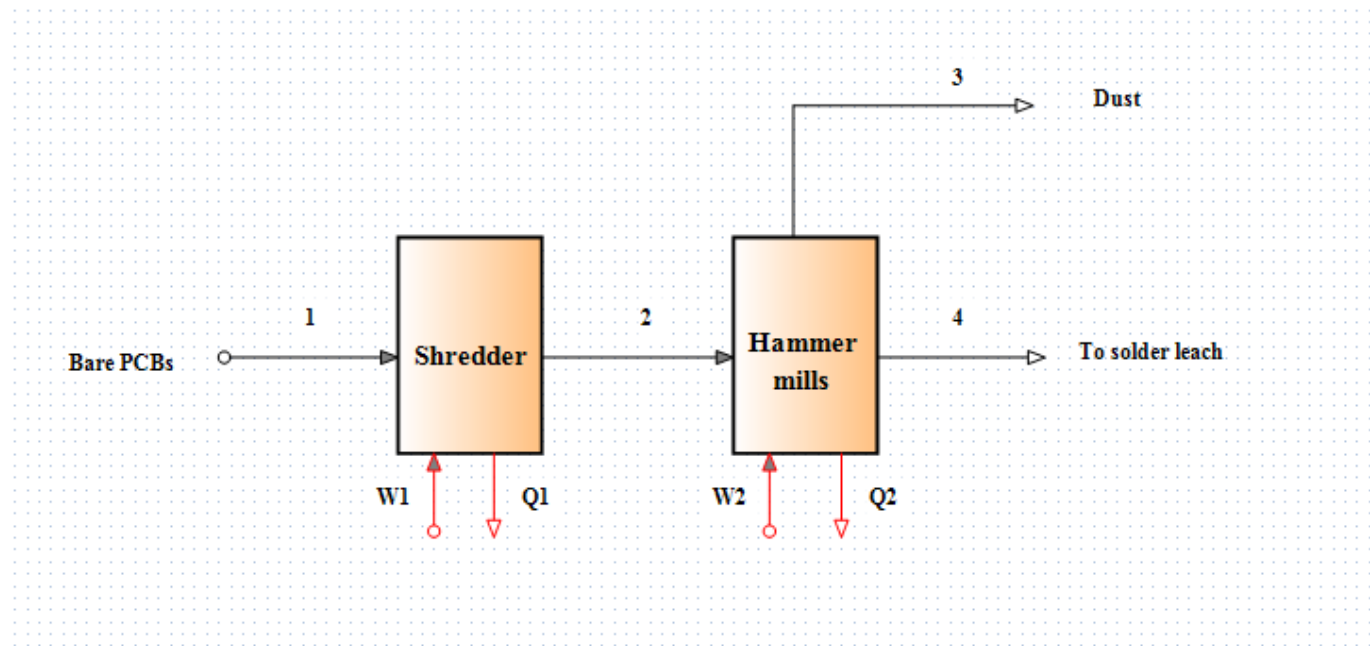
Figure 4-1: HSC Chemistry- Comminution Process Simulation
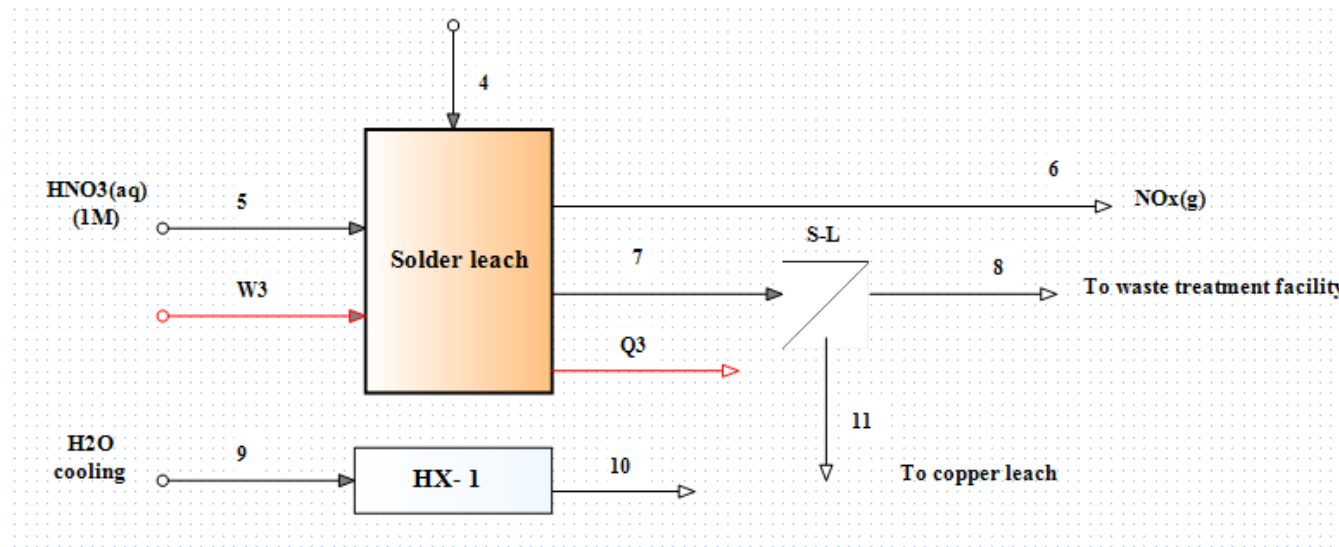
Figure 4-2: HSC-Sim - Solder Leach Simulation
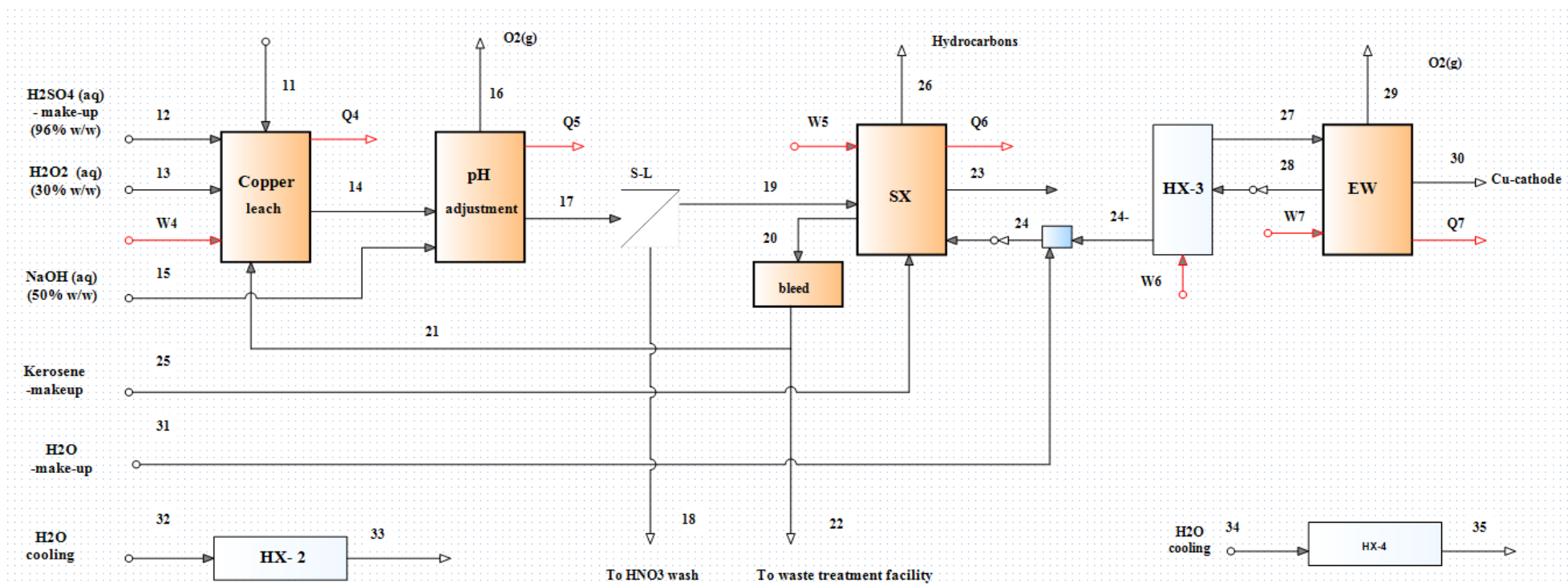
Figure 4-3: HSC-Sim- Copper Recovery Simulation
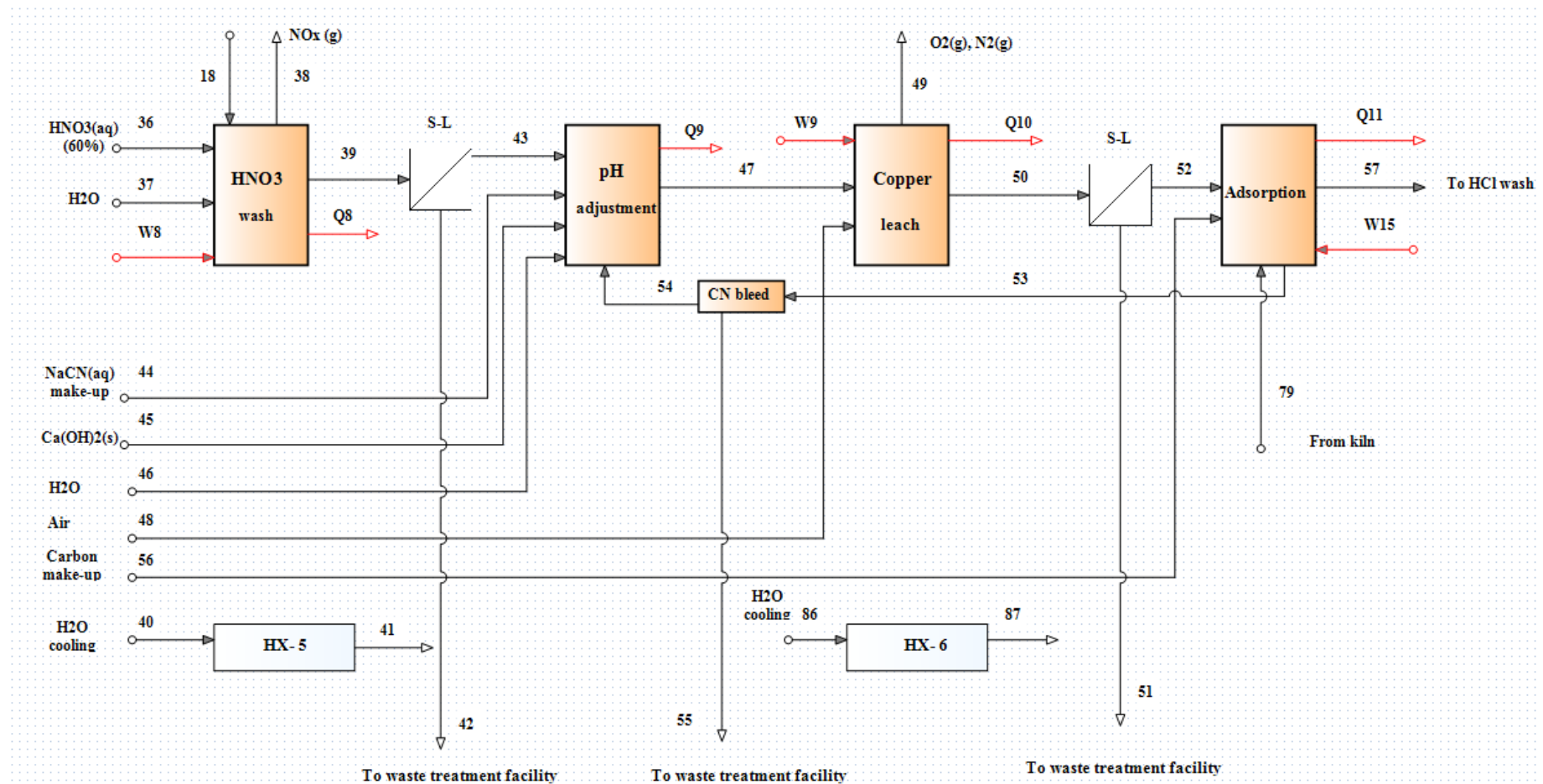
Figure 4-4: HSC-Sim - Gold Recovery Simulation (a)

81
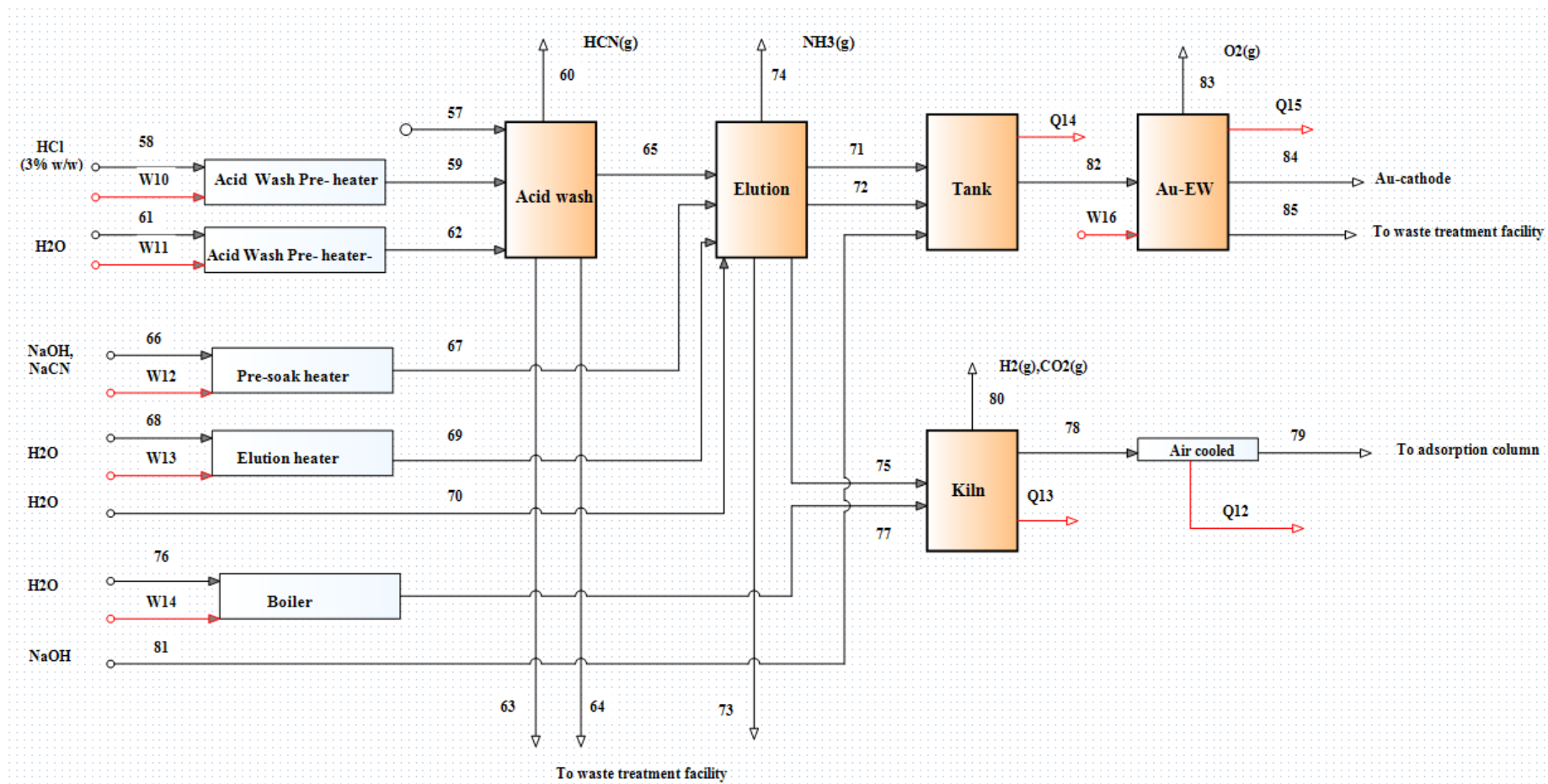
Figure 4-5: HSC-Sim- Gold Recovery Simulation (b)

4.1.1   Exergy and LCA in HSC-Sim

The HSC-Sim™ software offers extended functionalities such as the calculation of exergy values for each process stream in the developed flowsheet. It also enables the environmental assessment of the completed process or individual process units by converting each process stream to LCA-equivalent streams which can be directly imported to life cycle assessment software such as GaBi. Essentially the Life Cycle Inventory (LCI), the second phase of a life cycle study is created. The impacts of these flows i.e. the Life Cycle Impact Assessment (LCIA) can subsequently be performed by the GaBi software. The advantage of linking the HSC-Sim™ and computer based LCA tool is that the environmental performance of specific processes can be quantified from closed mass and energy balances. This eliminates the uncertainty that is often associated with the use of LCA databases that are based on average data.

As mentioned HSC- Sim™ automatically calculates the exergy values for each substance. The exergy values of each stream in Figures 4-1 to 4-6 are presented in Appendix A. This values where used to set up the exergy balances. HSC- Sim™ did not contain the standard chemical exergies of the following substances: kerosene, hydrocarbons due to the volatility of kerosene, activated carbon from coconut shells and were calculated using both literature data and the equation presented in section 2. The calculation of each of the aforementioned substances is demonstrated in Appendix B. The exergy of an aqueous substance in a stable and a completely dissociated state are different (Wall, 2009). The lixiviants used in this study are strong acids and therefore will completely dissociate as well as the ionic species formed in the leaching circuits. HSC- Sim™ does not calculate the standard chemical exergy of completely dissociated species for most substances used in this study and was therefore calculated by hand. An example is presented in Appendix B to demonstrate the basis of calculation of standard chemical exergies for completely dissociated species. The mixing of non-ideal solutions requires that the activities should be used instead of mole fractions. The Aqua-mode, a built-in feature in HSC Chemistry allows the calculation of activities of aqueous solutions. The Pitzer-equations were used to calculate the activity coefficients of the ionic species. The calculation of the mixing exergy of an aqueous species is demonstrated in Appendix B. A summary of the assumptions made for exergy calculations are enumerated below:

- Steady state conditions were assumed.
- Reference temperature and pressure is 25^0C and 1 atm respectively.
- Activity coefficients for liquid species are calculated using the Pitzer equations.
- Activity coefficients for solid and gaseous species are assumed to be 1.

- Complete dissociation of the lixiviants used was assumed for the process conditions considered.

- Standard species suggested by Szargut and Morris, (1986) were used to calculated exergy values for non-standard species.

4.2 GaBi

GaBi is a well-established life cycle assessment modelling tool developed by Thinkstep, also formerly known as PE international (Thinkstep, 2017) . It has a wide range of processes and impact assessment methodologies that allows the calculation of the environmental impacts of the whole system. After the simulation model is created in HSC-Sim™, all streams are collected and mapped as GaBi equivalent streams using the 'LCA-Evaluation' mapping tool. This mapping tool in HSC-Sim™ enables the search and selection of GaBi equivalent streams, normalising input and output streams to the main product as well as defining each stream as elementary (to and from the environment) or non-elementary flows (to and from the technosphere). The latter is an important step as it determines the final environmental impact of the overall process. After mapping, the data extracted from HSC-Sim™ are collected in a separate file which is imported into the GaBi software. The data are captured as a black box, showing only the in- and output elementary flows. The link between HSC-Sim™ to and GaBi are shown in Figure 4-67.
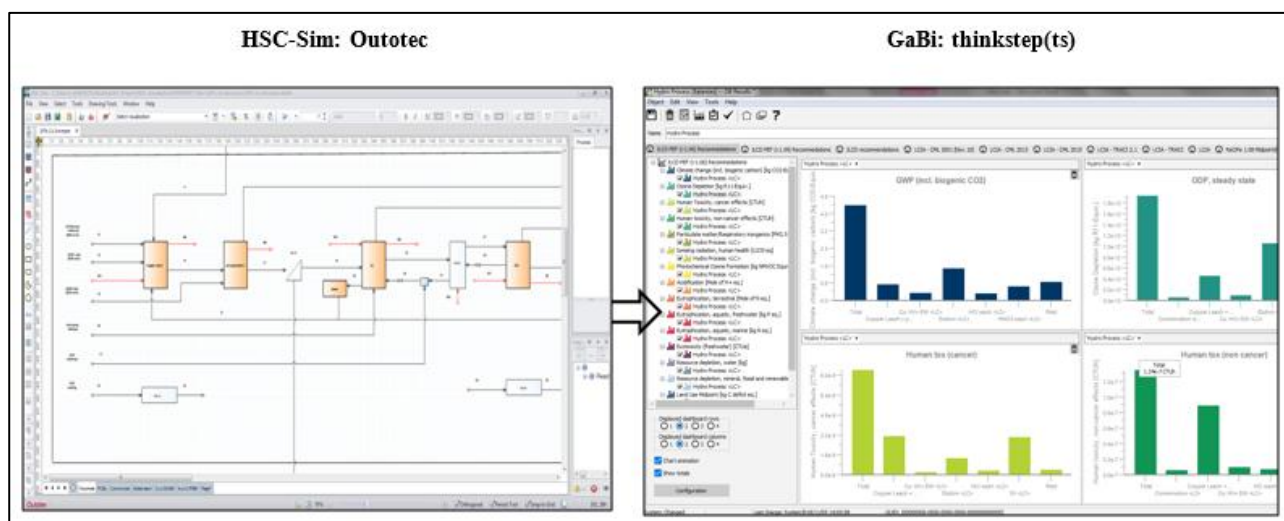
Figure 4-6: HSC-sim linked to GaBi

4.2.1   Life cycle assessment

The LCA methodology, according to the ISO 14040 standards was applied to a hydrometallurgical process aimed at the recovery of both copper and gold from waste printed circuit boards (WPCBs) (Latunussa *et al.*, 2016). The processing capacity is 30 000 metric tons/annum of waste printed circuits.

4.2.1.1 Goal of the Study

The **goal** of this study was to generate and assess environmental information relating to the WPCB treatment process, to identify the processing stages with the most significant environmental impacts and to discuss possible improvement opportunities for these processes based on the identified environmental hot spots.

The **motive** for conducting a LCA study are primarily to examine the environmental impact of hydrometallurgical process route for the treatment of waste printed boards where the two main products recovered is copper and gold. An exponential increase of waste electronic devices are noted annually, rendering metal recycling processes from such waste pivotal from both and economic and environmental management point of view. To date, various recycling technologies have been proposed in literature for metal recovery from WPCBs but formal analysis of the environmental burdens of the proposed processing routes is rarely done in a rigorous manner. Quantitative analysis of the environmental consequences associated with each process route may influence and guide future studies with process selection.

4.2.1.2 Scope of the Study

The **system** being studied is the hydrometallurgical treatment process for producing copper and gold. Detailed description of this process has been presented in **Chapter 3.**

The **functional unit (FU)** adopted for this study is defined as 30 000 metric tonnes/annum of bare PCBs i.e. the boards are stripped from all electronic components such as capacitors, transistors etc. All input and output data collected in the LCI phase are related to this functional unit. All impact scores obtained in the LCIA phase area also expressed in terms of this functional unit.

The **system boundary** is defined by adopting a **"cradle-to-gate"** approach which includes all the impacts related to the unit processes from comminution, metal extraction and metals refining, as shown in Figure 4-78. The environmental impacts of the unit processes outside of the dashed line are not considered. The **cradle-to-gate** approach defines the boundaries as from raw material collection (bare WPCBs entering the comminution section) to product i.e. secondary metals obtained from processes but not further.
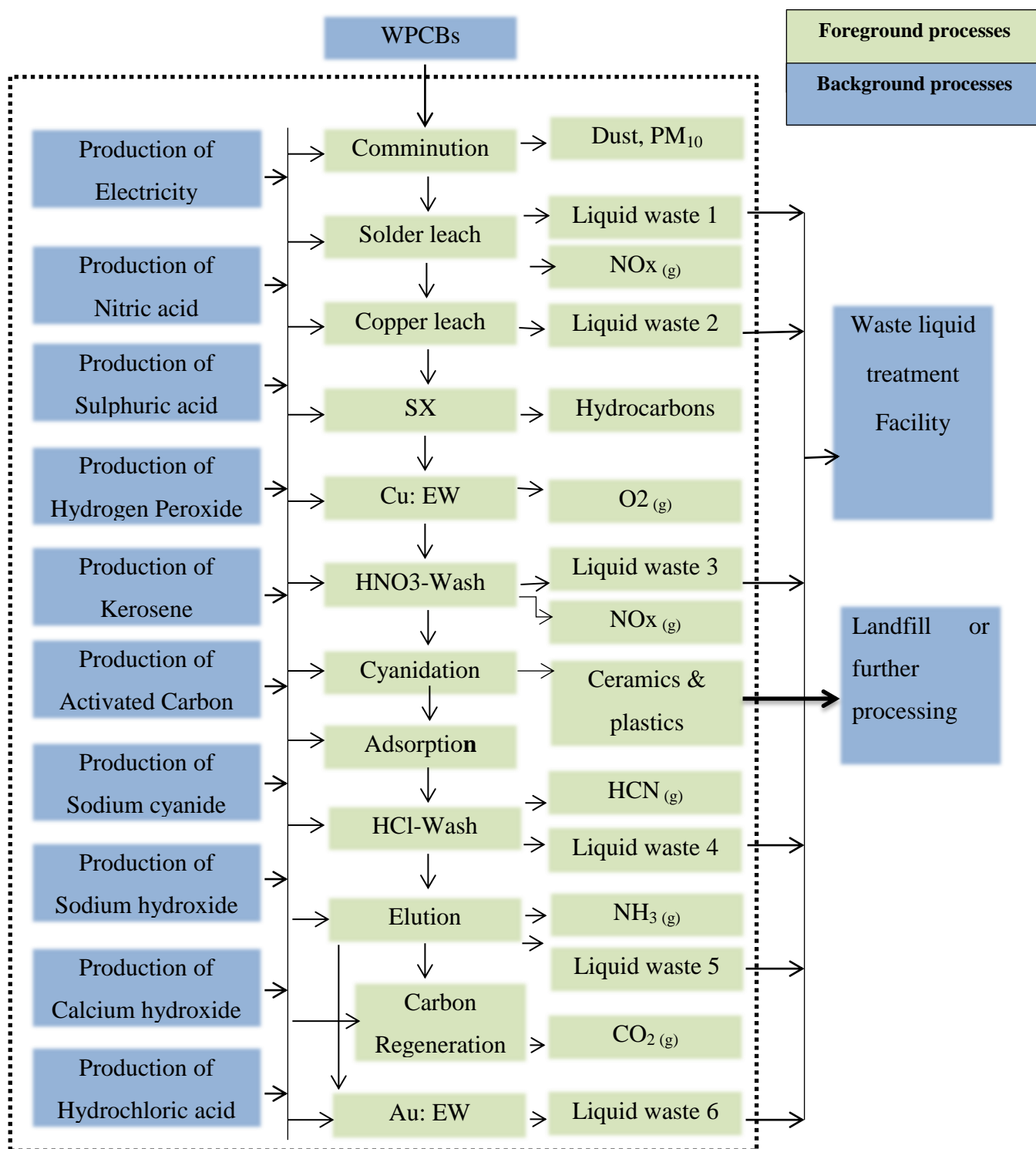
Figure 4-7: Schematic representation of the system boundary for the hydrometallurgical process

Considering that the discarded WPCBs is a waste stream, the zero-burden hypothesis was assumed (Ekvall *et al.*, 2007). This suggests that this waste stream does not carry any upstream

environmental burdens when delivered to the pre-treatment stage and therefore is not included in the environmental assessment. This **assumption** is commonly made in LCA studies of waste treatment (Ekvall *et al.*, 2007). This assumption also simplifies the comparison of different technologies treating the same waste. Impacts associated with transportation and the infrastructure of the plant i.e. construction and equipment is excluded due to a lack of information. The gas emissions from the process were assumed to be directly released to the environment, in order to consider a possible worst case scenario. The leachates from the solder leach (mainly Pb and Fe) and copper leach bleed (mainly Al) respectively are assumed to be treated in a separate industrial effluent plant. The environmental impacts of the waste water treatment plant were not considered. A LCA study of a similar hydrometallurgical process for the recovery of copper performed by Laura Rocchetti, Francesco Vegliò, Bernd Kopacek, (2013) reported that the wastewater treatment with hydrated lime was insignificant compared to other process units, hence the impacts of wastewater treatment was not considered. This also extends to the solids (both metals and non-metals) isolated from separation after the gold cyanidation process which is assumed to be further treated for recovery. Several uses for the non-metallic fraction have been reported in literature e.g. the plastics and ceramics can be reused in thermosetting resin matrix composites, thermoplastic matrix composites, concrete and viscoelastic material (Guo, Guo and Xu, 2009). Therefore, the non-metallic fraction is considered as a valuable product for further recovery.

All the **data** regarding the hydrometallurgical treatment process were obtained from both experimental works that were conducted by previous studies combined with well documented process information concerning technologies such as SX-EW, cyanidation and CIP (adsorption-elution-electrowinning) of gold. The background processes of electricity and material production were taken from the Professional database in GaBi. The South African electricity mix was selected for processes that require electricity input within the system boundary, while European conditions, more specifically Germany were considered for the production of materials. This was the only country within the database that had most of the available background datasets required for the process modelling; hence it was chosen to ensure consistency. The production of activated carbon and sodium cyanide were not available in the Professional database and was therefore constructed using literature data. A brief background and the construction of the datasets are discussed in the following sections.

4.2.1.2.1 Activated Carbon Dataset

Activated carbon (AC) can be produced from various carbon-containing materials. Traditionally, AC is manufactured from hard coal, wood or coconut shells but any material with a sufficiently high carbon content such as peat, rice husks, palm shells, olive wastes, scrap tires etc. were reported as suitable feedstock for AC production (Arena, Lee and Clift, 2016). Two types of processes can be employed to manufacture AC: chemical activation or steam activation. The latter process is most commonly used due to lower production cost. The carbon carrier and type of manufacturing process will determine the AC properties, as well as the hardness, purity and pore size distribution and can therefore be tailor made to the specifications of a process (Rogans, 2012; Arena, Lee and Clift, 2016).

Coconut shells are often utilized for AC production because it is readily available, has a high density and high purity (Arena, Lee and Clift, 2016). It is also the most suitable source for Carbon-in- pulp (CIP) or Carbon-in-leach (CIL) processes in gold recovery due to its high resistance to abrasion (Rogans, 2012). AC produced from coconut shells were used in the process modelling of WPCBs and thus forms part of the background processes in the LCA study. This particular process was not available in the GaBi Professional database; only processes that considered hard coal as raw material were available.

Lee *et al.*, (2016) evaluated the potential environmental impacts of AC production from coconut shells in Indonesia, which is one of the largest suppliers of AC. This study specifically aimed at quantifying the environmental performance of AC production from coconut shells due to the lack of information in literature. The system boundaries of this study included processes from the transportation of raw material acquisition to the delivery of AC, thus excluding the use and final disposal of AC. The production chain consisted mainly of two processes: carbonization and steam activation.

The results (Table 4-1) obtained from the mass and energy balances for the production of 1 ton of AC were used to construct a dataset (Figure 4-89) which was in turn used in the process modelling of WPCBs. It's worth mentioning that the environmental impact of AC transport to California (USA) was also investigated and were found to be negligible compared to the impact of AC production. This was assumed to be also true for delivery to South Africa.

Table 4-1: Elementary input and output flows for the production of 1 ton AC

Resource Consumptions	Unit	
Electric energy (Indonesian energy mix)	MJ	2160
Water	kg	1500
Air Emissions		
Carbon dioxide, biogenic	kg	6460
Water	kg	4220
Oxygen	kg	880
Nitrogen	kg	19000
Carbon monoxide	g	2440
Nitrogen oxides as NO2	g	1830
Dust	g	61
Tar (as naphthalene)	kg	3.9
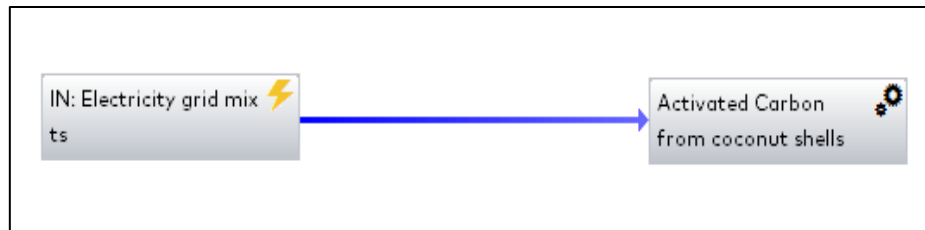
Figure 4-8: Activated carbon dataset used in LCA study

4.2.1.2.2 Sodium cyanide dataset

Cyanides can be either produced by the melt process or by the most commonly used processes using aqueous hydrogen cyanide as the source (Gail *et al.*, 2012). Hydrogen cyanide is principally produced from the Andrussouw process in which ammonia, oxygen and methane gas are used as raw materials (Engelbrecht, 2015a). Gaseous hydrogen cyanide (HCN), water and other combustion products are produced by the catalytic conversion of ammonia and methane gas in the presence of air. The theoretical reaction is presented below (Gail *et al.*, 2012; Engelbrecht, 2015b).

Equation 4-1

$$NH_3 + CH_4 + \frac{1}{2}O_2 \rightarrow HCN + 3H_2O$$
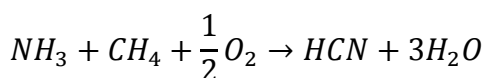
After cooling, the HCN is then reacted with 50 per cent sodium hydroxide (NaOH) solution to produce sodium cyanide (NaCN) with an approximate strength of 30 per cent w/w (Engelbrecht, 2015b). The stoichiometric reaction is given by Equation 4-2. This reaction was used to construct the NaCN (30% w/w) dataset (Figure 4-910) since both HCN production from the Andrussouw process and the production process of NaOH (50% w/w) were available in the Professional database. The dataset is based on the production of 1 kg NaCN.

$$HCN + NaOH \rightarrow NaCN + H_2O$$
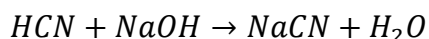
Equation 4-2
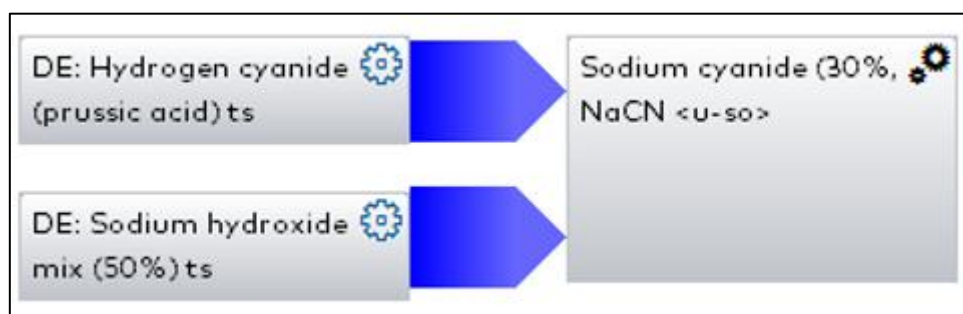
Figure 4-9: Sodium Cyanide Dataset

4.2.1.3   Life cycle inventory (LCI)

The LCI were obtained by considering all the input and output flows of each component within the product system using mass and energy balances that were obtained from the process simulation in HSC-Sim. The LCI was created by following the steps as discussed in section 4.2. The foreground data used for the analysis was extracted from experimental work performed at the University of Stellenbosch specifically for the solder and copper leaching stages respectively. Other processes such as the gold cyanidation, electrolysis processes, CIP circuit and solvent extraction were derived from literature. This data represent the expected recoveries for mainly ores such as copper and gold and is assumed to be similar for secondary treatment of waste such as printed circuit boards. The mass and energy balances of the foreground system that were simulated in HSC-Sim were mapped and imported into the GaBi software. The foreground processes are presented in Figure 4-101. The background data, related to the electricity mix and raw material production processes were obtained from the Professional database in GaBi except for activated carbon and sodium cyanide, which were constructed within GaBi using literature data. Since attributional-LCA modelling has been adopted in this study, these processes uses average data. The overall process (both foreground and background processes) that was simulated in GaBi is shown in Figure 4-112:
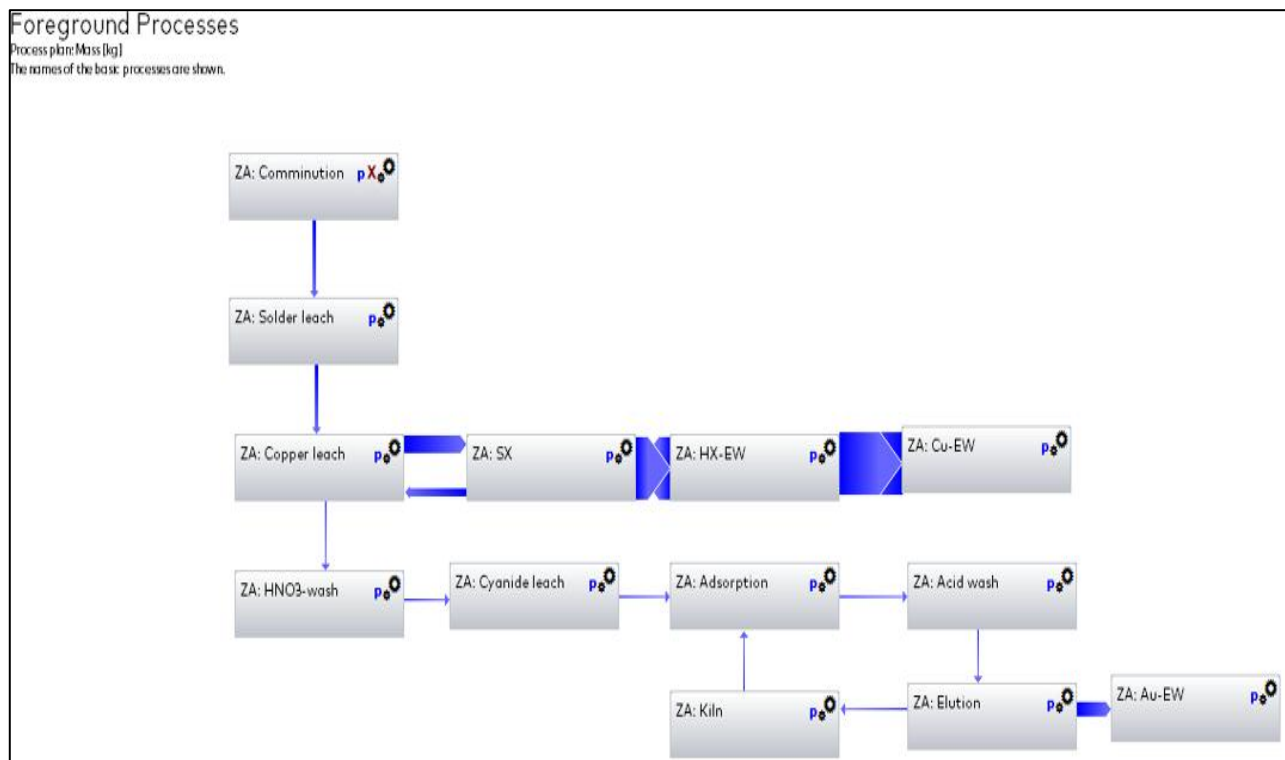
Figure 4-10: Unit processes of the foreground system
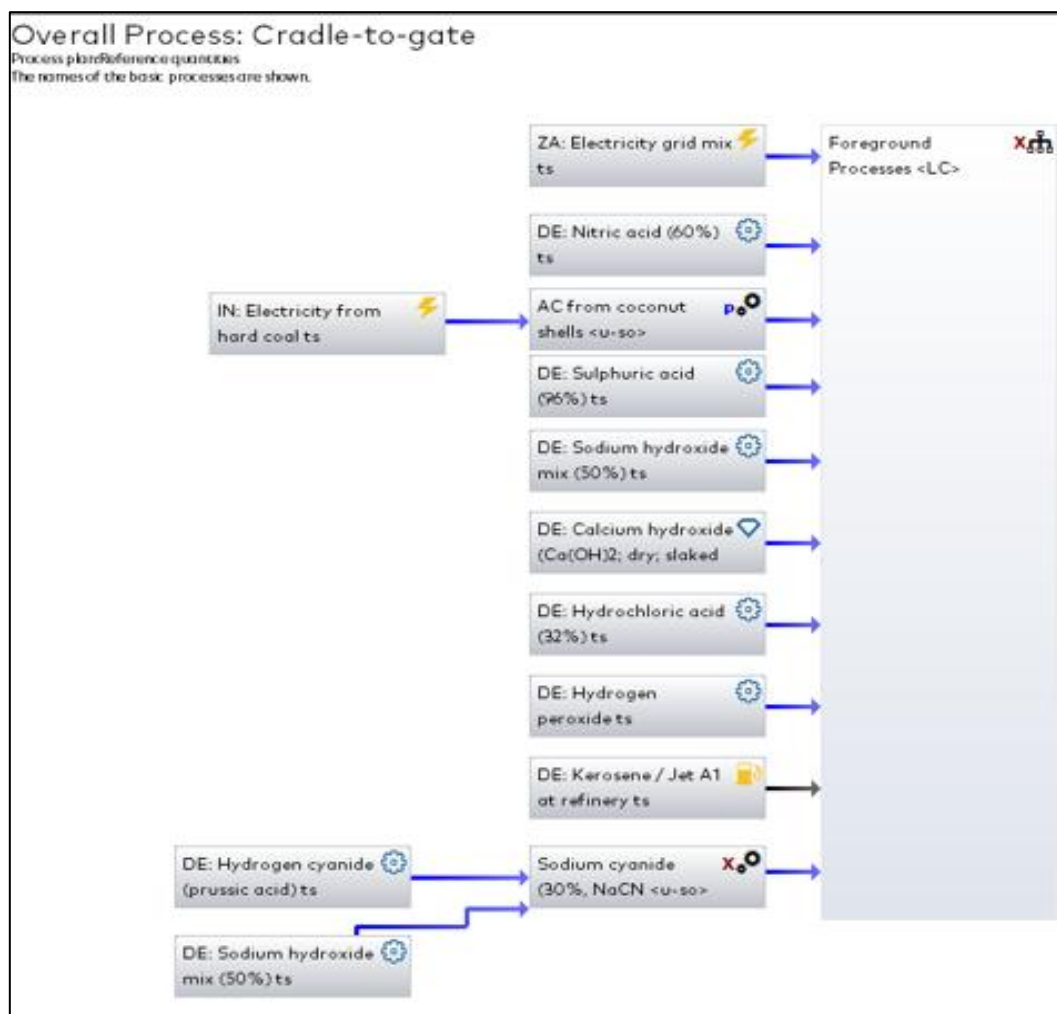
Figure 4-11: Overall process considered in LCA study

4.2.1.4   *Life cycle Impact assessment (LCIA)*

The Life Cycle Assessment (LCIA) has been modelled with the GaBi software version 8. To translate the inputs and outputs into potential environmental equivalents the CML- 2001 impact assessment method was selected in this study. The CML-2001 methodology is defined as a midpoint or problem- oriented approach that was developed by the Institute of Environmental Sciences of the University of Leiden, The Netherlands (Menoufi, 2011). This method was used in most LCA studies regarding the treatment of electronic waste (Hischier and Wäger, 2005; Laura Rocchetti, Francesco Vegliò, Bernd Kopacek, 2013; Xue *et al.*, 2014; Iannicelli-zubiani *et al.*, 2017) and are among the most frequently methods used in the South African manufacturing industry (Brent, 2004).

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The CML method (baseline version) consist of 10 impact categories which are chosen for this study and are enumerated as follows: Climate change potential (GWP), human toxicity potential (HTP), acidification potential (AP), eutrophication potential (EP), abiotic depletion potentials (ADP), stratospheric ozone depletion potential (SODP), photochemical oxidation potential (POP), freshwater aquatic eco-toxicity potential (FAETP), marine aquatic eco-toxicity potential (MAETP) and terrestrial eco-toxicity potential (TETP). Considering the uncertainties associated with normalisation, it was chosen to not perform this step in this study. Global warming is evaluated considering a 100-year time scale. The regional validity of the impact categories is global except for acidification and photochemical oxidation, which are calculated from average European values (Menoufi, 2011).

5.   RESULTS AND DISCUSSION

This chapter presents and discusses the results obtained from the simulation processes described in Chapter 4. Various process conditions and operating philosophies were simulated to determine the best operating conditions in terms of resource efficiency and environmental impact.

5.1   Process Summary

Exergy analysis and LCA were performed using the mass and energy balances of the developed flow sheet. The logic behind the development can be viewed in Chapters 3 and 4. The simulation results of the mass, energy and exergy values are shown in the Appendix A. Table 5-1 gives the process summary in terms of metal recovery and energy consumption.

Table 5-1: Process Summary

Section	Target Metal	Recovery	Purity	Energy Consumption (kWh/hr)
Comminution	N/A	N/A		205,32
Solder Leach	Pb/Sn	63%	2%	53,04
Copper Recovery	Cu	81%	100%	1247,58
Precious Metal Recovery	Au	97%	100%	2049,98

5.2   Exergy Analysis

Exergy destruction and overall exergy efficiency of the entire process were used to determine the thermodynamic performance of the overall process.

5.2.1   Exergy accounting of the overall process

Accounting for exergy resources distribution in a process chain is imperative for assessing its performance from a thermodynamic point of view. This section presents the account of all exergetic input of the overall process and its individual units. Figure 5-1 shows that only 0.85% of exergy input to the overall process is converted to valuable product streams, 82.55% was lost through waste streams while 16.6% was destroyed in the process due to irreversibilities. It appears that most of the valuable exergetic input was lost as waste. This can be ascribed to the high exergetic value associated with the non-metallic fraction of WPCBs that remains inert during the process.

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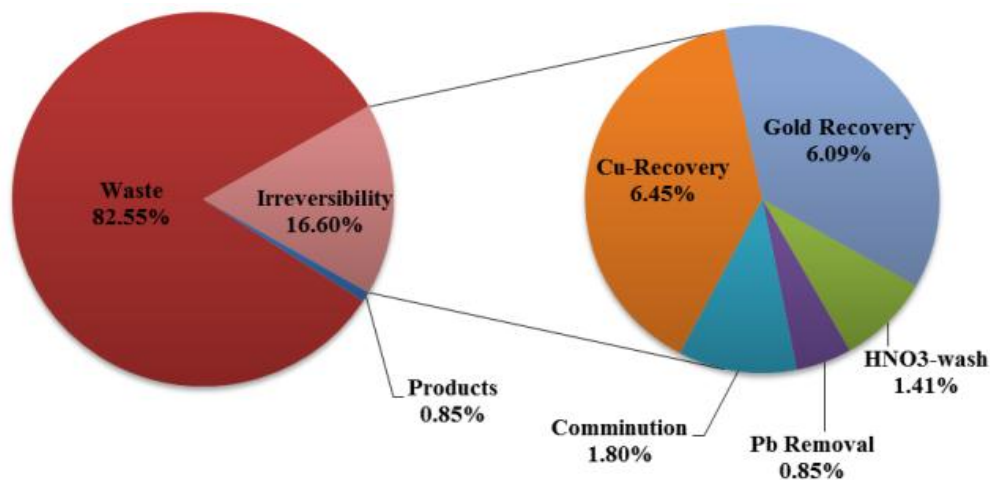
Figure 5-1: Exergy input distribution

5.2.2   Exergy Destruction

Exergy destruction, calculated from the exergy balance is the difference between the exergy in the process input and output streams as presented in section 2. This parameter quantifies the entropy production i.e. irreversibility of the overall process or process components. The entropy production or the exergy destruction associated with a process are a direct measure for resource consumption of a process (Goßling-Reisemann, 2008). The results from this equation applied to the individual process components as well as to the overall process were used to evaluate and understand the sources of inefficiencies in each unit operation. The sources of the irreversibilities are described by the phenomena that create these irreversibilities. These include friction, heat transfer over finite temperatures, spontaneous chemical reaction mixing etc. (Dogbe, Mandegari and Görgens, 2018b). The process under consideration involves more than one of these irreversibilities, hence the predominant phenomena(s) are considered as the main cause of irreversibility. It is a powerful tool which can be used to optimise the various process units. A breakdown of the overall exergy destruction distribution is shown in Figure 5-2.

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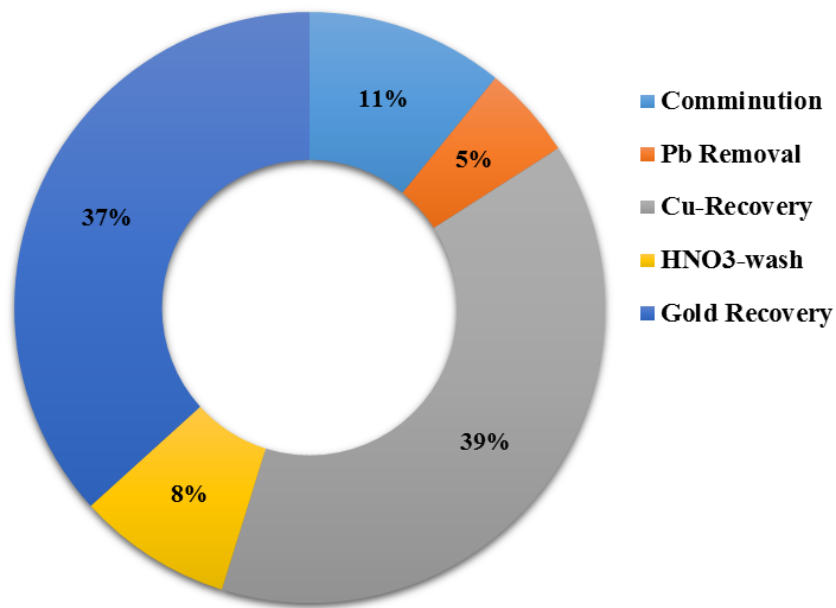
Figure 5-2: Process Exergy Destruction Summary

The results indicate that the gold recovery and copper recovery process units are the main contributors to the overall process inefficiencies. The exergy destruction rates in these processes should thus be prioritised in order to improve the overall thermodynamic efficiency.

5.2.2.1 *Copper Recovery Circuit*

The copper recovery section showed that 27.92% of the exergy destruction occurs within the leaching and pH correction steps. This is graphically presented in Figure 5-3.
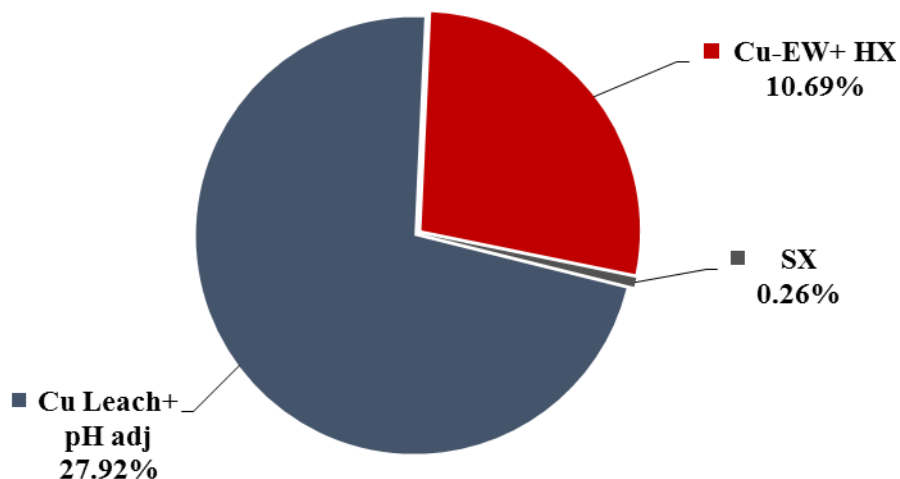
Figure 5-3: Cu-Recovery- Exergy destruction

The irreversibilities within the various process units are normally due to work lost in the form of heat, friction losses (external and internal), spontaneous chemical reactions, heat transfer and the mixing of fluids (Dogbe, Mandegari and Görgens, 2018a). Consideration of the copper recovery process, all the above phenomena are present in the process. When analysing the leaching circuit the following elements is highlighted as the biggest contributors of irreversibilities within the copper recovery circuit is the following:

- Leaching circuit:
    i. Mixing

The leaching requires an intensive mixing process to assist with the reaction kinetics and to keep the solids in suspension within the leaching vessel. During this process, friction losses and heat generation occurs which adds to the system irreversibility.

    ii. Heat Exchange

The temperature within the reactor is being managed with a cooling jacket at 25^0C, which is also the temperature of the ambient environment. The return water from the jacket enters the cooling tower unit process at 60^0C and returns back to the system at 25^0C. This creates irreversibility in the process because of temperature transfer over finite temperature differentials. Work input that is lost as heat to the system is also a contributing factor to the irreversibility within this section of the process. The difference in physical exergy between the in-and outlet indicates that approximately 3.8% of the total exergy destruction in the leaching circuit is due to cooling.

    iii. Reaction Chemistry

The copper leaching reaction is a multiple step reaction which is done in the presence of a strong oxidising agent in the form of hydrogen peroxide (Mecucci and Scott, 2002):

$$H_2O_2 \rightarrow H_2O + \frac{1}{2}O_2$$ **Equation 5-1**

$$Cu + H_2O_2 \rightarrow CuO + H_2O$$ **Equation 5-2**

$$CuO + H_2SO_4 \rightarrow CuSO_4 + H_2O$$ **Equation 5-3**

$$Cu + H_2O_2 + H_2SO_4 \rightarrow CuSO_4 + 2H_2O$$ **Equation 5-4**

Throughout the course of leaching, the formation of copper sulphate participates in several reactions as shown by the latter equations. Each reaction contributes to the irreversibility of the process. A

change in lixiviant and process operating conditions can possibly reduce the irreversibility within the process. The selection of a more element selective leaching agent may reduce the unit's exergy destruction, because it will limit the intermediate reactions from occurring. The difference in physical exergy between the in-and outlet indicates that approximately 96.2% of the total exergy destruction in the leaching circuit is due to cooling.

- Copper EW circuit
    i. Heat Transfer

After the SX circuit the AE solution requires heating. This is done with the assistance of a heat exchanging unit. The AE solution temperature is taken from 25°C to 45°C. The temperature differential between the AE and heated AE as well as the EW circuit and the environment destroys a portion of the exergy fed into the circuit.

The exergy values of the various process inputs and outputs are expressed graphically in the Grassmann-Diagram in Figure 5-4. The width of the arrows shown is proportional to the exergy value of that stream.
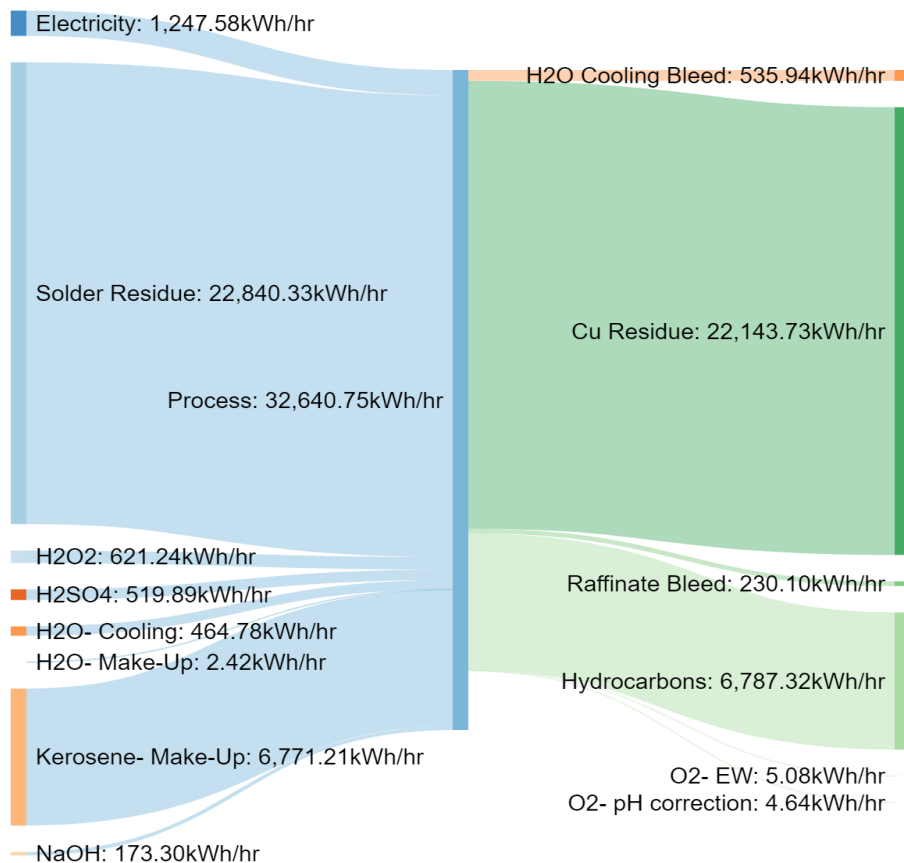
Figure 5-4: Copper Process Grassmann- Diagram

5.2.2.2 *Gold Recovery Circuit*

A breakdown of the overall exergy destruction for the gold recovery process is depicted in Figure 5-5. Consideration of the relative exergy destruction rate in the gold recovery process showed that the elution circuit and the hydrochloric acid wash process are the biggest contributors to process inefficiencies.
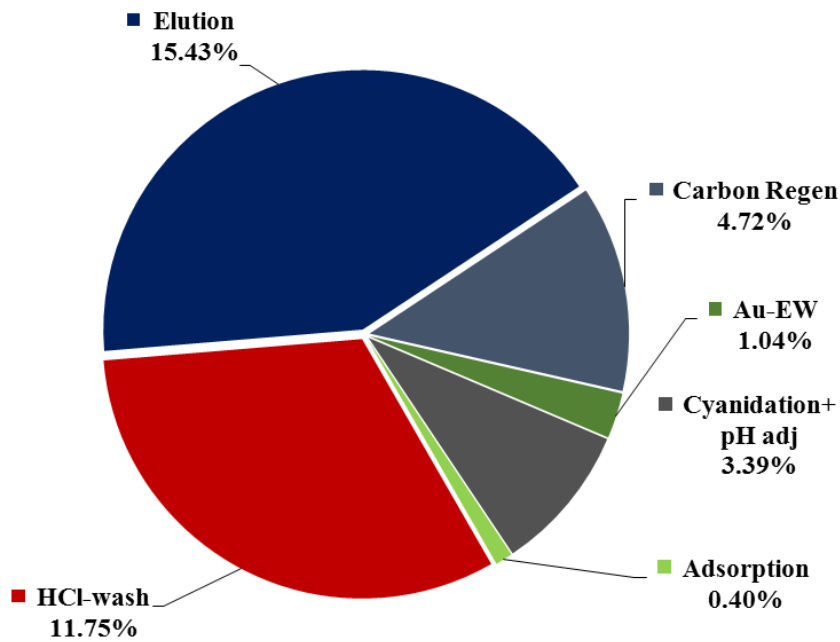
Figure 5-5: Au-Recovery- Exergy destruction

The gold elution circuit is an energy intensive process where various process streams require pre-heating and mixing before it enters the system. The elution circuit in this process was operated at 110^0C. All of the reagents and systems conditioning chemicals require pre-heaters which take the various components from 25^0C to the required temperature. Therefore the main cause of process irreversibility is due to heat transfer over finite temperature. The physical exergy difference between in-and outlet for the elution and HCl washing stages shows that 99.78% and 99.93% of the exergy destruction in these respective units are attributed to the increase in temperature. The remainder are due to chemical reactions, frictional losses etc. The exergy values of the various process inputs and outputs for the gold recovery processes are expressed graphically in the Grassmann-Diagram in Figure 5-6.

Figure 5-6: Gold Recovery Grassmann Diagram

The exergy destruction is predominantly attributed to physical exergy changes due to increase in temperature of process streams. Process integration is not only of critical importance to recover the exergy losses but the intermediate/ inter-stage heating may reduce overall irreversibility due to heating of streams with smaller temperature differentials. Alternative stripping technologies should also be evaluated. If the stripping process can be operated close to ambient temperature the exergy destruction might be reduced significantly. Alternative processes can include the Merrill Crowe process or Ion exchange technologies. The details of these processes are discussed in section 2.7.4.3.

5.2.3 Exergy Efficiency

Exergy efficiency is a powerful optimisation tool when used in conjunction with the exergy destruction tool. It quantifies and benchmarks the system's performance and highlights the effect of process improvements on the overall process efficiency.

The exergetic efficiency, derived from Equation 2-53can be defined by the following equation:

$$\Psi = \frac{\sum E_{desired\ Products}}{\sum E_{inputs}}$$

Equation 5-5

The products defined in this equation are the desired products produced by the process. In the case of the designed process, it will be the recovered gold and copper. The inputs are all of the resources required to drive the process, this includes the primary feed source (PCB), all chemical reagents and the electrical inputs. Using exergy to determine the efficiency of the process creates a tool where the streams with various dimensions (mass and energy) is transformed into a single manageable parameter (exergy), which also takes into account the thermodynamic limitation of a given stream in terms of the first and second laws. Process improvement can be done by considering the exergy destruction analysis results and by applying the exergy efficiency principle. Table 5-2 classifies the various process streams according to the exergy efficiency definitions.

Table 5-2: Classified Exergy Flow Analysis in Base Case

Stream nr	Component	Exergy Flows (kWh/ton PCB)		
		Input	Output	
			Desired Product	Waste
1	PCBs	5372,11		
5	HNO3(aq)	28,84		
9	Cooling water	27,42		
12	H2SO4-96wt%	113,54		
13	H2O2-30wt%	135,68		
15	NaOH-50%	37,85		

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25	Kerosene-makeup	1478,83		
31	H2O-makeup	0,53		
34	Cooling water			194.45
35	Cooling water			224.22
36	HNO3-60%	7,11		
37	H2O-dilution	0,74		
44	NaCN(aq)-30%-makeup	0,24		
45	Ca(OH)2(s)	2,68		
48	Compressed air	0,00		
56	Carbon makeup	59,76		
58	HCl-3wt%	46,57		
61	Acid wash rinse water	6,05		
66	NaCN/NaOH soak soln	168,43		
68	Eluant	19,08		
70	Final rinse water	19,08		
76	H2O	1,26		
81	NaOH-50%	0,21		
30	Cu-Cathode		74,65	
84	Au cathode		0,01	
W	Electricity	1040,27		
3	PCBs- dust			312,43
6	NOx(g)			15,26
8	Fe,Pb-Nitrate Solution			20,18
10	Cooling water			31,62
16	O2(g)			1,02
26	Hydrocarbons			1482,35
29	O2(g)			1,11
22	Raffinate- bleed waste-43%			50,25
38	NO2(g)			45,35
49	N2(g),O2(g)			0,01
60	HCN(g)			0,12
74	NH3(g)			0,02

83	O2(g)/H2(g)			0,02
85	Barren gold solution			41,51
73	Pre-soak solution-discharge			183,08
80	Combustion gases			79,29
63	HCl solution discharge			60,10
64	Wash water discharge			10,86
55	CN bleed-5%			0,48
51	Au-residue			4677,52
42	Nitrate salts			-1,55
41	Cooling water			48,09
87	Cooling water			19,11
89	Cooling water			0,90
Total		**8667,80**	**74,66**	**7497,8**

The difference between the process outputs and the inputs are the exergy destruction. This is due to the thermodynamic irreversibilities within the process. This yields an overall exergy destruction of 16.6% and a base case exergetic efficiency of 0.85%. This low exergetic efficiency is largely due to relatively small volume of product produced when compared to the feed flow. 81.67% of the total exergy input reports to the waste streams.

5.2.3.1 Exergy losses

The hydrometallurgical process generates various waste streams from the different process units. The waste streams are in gas, liquid and solid form each with associated qualities. Analysis in Table 5-2 shows that the emission streams still contain value and an opportunity exists to recover some of this quality for internal process use or as additional saleable products. Table 5-3 is a summary of the valuable waste streams and their associated exergetic value. The various waste streams were analysed in terms of recoverable materials. The streams with material that can be recovered with traditional mineral processing equipment was analysed in terms of its inherent chemical, physical and mixing exergy values. The streams with no intended recovery goal were not considered in the analysis.

Table 5-3: Waste Streams- Exergy Analysis and Resources to be recovered

#	Stream Description	Goal	Chemical Exergy (KWh)/hr	Physical Exergy (KWh)/hr	Exergy of mixing (KWh)/hr	Total Exergy (KWh)/hr	Total Exergy (kWh/ton PCBs)
3	Dust	Desired Product (Cu)	2,73			2,73	0,60
6	NO_x	NO_3 production	71,46		-1,60	69,86	15,26
8	Fe, Pb- Nitrate Solution	-				0,00	0,00
10	Cooling water	Heat Recovery		19,23		19,23	4,20
16	$O_2(g)$	-				0,00	0,00
26	Hydrocarb2ons	-				0,00	0,00
29	$O_2(g)$	-				0,00	0,00
22	Raffinate-bleed waste- 43%	Desired Product (Cu)	33,45		-12,43	21,02	4,59
22		Add. Desired Product (Ni)	2,25		-1,27	0,98	0,21

#	Stream Description	Goal	Chemical Exergy (KWh)/hr	Physical Exergy (KWh)/hr	Exergy of mixing (KWh)/hr	Total Exergy (KWh)/hr	Total Exergy (kWh/ton PCBs)
2		Add. Desired Product (H_2SO_4)	121,70		-15,63	106,07	23,17
29	$NO_2(g)$	NO_3 production	207,64			207,64	45,35
49	$N_2(g),O_2(g)$	-				0,00	0,00
60	$HCN(g)$	Cyanide Production	0,54			0,54	0,12
74	$NH_3(g)$	Ammonia Production	-				
83	$O_2(g)/H_2(g)$	-				0,00	0,00
85	Barren gold solution	Water Recovery	174,83		-0,16	174,66	38,15
73	Pre-soak solution	Water Recovery	83,01	68,53	-7,46	144,08	31,47
73		Cyanide Recovery	674,39		-6,27	668,13	145,92

#	Stream Description	Goal	Chemical Exergy (KWh)/hr	Physical Exergy (KWh)/hr	Exergy of mixing (KWh)/hr	Total Exergy (KWh)/hr	Total Exergy (kWh/ton PCBs)
73		Heat Recovery		13,93		13,93	3,04
80	Combustion gases	Heat Recovery		3,83		3,83	0,84
63	HCl solution	HCl Recovery	100,63		-5,4	95,19	20,79
63		Water Recovery	127,14		-10,0	117,13	25,58
63		Heat Recovery		62,89		62,89	13,74
64	Wash water discharge	Water Recovery	27,71			27,71	6,05
64		Heat Recovery		22,00		22,00	4,81
55	CN bleed-5%	Water Recovery	2,17		-0,0005	2,17	0,47
55		Cyanide Recovery	0,01		-0,0008	0,01	0,00
51	Au-residue	N/A				0,00	0,00

#	Stream Description	Goal	Chemical Exergy (KWh)/hr	Physical Exergy (KWh)/hr	Exergy of mixing (KWh)/hr	Total Exergy (KWh)/hr	Total Exergy (kWh/ton PCBs)
42	Nitrate salts	Water Recovery	21,29			21,29	4,65
41	Cooling water	Heat Recovery		29,24		29,24	6,39
87	Cooling water	Heat Recovery		11,62		11,62	2,54
89	Cooling water	Heat Recovery		0,54		0,54	0,12
	Total		1651,07	231,82	-60,28	1822,62	398,04

The table shows that 398,04 kWh/ton out of the 7497,8 kWh/ton of current waste streams that can be recovered as desirable products. To realise these process efficiencies the following technologies will have to be introduced into the system:

5.2.3.2   Heat Recovery

Various streams still contain valuable physical exergy. This includes the cooling systems and the heated waste streams from the gold recovery process. The thermal energy can be utilised in the system pre-heaters to reduce the electricity demand of the process. To achieve this, the hot streams will be moved internally and sent to heat exchange units.

5.2.3.3   Water Recovery

The liquid streams generated in the process are currently being sent to waste management processes outside of the process boundaries. This is currently not being seen as a desirable product, only if the water is recovered and re-used within the process boundaries or sold as a fit-for-purpose water (drinking, irrigation, etc.). This can be done by utilising water purification technologies. This can include reverse osmosis, nano-filtration or ion exchange technologies.

5.2.3.4 Copper Recovery

There are two main copper streams produced in the process- the raffinate bleed and the gold recovery circuit's nitric acid wash. The raffinate streams still contains a high purity copper sulphate streams, which can be recovered with a downstream direct-EW process or sold as high concentration copper liquor to another processing plant. The copper in this bleed stream exist because of the internal process water and acid concentration management- returning 100% of the raffinate to the internal process will upset the operating conditions. The copper in the nitric acid wash process exist as $Cu(NO_3)_2$. The problem with this stream is the fact that it contains various other base metals. The liquor can be sold to a tertiary metal processor.

5.2.3.5 Sulphuric Acid Recovery

The sulphuric acid that is present in the raffinate bleed stream can be recovered with the additional copper recovery process.

5.2.3.6 Nickel Recovery

Nickel is available in the nitric acid wash process. Nickel is present as $Ni(NO_3)_2$ in a liquor with other base metals. The nickel can be selectively be recovered by a downstream SX-EW process or the liquor can be sold to a tertiary metal processor.

5.2.3.7 Cyanide Recovery

Cyanide is available in the cyanide bleed and the solution discharges from the gold recovery processes. Various technologies can be employed to upgrade the cyanide in the waste streams to the required purity and quality for the process. This can include membrane technologies or ion exchange.

5.2.3.8 HCl Recovery

The gold hydrochloric acid wash streams contain a high volume of hydrochloric acid. The acid can be recovered selectively with acid resistant membrane technologies.

5.2.3.9 Nitric Acid Production

NO_x gas streams are generated within the solder removal and the gold washing processes units. The gasses generated from these units can be captured by a gas-water scrubbing unit and nitric acid can be produced in this manner under the appropriate operating conditions.

Each of the suggested process efficiency improvement techniques may improve the overall process efficiency if introduced into the system. All of these steps requires additional equipment capital and

introduces new complexities and thermodynamic irreversibilities into the system. The changes should thus be subjected to an economic analysis.

Klaasen *et al.*, (2010) conducted an exergy analysis for the recycling of zinc via a pyrometallurgical route. In this study other possible recoverable products are also considered and included in the calculation of the exergetic efficiency. This is done to determine the maximum possible exergetic efficiency if these identified streams with potential value is considered for the purposes of the study as valuable products. A similar approach is followed in this study to determine the maximum possible exergetic efficiency. Table 5-4 summarises the effect of the process improvement suggestions. The water recovery system yielded the biggest increase in the system's exergetic efficiency and the increase in desirable products, copper and nickel, had an almost insignificant effect on the system performance.

Table 5-4: Process Improvement Exergy Efficiencies

Process Improvement	Exergy (kWh/ton)	Ψ
Water Recovery	106,37	2,08%
Heat Recovery	35,66	1,26%
Copper Recovery from Waste Streams	5,19	0,91%
Cyanide Recovery	146,04	2,54%
HCl Recovery	20,79	1,09%
H2SO4 Recovery	23,17	1,12%
Nitric Acid Production	60,61	1,55%
Nickel Recovery	0,21	0,85%
Combined		5,44%
Base Case		**0,85%**

5.2.4   Sensitivity Analysis

A sensitivity analysis was conducted to show the sensitivity of the process with regards to the process assumptions. Chapter 4 showed that the process has numerous input streams which might all have a significant influence on the performance of the system in terms of the actual metal recovery as well as the environmental impact and the efficiency of the process. Based on the results displayed in section 0 the process sensitivity will evaluate the performance with the change in electricity input and a change in the feed copper and gold concentrations.

5.2.4.1   Energy

When a system is operational the required electricity may vary depending on the operating philosophy, human factors and the actual equipment installed. During the lifespan of a process unit various components lose efficiency and with the loss in efficiency the actual electrical input can potentially increase. This might also happen when bigger motors or new systems are introduced to the process while in operation. This increase in electricity may have a significant impact on the resource efficiency and the environmental impact of the process. Figure 5-7 shows the breakdown of the total exergy destruction distribution for an increase in electricity.
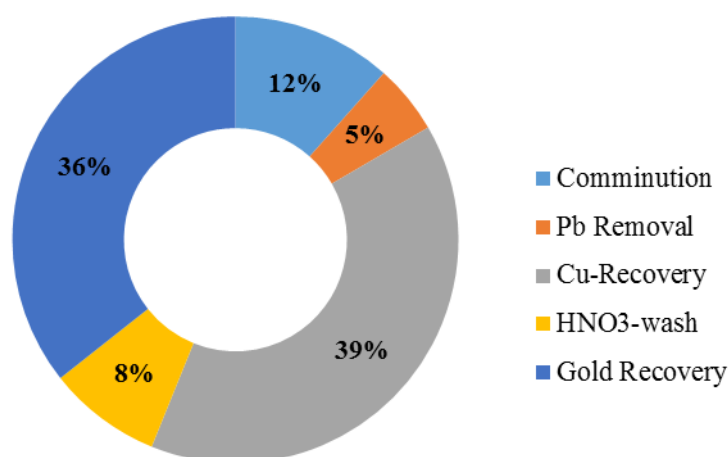
Figure 5-7: Total Exergy Destruction with 10% Electricity Increase

The stages that are energy intensive are the comminution, copper electrowinning, elution and HCl washing stages (Figure 5-8 and Figure 5-9). An increase in electricity affected largely the comminution stage with regards to overall process inefficiencies. Inefficiencies in the comminution section are attributed to conversion of valuable energy to heat loss to the environment. Radziszewski, (2013) highlights this inefficiency in comminution circuits and gave suggestions for the recovery of waste heat. Without regard for the increase in exergy destruction for the comminution section, the copper and gold recovery sections remain the major contributors to the overall process irreversibility.

Figure 5-8 and Figure 5-9 depicts the relative contribution to the total exergy destruction for the gold and copper recovery circuits.
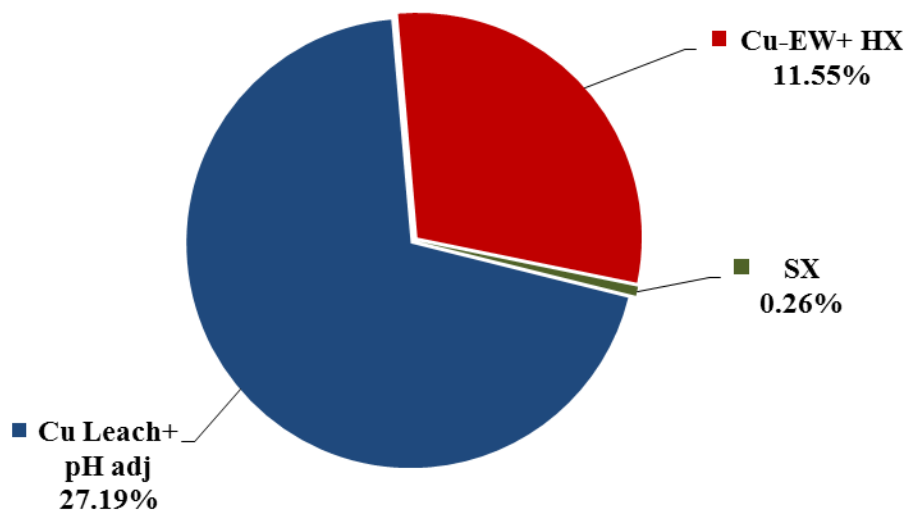
Figure 5-8: Cu-Recovery- Exergy destruction 10% Electricity Increase
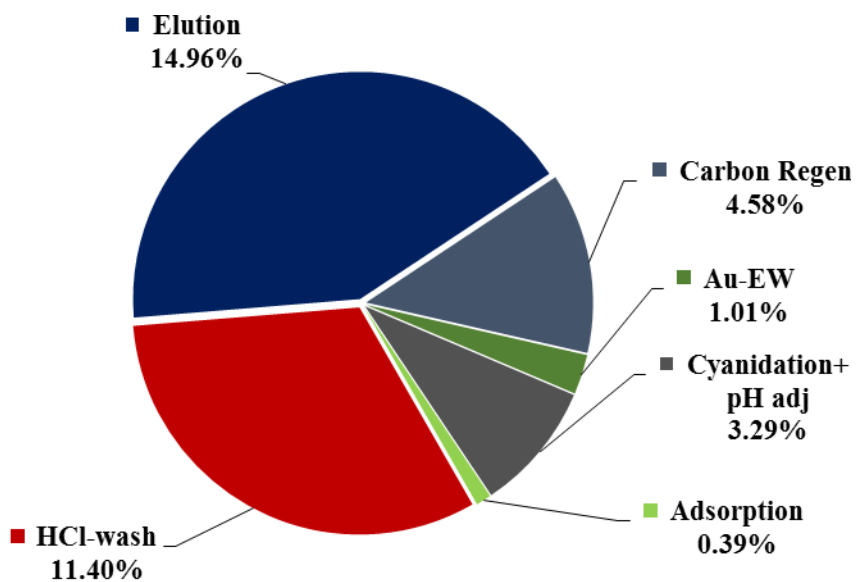
Figure 5-9: Au-Recovery-Exergy destruction 10% Electricity Increase

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A similar approach was followed to investigate the effect of a decrease in total electrical energy consumption. As with electricity increase the plant electricity requirement supply can also decrease. This can also be due to equipment and operating changes as well as human interference. The exergy destruction contribution of the various plant sections are summarised in Figure 5-10. The decrease in electricity does not influence the relative importance of the various sections with regards to the total exergy destruction. However it is noteworthy that the gold recovery section is significantly affected by a reduction in electricity consumption. This highlights the importance of recovering the physical exergy that are lost as thermal energy as discussed in section 5.2.3.1. The increase noticed for the copper recovery section is mainly due to the transformation of chemical exergy in the leaching circuit. It may be worthwhile to investigate alternative lixiviants for comparison to recover copper. A breakdown of the relative contribution of the copper and gold sections is given in Figure 5-11 and Figure 5-12.
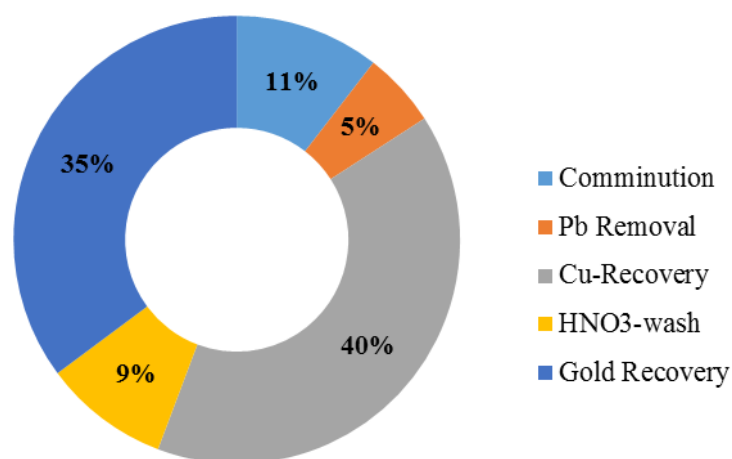
Figure 5-10: Process Exergy Destruction- 10% Electricity Decrease
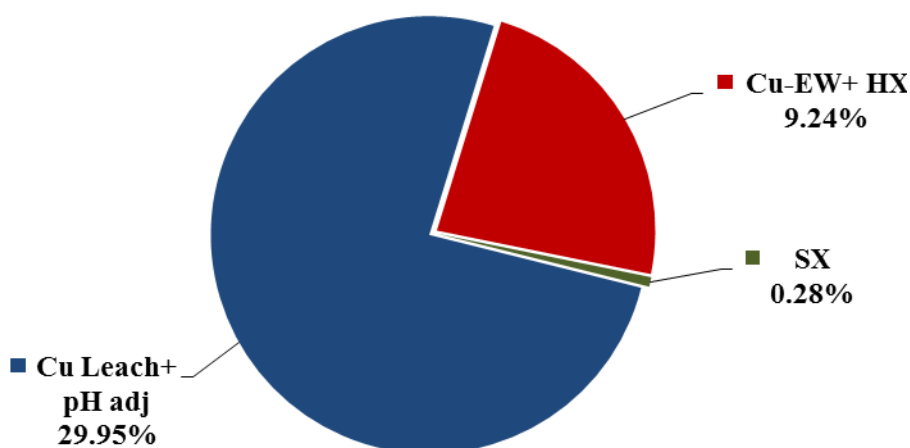
Figure 5-11: Cu-Recovery- Exergy destruction 10% Electricity Decrease

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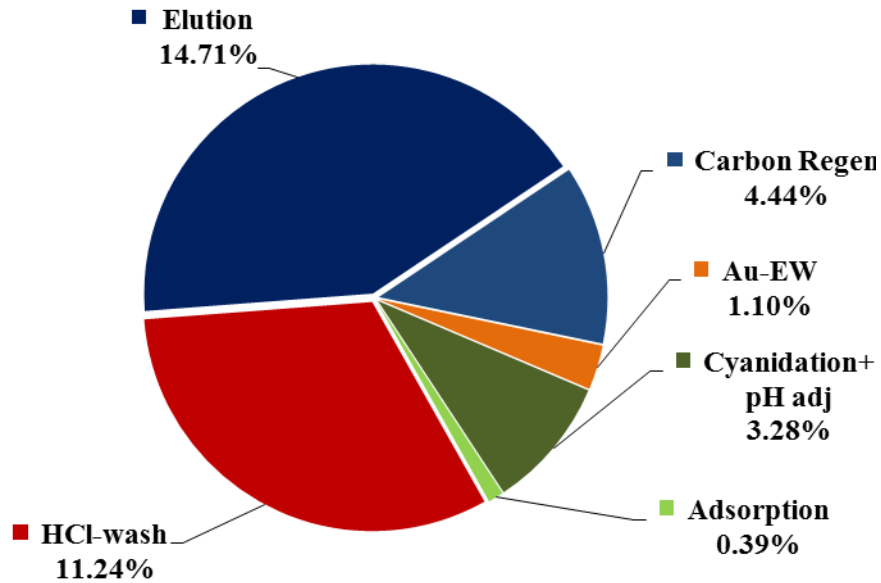
Figure 5-12: Au-Recovery- Exergy destruction 10% Electricity Decrease

A summary of the effect of electrical energy relative to the base case scenario are depicted in Figure 5-13. A consideration of the results showed that the nitric acid wash and solder leach circuits are relatively unaffected, but the comminution, copper recovery and gold circuits vary significantly in response to the electrical energy consumption. More energy efficient process solutions and technologies should thus be considered.
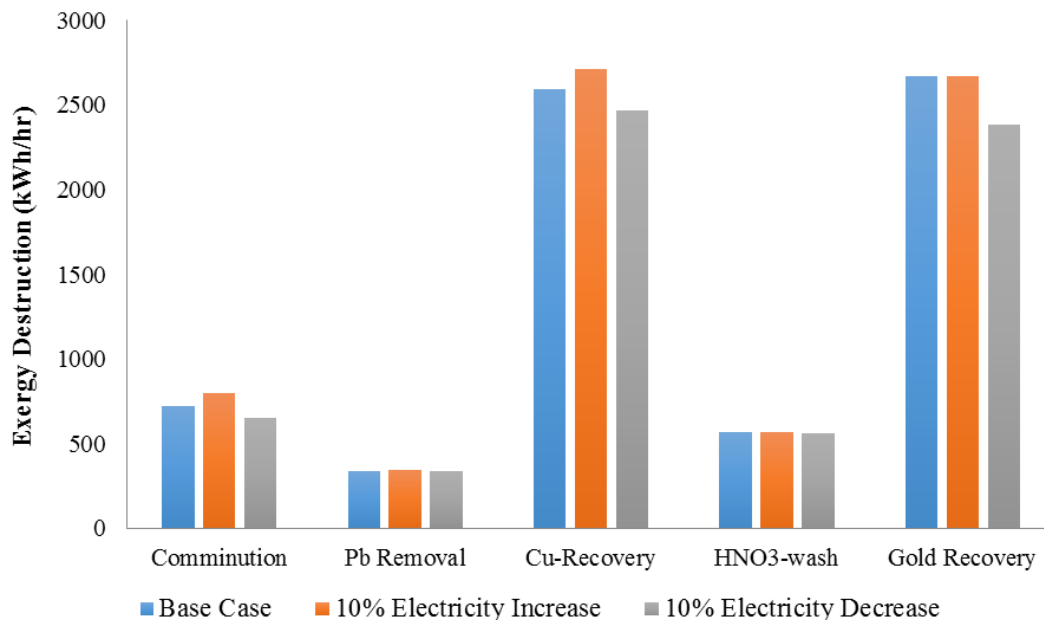
Figure 5-13: Electricity Sensitivity Analysis Comparison

5.2.4.2   Feed Concentration

PCBs contain a range of metals as described in section 2.2. The composition varies depending on the manufacturer, manufacturing date and the type of equipment. Feed metal concentration will thus vary depending on the various recyclers and the type of equipment liberated from waste dumps. This change in concentration has a significant effect on the process economics, environmental impact and the resource efficiency as well as resource requirements. Gold and copper is the main economic drivers for the process, and it is important to understand the influence of the change in concentrations on the process inefficiencies. Typical PCB has a copper concentration of 56.93 wt. % and a gold contribution 0.05 wt. % (when only the metallic fraction is considered). Gold is inert during the upstream leaching processes and only participate in the gold leaching reactions. Copper reacts throughout the process, with the exception of the solder leach reactions (low nitric acid concentration) and is also present during the gold recovery process. A variation in the copper concentration are expected to contribute more to the overall system performance, because of its relative concentration when compared to other metals and its interaction or potential interaction in all of the process steps.

5.2.4.2.1 Copper Concentration

Technological advancements and the cost of various process raw materials may change the concentration of copper used in EE-equipment. This combined with the general variations of the expected feed concentrations creates a need to understand the influence of a change in copper concentration in the overall process resource efficiency and environmental impact.

The change in concentration was done by applying the $\pm$ 10% variation on base case copper concentration and adjusting the relative composition of the other metals to maintain the same feed flow. All of the processes operating conditions were kept constant for the simulation. Table 5-15 summarises the feed analysis input into the HSC modelling program.

Figure 5-14 and Figure 5-15 shows the effect of the copper concentration increase and decrease on the overall process exergy destruction. Consideration of the results indicates that the relative exergy destruction distribution of the major process components did not change significantly. This show that even with the change in exergy destruction created by a metal concentration change, the individual processes should still be optimised to reduce the inefficiencies within the process. The comparative exergy destruction values for the overall process are shown in Figure 5-16 and Figure 5-17.

Table 5-5: Feed Composition- Change in Copper Concentration

Metal	Base Case kg/hr	10% Increase kg/hr	10% Decrease kg/hr
Cu	729,81	759,55	696,48
Al	118,84	112,44	126,01
Fe	102,86	97,32	109,07
Sn	80,60	76,26	85,46
Ni	17,93	16,97	19,01
Zn	98,48	93,17	104,42
Pb	131,14	124,08	139,06
Au	0,58	0,55	0,62
Ag	1,82	1,72	1,93
Total	**1282,05**	**1282,05**	**1282,05**
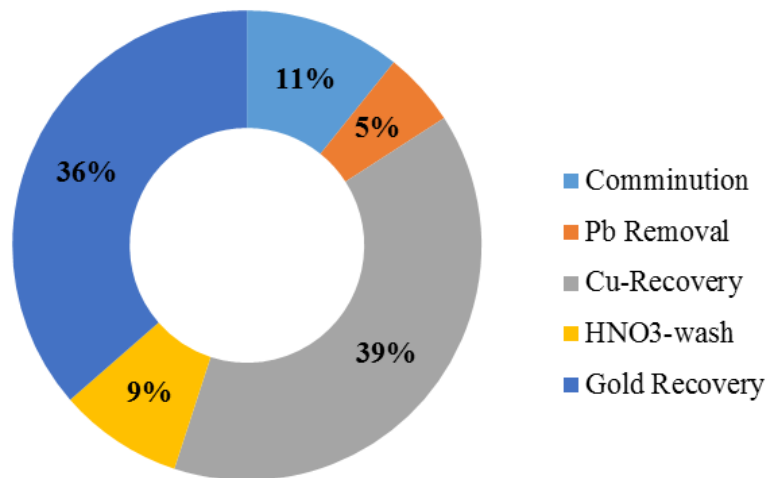
Figure 5-14: Relative Process Exergy Destruction- 10% Copper Increase
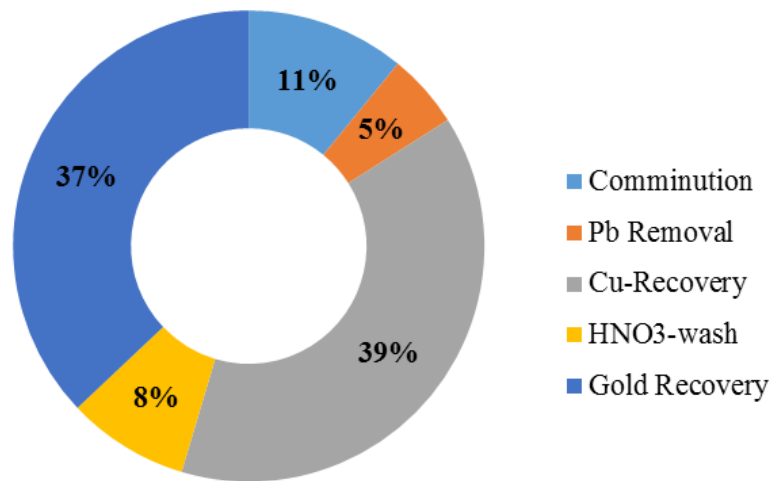
Figure 5-15: Relative Process Exergy Destruction- 10% Copper Decrease
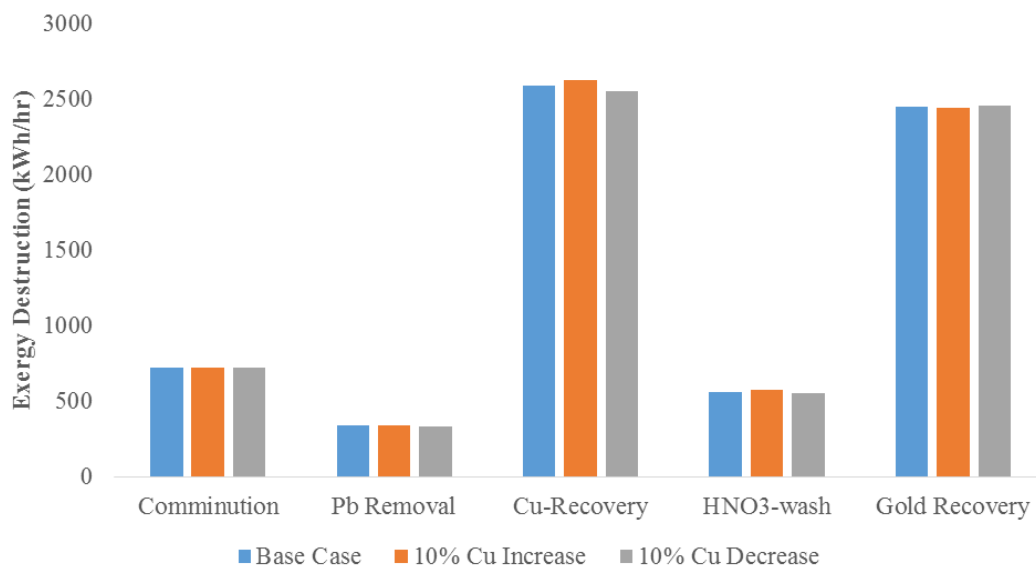
Figure 5-16: Effect of Copper concentration on major components

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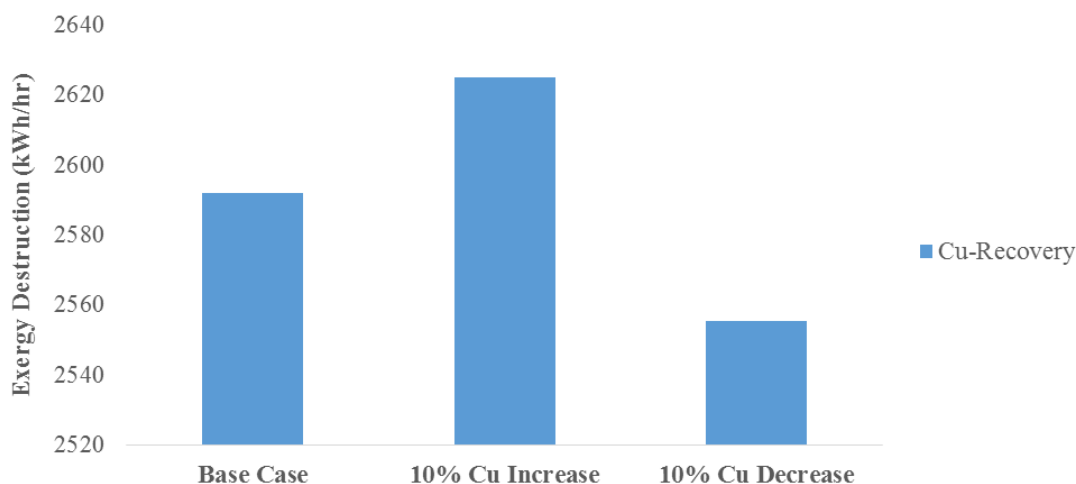
Figure 5-17: Copper Recovery Exergy Destruction- Sensitivity Comparison

5.3 Life Cycle Assessment

The interpretation is the final stage of a LCA study and according to the ISO standards the objective of this phase is to analyse results, discuss limitations and provide recommendations that are aligned with the defined goal and scope of the study. This chapter presents the environmental profile of the hydrometallurgical processing route for the production of copper and gold from waste printed circuit boards. Individual contributions to each impact category are discussed and the major contributors are emphasised. A sensitivity analysis was also undertaken to analyse the influence of variability in the input parameters.

5.3.1 Life cycle inventory (LCI)

Table 5-6 presents the mass and energy streams of the overall system. All results are normalised to 1kg WPCB. The tracked flows (x) refer to the data sources while the waste flows (*) are streams that require additional processing outside the current system. The remaining flows indicate the elementary flows specifically to the foreground system. The elementary flows of the overall system (foreground and background data) are presented in Table 5-7. These are flows at the system-environment interface i.e. streams that directly enter or leave the system in the form of resources, emissions to air, fresh water, sea water and soil.

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Table 5-6: Life cycle inventory (LCI) data

Parameter	Quantity	Amount	Unit	Tracked / Waste flows
Inputs				
Activated carbon [Organic intermediate products]	Mass	0,008	kg	X
Air [Renewable resources]	Mass	0,010	kg	
Calcium hydroxide [Intermediate products]	Mass	0,010	kg	X
Electricity [Electric power]	Energy (NCV)	3,745	MJ	X
Fresh water, regionalized, ZA [Water]	Mass	7,884	kg	
Hydrochloric acid (32%) [Intermediate products]	Mass	0,185	kg	X
Hydrogen peroxide (50%) [Intermediate products]	Mass	0,328	kg	X
Kerosene [Refinery products]	Mass	0,124	kg	X
Nitric acid (60%) [Inorganic intermediate products]	Mass	0,249	kg	X
Nitric acid (60%) [Intermediate products]	Mass	0,561	kg	X
Printed wiring board (unpopulated) [Parts]	Mass	1,000	kg	X
Sodium cyanide [Intermediate products]	Mass	0,251	kg	X
Sodium hydroxide (50%; caustic soda) [Intermediate products]	Mass	1,529	kg	X
Sulphuric acid aq. (96%) [Intermediate products]	Mass	0,386	kg	X
Outputs				
Ammonia [Inorganic emissions to air]	Mass	0,000	kg	
Carbon dioxide [Inorganic emissions to air]	Mass	0,023	kg	
Copper cathode (>99.99 Cu) [Metals]	Mass	0,129	kg	X
Dust (PM10) [Particles to air]	Mass	0,037	kg	
Gold [Metals]	Mass	0,000	kg	X
Hydrocarbons, aromatic [Group NMVOC to	Mass	0,124	kg	

air]				
Hydrogen [Inorganic emissions to air]	Mass	0,002	kg	
Hydrogen cyanide (prussic acid) [Inorganic emissions to air]	Mass	0,000	kg	
Landfill of plastic waste [Consumer waste]	Mass	0,716	kg	*
Nitrogen (atmospheric nitrogen) [Inorganic emissions to air]	Mass	0,008	kg	
Nitrogen dioxide [Inorganic emissions to air]	Mass	0,014	kg	
Nitrogen dioxide [Inorganic emissions to air]	Mass	0,135	kg	
Nitrogen oxides [Inorganic emissions to air]	Mass	0,013	kg	
Oxygen [Inorganic emissions to air]	Mass	0,064	kg	
Pit steam [Other emissions to air]	Mass	0,068	kg	
Waste heat [Other emissions to air]	Energy (NCV)	1,581	MJ	
Water (waste water, untreated) [Flows]	Mass	4,151	kg	*

Table 5-7: Elementary flows of overall system

Flows	Hydro Process (kg)
Resources	3059,51
Deposited goods	9,73
Emissions to air	60,01
Emissions to fresh water	3081,64
Emissions to sea water	3,54
Emissions to agricultural soil	-1,58E-06
Emissions to industrial soil	1,74E-05
Total	**6214,43**

5.3.2 Life cycle impact assessment (LCIA)

The impacts caused by the overall process were calculated from the results generated in the LCI phase. These impacts were calculated at midpoint level using the CML methodology and are presented in Table 5-8. These midpoint categories are based on the relative contribution to the three main areas of protection (AoP): natural resources, human health and ecosystem quality. The relative

contributions of the foreground and background processes to the overall impacts are also pointed out in Table 5-8 and Figure 5-18.

Table 5-8: Total impacts associated with the overall process from cradle-to-gate

Impact Category	Unit	Score	Foreground Processes	Background Processes
Abiotic Depletion (ADP elements)	kg Sb eq.	1,3E-05	0,0%	100,0%
Abiotic Depletion (ADP fossil)	MJ	5,9E+01	0,1%	99,9%
Acidification Potential (AP)	kg SO_2 eq.	1,0E-01	79,9%	20,1%
Eutrophication Potential (EP)	kg Phosphate eq.	2,3E-02	91,4%	8,6%
Freshwater Aquatic Eco toxicity Pot.	kg DCB eq.	7,2E-03	0,0%	100,0%
Global Warming Potential (GWP 100 years)	kg CO_2 eq.	4,4E+00	0,6%	99,4%
Global Warming Potential (GWP 100 years), excl. biogenic carbon	kg CO_2 eq.	4,3E+00	0,6%	99,4%
Human Toxicity Potential (HTP inf.)	kg DCB* eq.	4,8E-01	46,8%	53,2%
Marine Aquatic Eco toxicity Pot. (MAETP inf.)	kg DCB eq.	2,9E+02	0,0%	100,0%
Ozone Layer Depletion Potential (ODP, steady state)	kg R11 eq.	1,9E-12	0,0%	100,0%
Photochem. Ozone Creation Potential (POCP)	kg Ethene eq.	5,7E-03	80,1%	19,9%
Terrestric Eco toxicity Potential (TETP inf.)	kg DCB eq.	5,8E-03	0,0%	100,0%

DCB is 1,4 dichlorobenzene

It is evident that the background processes contributes entirely to the overall impacts except for the AP, EP and POCP categories, which was mainly caused by the core processes. The background processes refers to the data sources that are needed to run and operate the core processes. As mentioned earlier the effect of downstream processes such as waste water treatment was not considered in this study. The relative contributions of the individual processing units to each of the considered impact categories are shown in Figure 5-19. The results highlight the roles of Elution,

HNO_3 wash and Copper leach as the major contributors to the overall impact. Their contribution respectively ranges from a minimum of 2.62% to 74.2%, .44% to 77.9% and 3.17% to 29.8% across the different impact categories. All the remaining processes excluding SX, HCl wash, Solder leach and Comminution contributes almost insignificantly to the overall impact.

5.3.3   Contribution of substances to the key categories

From Figure 5-19 it is evident that the production of electricity from hard coal, sodium hydroxide and nitric acid are the major contributors to the *Global Warming* impact category. Electricity accounts for 32.10% of all the contributions to the global warming whereas sodium hydroxide and nitric acid accounts for 23.5% and 20% respectively. The inorganic substances, carbon dioxide and methane from these processes are the main contributors to climate change, each with a share of 71.15% and 4.61% respectively.

Chlorodifluoromethane (R-22) is the dominant substance that contributes to the *Ozone layer depletion* impact category. This substance is traced back to the production of sodium hydroxide and electricity, each with a contribution of 57.81% and 20% respectively. The emission of hydrogen fluoride to air is the predominant substance that contributes to *Marine Aquatic toxicity*, which is mainly due to the production of electricity from coal and sodium hydroxide. The relative contribution of each process in this category is 50% and 32.26% respectively.

The use of crude oil, hard coal and natural gas as feedstock for the production of kerosene, electricity, hydrogen cyanide, sodium hydroxide, nitric acid and sulphuric acid significantly contributes to *Abiotic depletion (fossil)*. Each process contributes 10.4%, 23.3%, 16.6%, 19.38%, 10.8% and 7.39% to all of the contribution of this impact category. Sodium chloride (rock salt) is the major contributor to *Abiotic depletion (elements)*, with copper, gold, lead, molybdenum, sulphur and yttrium contributing to a lesser extent. The impact is mainly caused by the production of sodium hydroxide with a share of 90.61% of all the contributions to this category.

The foremost substance contributing to *Terrestrial Eco toxicity* is mercury. Nickel, selenium, tin, vanadium, zinc and beryllium are additional dominating substances in this category. The latter substances are due to electricity production and mercury is predominantly due to the production of hydrogen peroxide. Each process contributes respectively 29.7% and 51.8% to this impact category.

The emissions of nickel, copper, cadmium, vanadium, barium, phenol (hydroxyl benzene) and naphthalene to water mainly contributes to the impact category of *Freshwater Aquatic Eco toxicity*.

The production of kerosene, sulphuric acid sodium hydroxide and electricity each contribute 29.8%, 21.2%, 19.7% and 15.1% to the overall contribution of this category.

Figure 5-18: Relative impact percentages of unit processes
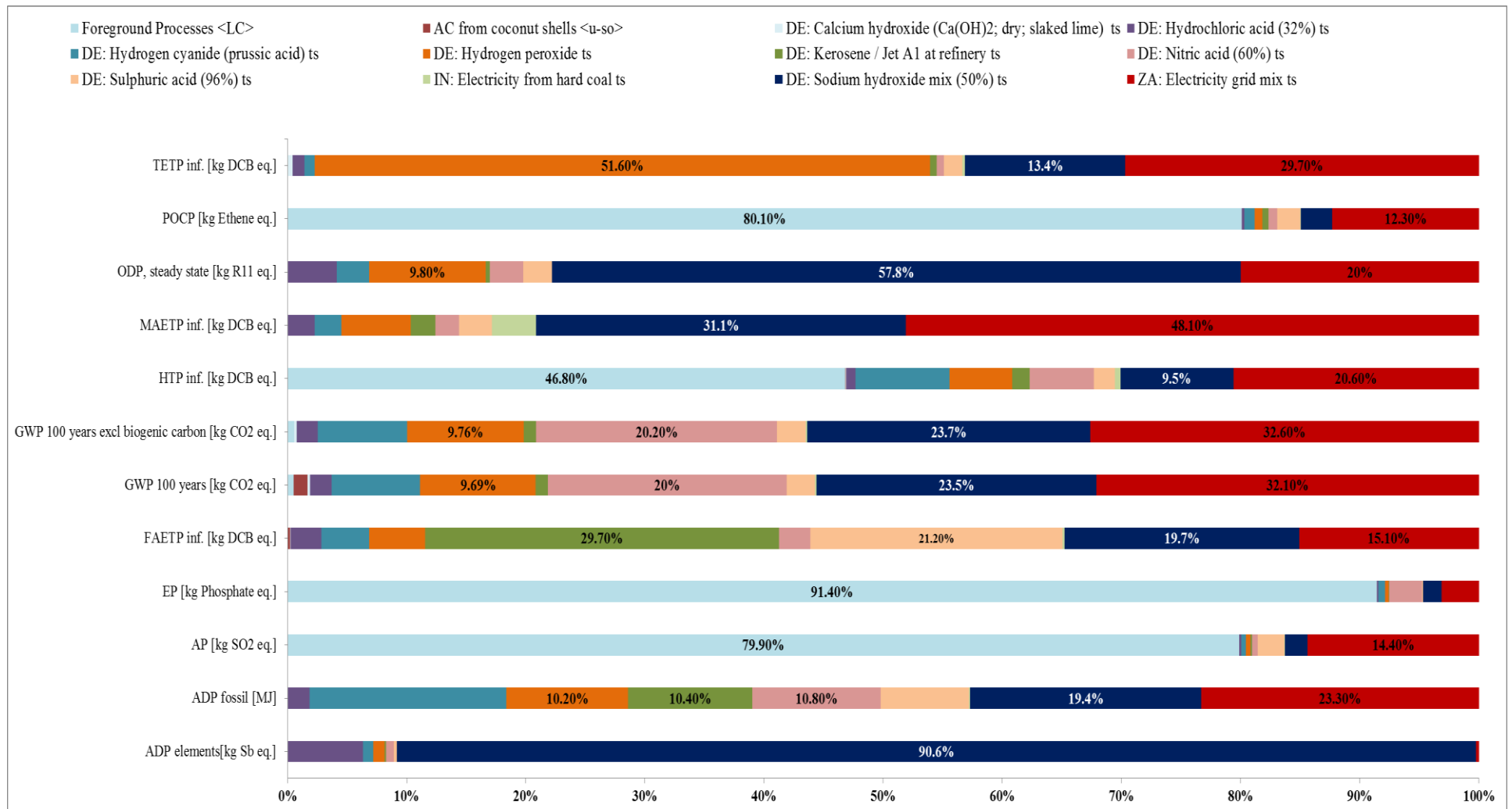
Figure 5-19: Relative impact percentages of Foreground and Background processes

The foreground system (hydrometallurgical process) contributes 80.1%, 80% and 91.4% respectively to the *Photochemical Ozone Creation*, *Acidification* and *Eutrophication* impact categories. The emission of NOx gasses (nitrogen dioxide and nitrogen oxide) are the predominant substances in all three categories with ammonia contributing to a lesser extent to the *Acidification* and *Eutrophication* impact categories. This observation is expected since no treatment of the off-gasses emitted from the nitric acid leaching and elution stages was considered; instead it is assumed all the gasses are emitted directly to the atmosphere. The production of electricity is the second major contributor to these impact categories. The emission of nitrogen oxides contributes to all three categories with sulphur dioxide to the first two categories.

The emissions of NOx and ammonia gasses as well as dust from shredding and milling stages, contributes collectively 47.1% of the overall contributions to *Human toxicity*. The remainder is caused by the production of electricity (20.7%), sodium hydroxide (9.52%) and hydrogen cyanide (7.93%). Major substances emitted from the latter processes include arsenic (+V), selenium, dioxins (unspecified), nickel and hydrogen fluoride.

5.3.4 Interpretation of base case results

It is evident from the scores presented that the production of sodium hydroxide followed by coal-based electricity generation is the dominant processes for all impact categories considered. Therefore, the reduction of these process inputs in the process units with the highest consumption thereof is desirable. As shown in Figure 5-18 and Figure 5-19 the process units with the highest electricity consumption are the carbon stripping and electrolysis processes. The pH adjustment of the copper- PLS prior to solvent extraction contributes 85.6% to the total sodium hydroxide consumption while the remainder is used for carbon stripping and sodium cyanide production. The role of nitric acid production from ammonia and the use thereof to the overall impact is also highlighted. The consumption of nitric acid produces NOx gasses which contribute largely to the *Human toxicity, Photochemical Ozone Creation*, *Acidification* and *Eutrophication* impact categories when released to the air. An abatement measure would be to recover the NOx gasses as nitric acid which in turn can be recycled back to the system.

Even though the LCA of waste printed circuit board has been extensively studied (Xue *et al.*, 2014; Iannicelli-zubiani *et al.*, 2017) the potential environmental impact of WPCB treatment via a hydrometallurgical route widely varies for example Xue *et al.*, (2014) investigated the environmental impacts for a recycling chain that includes waste liberation through metal refining.

Similar to the assumptions made in this study, gas emissions were emitted to the environment and the waste water were sent to a waste treatment facility. The leaching stages that use aqua-regia (hydrochloric acid and nitric acid mixture) as lixiviant were highlighted to engender the most significant impact across the impact categories considered. This was attributed to the production and consumption of hydrochloric acid and nitric acid mixture. Based on the study done by Iannicelli-zubiani *et al.*, (2017) the use of nitric acid for leaching was also emphasised as the foremost contributor to overall environmental impact. In addition to the effect of nitric acid usage, sodium hydroxide also had a significant impact on the environment. In the latter study, sodium hydroxide was used to neutralise the NOx gasses emanating from the nitric acid leach (Iannicelli-zubiani *et al.*, 2017). Without regard to the different operating conditions considered, process uncertainties, geographical variability and difference in overall environmental burdens between different studies similar findings were highlighted in this study.

5.3.5   Sensitivity analysis

A sensitivity analysis has been carried out to understand how the results are influenced by the variability in the process parameters and assumptions made. A consideration of previous work done Xue *et al.*, (2014) a similar approach for the sensitivity analysis was followed in study. Considering the key role of electricity consumption specifically in comminution, carbon stripping and electrolysis processes, a ± 10% electricity variation of the total base case requirement was investigated. The South African electricity mix considered in this study is based on the utilization of hard coal (it is assumed the core process will be located here). To investigate the impact of a different location, an alternative electricity mix that is located in the same region as the background processes (in this case Germany (DE)) was also investigated.

Similarly to electricity, the sodium hydroxide consumption has shown a significant contribution to the overall impact. Adjustment of the PLS pH prior to SX are the key contributor to sodium hydroxide consumption as mentioned earlier. Therefore, a **5%** increase in sodium hydroxide consumption in the copper leach was considered. Alternative to sodium hydroxide hydrated lime can also be used to adjust the pH of the copper-PLS, hence the use of hydrated lime on the overall impact was also considered. The required lime to adjust the pH to 1.8 was calculated from mass balances. The use of nitric acid is important for the removal of base metals that particularly hinders efficient copper and gold recovery. Therefore, a **5%** increase in nitric acid consumption was also investigated. Sulphuric acid and hydrogen peroxide consumption was also increased by **5%**. The

emissions from the core process that are directly affected by the usage of the aforementioned parameters are linearly adjusted. A summary of the different scenarios are given in Table 5-9.

Table 5-9: Scenario modelling for the hydrometallurgical process

Scenario	Description	Region
S1	Energy consumption was increased 10% relative to the base case value.	ZA
S2	Energy consumption was decreased 10% relative to the base case value.	ZA
S3	Sodium hydroxide consumption was increased by 5%.	DE
S4	Nitric acid consumption was increased by 5%.	DE
S5	Sulphuric acid consumption was increased by 5%.	DE
S6	Hydrogen peroxide consumption was increased by 5%.	DE
S7	Location of electricity mix production was changed with a similar voltage output.	DE
S8	PLS pH adjustment from copper leach was changed to calcium hydroxide.	DE

The comparison of scenarios 1, 2 & 7 to the base case are shown in Figure 5-20. Consideration of the results from S1 and S2, it is important to note that the comminution, electrolysis and carbon stripping processes are energy intensive compared to the other processes in the recycling chain. Therefore, when the required energy increased or decreased by 10% the consequential environmental impact changed accordingly. All impact category scores increased except for *Eutrophication* and *Abiotic depletion (elements)* for S1, whereas the scores decreased for all categories except *Abiotic depletion (elements)*. The impact category *Marine Aquatic toxicity* was mostly influenced by the perturbation, resulting in a 5% increase for S1 and 4.8% decrease for S2. From Figure 5-19 electricity consumption had the greatest impact in this category. For all the other impact categories the changes, both positive and negative were less than 3.5%. The impact of electricity production in a different country is also shown in Figure 5-20. Significant decreases, with a minimum of 3% to a maximum of 23% were observed for all impact categories except for *Abiotic depletion (elements)* and *Ozone layer depletion*. The difference of the raw material composition between the electricity mixes are shown in the Figure 5-21 and below. The data was obtained from the GaBi LCA program database.
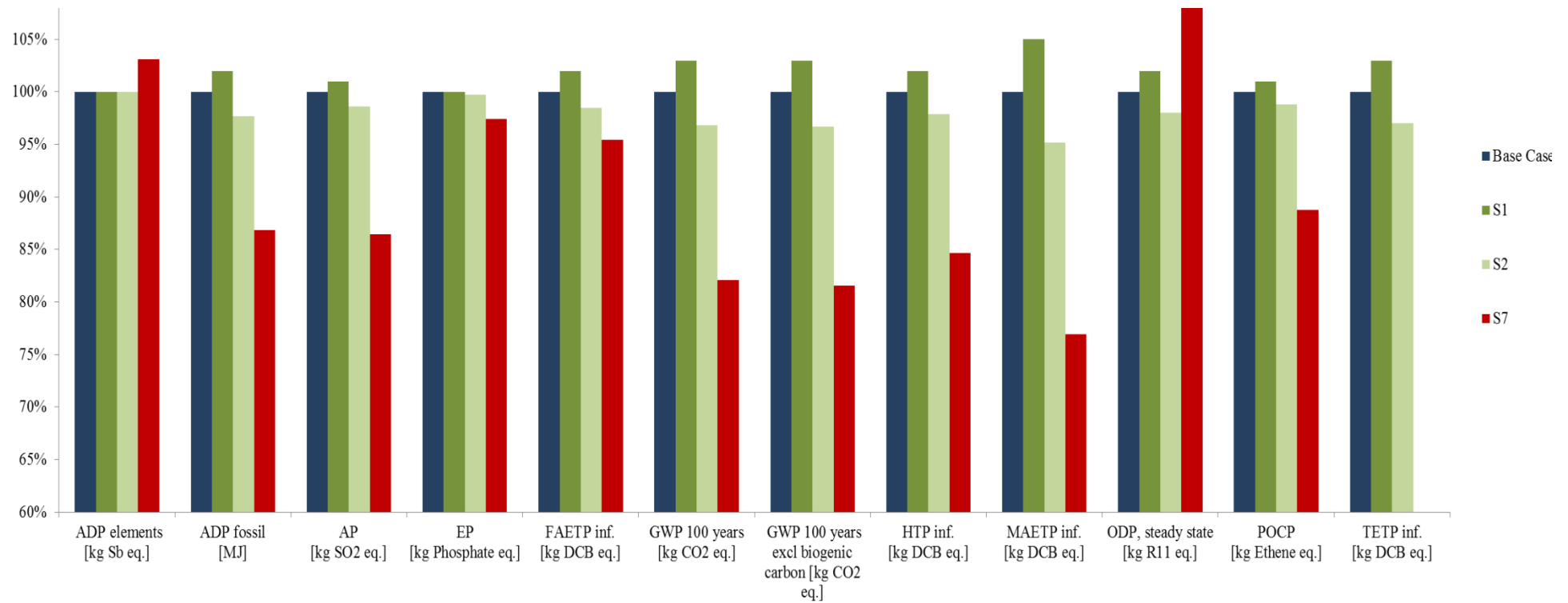
Figure 5-20: Comparison of the overall environmental impact for Scenarios 1, 2&7
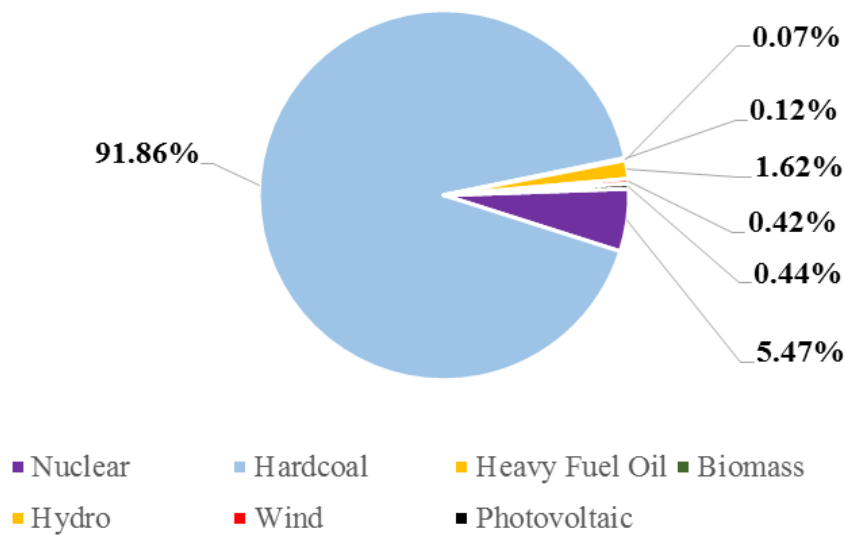
Figure 5-21: South African Electricity Grid Mix
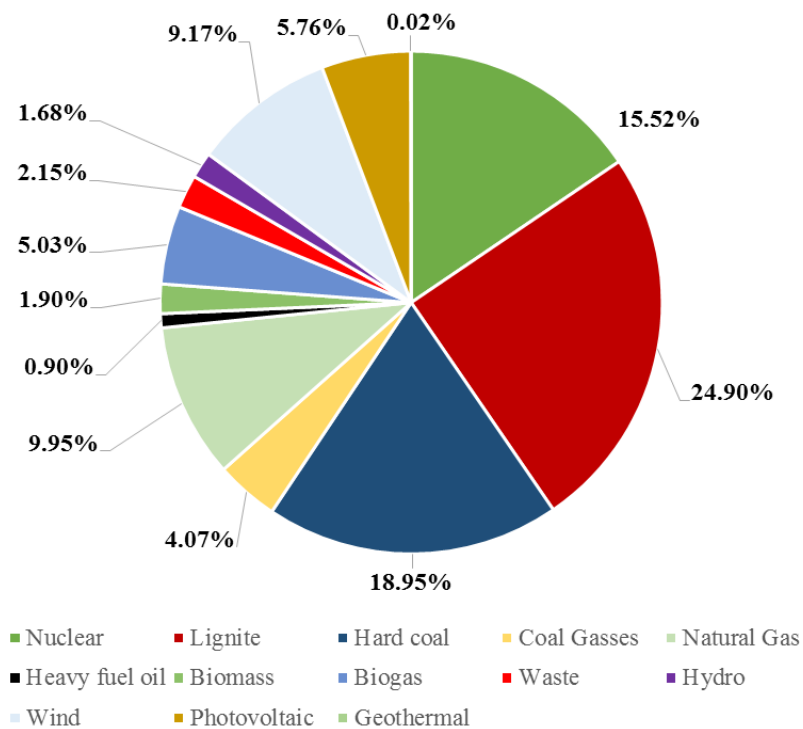
Figure 5-22: German Electricity Grid Mix

The figures show that the South African electricity is primarily produced with hard coal and the German grid is a mix between coal sources and cleaner energy. Hard coal is one of the best sources of carbon for electricity generation, because it has high carbon content when compared to the lignite used in the German grid. Lignite, brown coal, has relatively low carbon content with high volatiles

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and ash in its make-up. The main difference between the two grids is the overall make-up of the grids and the contribution of this to the environment. The locality of the process plant, and the electricity source, is thus important when considering the impact of the process plant. The contributions of the various sources are summarised in Table 5-10 and Table 5-11.

Table 5-10: South African Grid- Electricity Make-Up

Energy Carrier Specific Power Plant	Units	Heavy Fuel	Hard coal	Biomass
CO_2 emissions	(kg/TJ Fuel output)	77400	94454	99395
CO emissions	(kg/TJ Fuel output)	80	32,5	500
SO_2 emissions	(kg/TJ Fuel output)	1739,7	753,1	122
NO_x emissions	(kg/TJ Fuel output)	250	397,9	170
Share of electricity from CHP plant (%)	%	0	0	0
Efficiency of Electricity Plant	%	35,2	31,4	25
Overall efficiency of CHP plant	%	-	-	-
Share of electricity of thermal efficiency within CHP Plant	%	-	-	-
Grid losses related to < 1kV electricity Supply	%	9	9	9
Grid losses related to 1-60kV electricity Supply	%	2,9	2,9	2,9
Thermal Efficiency of heat plant	%	100	100	100
Thermal Efficiency of heat plant	%	85;90;95	85;90;95	85;90;95

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Table 5-11: German- Electricity Make-Up

Energy Carrier Specific Power Plant	Units	Natural Gas	Coal gasses	Biogas	Heavy oil	Hard coal
CO2 emissions	(kg/TJ Fuel output)	5600	225000	101137	80	94454
CO emissions	(kg/TJ Fuel output)	17.2	30.4	150	1739.7	32.5
SO2 emissions	(kg/TJ Fuel output)	0.4	0	75.6	250	753.1
NOx emissions	(kg/TJ Fuel output)	38.4	212.4	100	0	397.9
Share of electricity from CHP plant (%)	%	83.6	8	72.2	35.2	0
Efficiency of Electricity Plant	%	50.8	40.7	37.6	38	31.4
Overall efficiency of CHP plant	%	71.1	56.6	58.8	57.5	79.8
Share of electricity of thermal efficiency within CHP Plant	%	61.6	95.9	94.9	91.3	33.6
Grid losses related to < 1kV electricity Supply	%	4.4	4.4	4.4	4.4	4.4
Grid losses related to 1-60kV electricity Supply	%	1.4	1.4	1.4	1.4	1.4
Thermal Efficiency of heat plant	%	100	100	100	100	100
Thermal Efficiency of heat plant	%	85;90;95	85;90;95	85;90;95	85;90;95	85;90;95

The sensitivity of the different lixiviants used is shown in Figure 5-23. An increase in sulphuric acid consumption (scenario 5) showed similar overall impact as the base case except for the impact category *Freshwater Aquatic Eco toxicity* which increased by 1%. This suggests that sulphuric acid consumption is not the primary source of environmental impact. For scenario 6, an increase in hydrogen peroxide consumption resulted in a 1% and 3% increase in the *Abiotic depletion (fossil)* and *Terrestric Eco toxicity* impact categories respectively. Increased sodium hydroxide consumption in the copper leach (scenario 3) resulted in a 1% increase in both the *Abiotic depletion (elements)* and *Ozone layer depletion* impact categories. From Figure 5-19 sodium hydroxide has the greatest contribution to the aforementioned impact categories. An increase in nitric acid consumption (scenario 4) resulted in a 5% increase in *Eutrophication* impact score and a 4% increase in the *Photochemical Ozone Creation* and *Acidification* impact values. The total *Human toxicity* impact score increased by 2%. The increased contribution to the aforementioned impact categories is a result of the core process which releases NOx gasses to the atmosphere as pointed out in section 5.3.3. The 1% increase in *Abiotic depletion (fossil)* and *Global Warming* impact scores are due to the production of nitric acid from ammonia. This suggests that the emission of NOx gasses to the atmosphere has a greater impact on the environment than the production of nitric acid from ammonia. Therefore, investigating the effect of nitric acid production from NOx gasses on the environment may be of value.
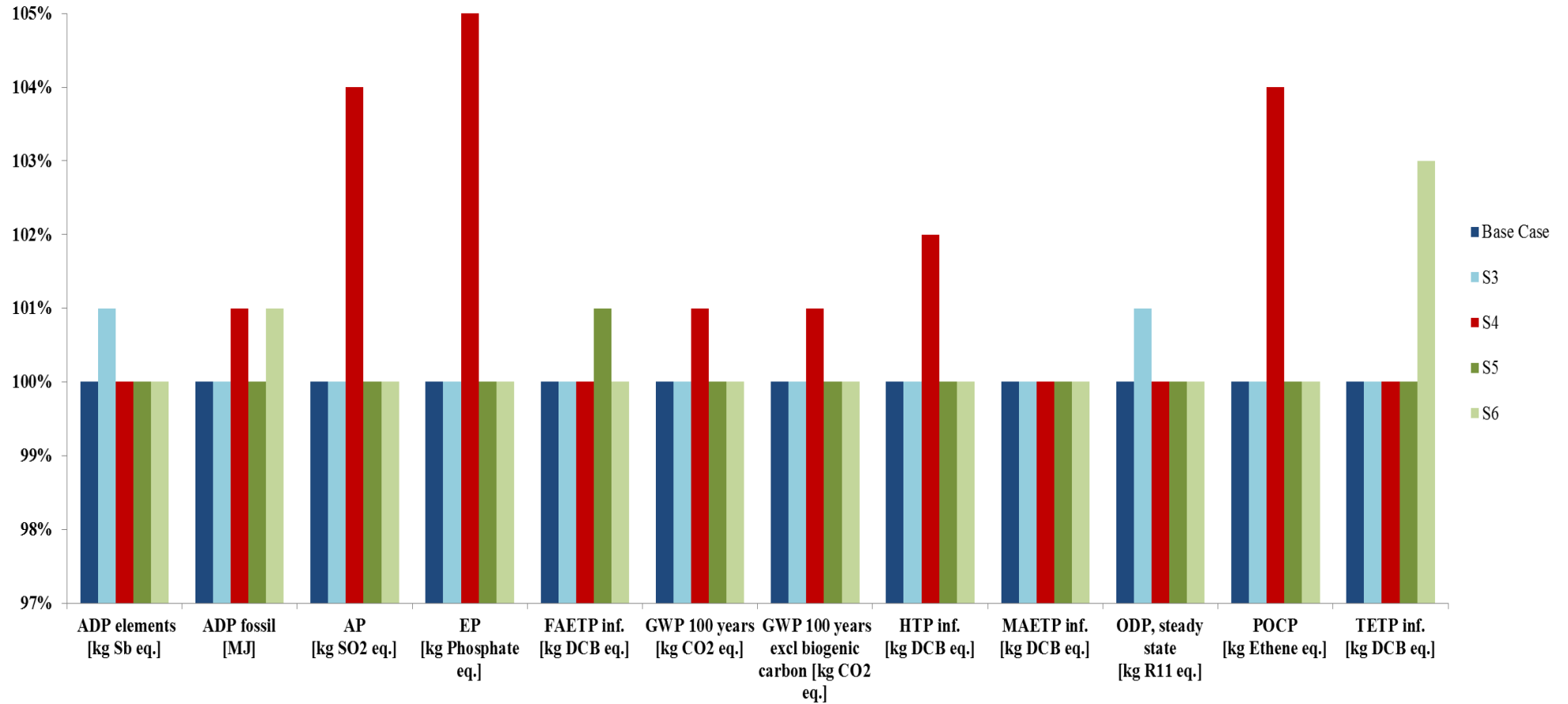
Figure 5-23: Comparison of the overall environmental impact for Scenarios 3-6

As previously discussed the contribution of sodium hydroxide to the overall environmental impact is primarily caused by the use thereof in the copper leach. The environmental impact of using calcium hydroxide compared to the base case is shown in Figure 5-24. All of the impact categories except for *Terrestric Eco toxicity* decreased by a minimum of 0.43% to a maximum of 17.2%. This suggests that the production of calcium hydroxide is more environmentally benign than sodium hydroxide. The increase of the *Terrestric Eco toxicity* impact value by 3.46% is due to the release of mercury to the air. Hydrogen production still remains the major contributor to the total impact of the latter impact category. Figure 5-25 and Figure 5-26 present the contribution of how the respective contribution of sodium hydroxide consumption and calcium hydroxide consumption to the overall impact changes for the base case and scenario 8. The impacts of the other background as well as the core process are blanked out to in order to emphasise the contribution of the aforementioned processes. Regardless of the decrease in overall impact (Figure 5-24) that is notice for substituting the bulk of sodium hydroxide that is consumed in the copper leach, the impacts caused by sodium hydroxide consumption in the elution stage still remains pronounced. This suggests that sodium hydroxide production should be avoided at all cost when possible in order to reduce the overall environmental footprint of the process. Sodium production is traditionally produced with the Castner-Kellner process. This process is highly energy intensive process and utilises an electrolytic cell to produce the final product. A brine solution (NaCl) is fed into the cell and the sodium hydroxide is formed with chlorine gas and hydrogen peroxide as by products. These products are harmful to the environment and the production of caustic is thus always balanced with the potential off-take of a chlorine based product. Calcium hydroxide is a naturally occurring product and is mined from shallow surface deposit throughout South Africa. This combined with the lower energy input required to produce the product makes hydrated lime a more environmentally sustainable solution for the neutralization process steps. Current examples of this in a South African context include Sasol and NCP who produces sodium hydroxide via this process.
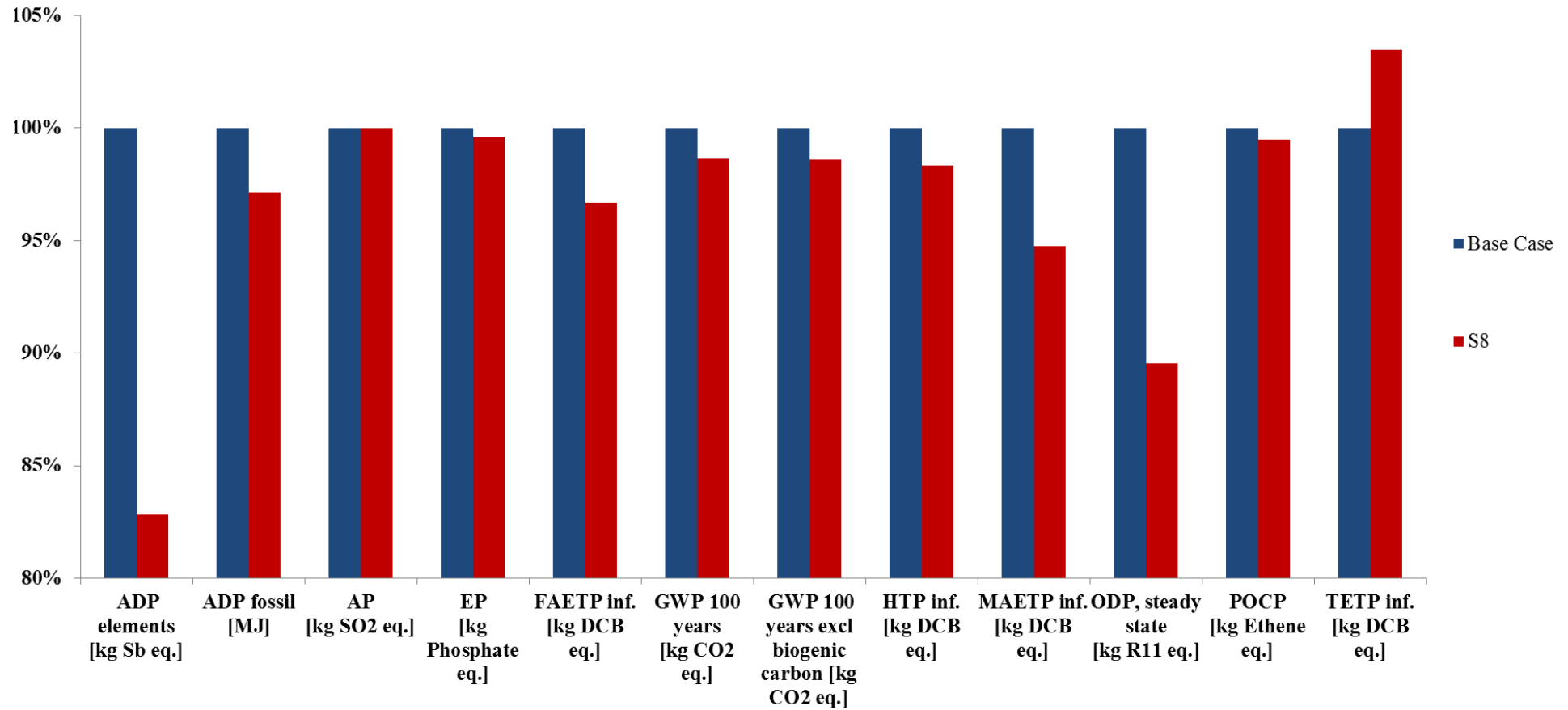
Figure 5-24: Comparison of the overall environmental impact for Scenarios 8
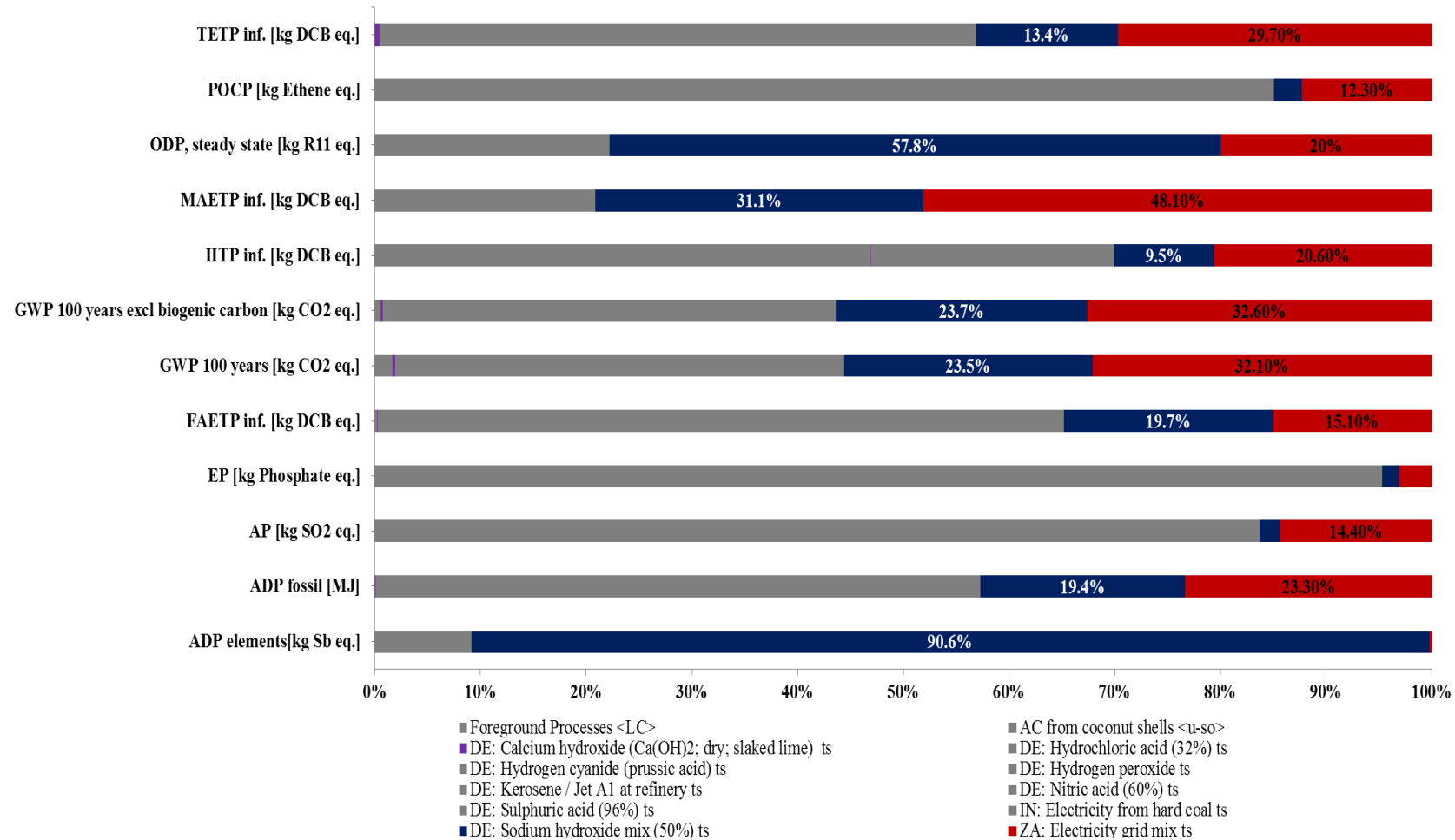
Figure 5-25: Relative contributions of sodium hydroxide and calcium hydroxide to the overall environmental impact for Base case
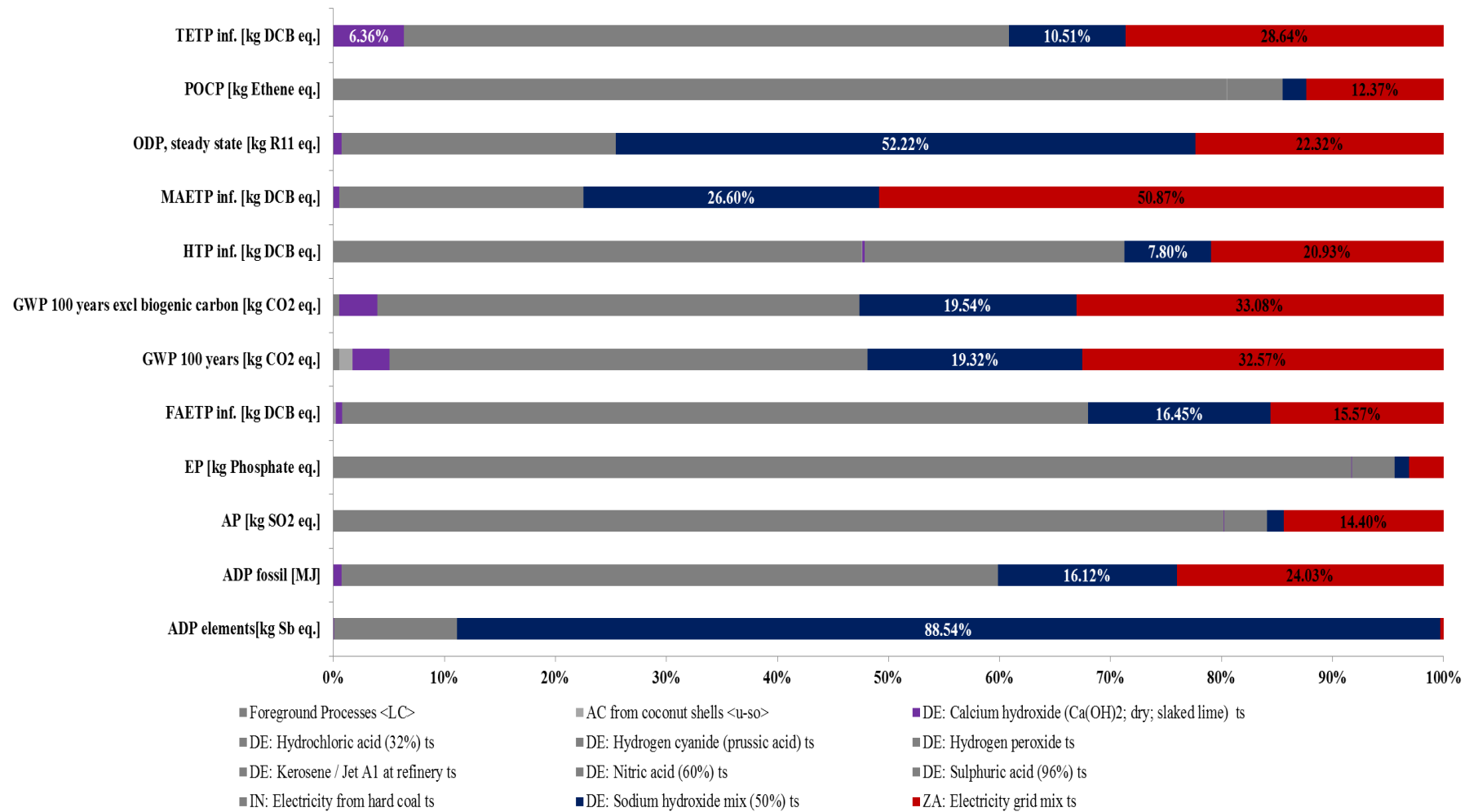
Figure 5-26: Relative contributions of sodium hydroxide and calcium hydroxide to the overall environmental impact for Scenario 8

5.3.6   Improvement potential and future decision making support

As analysed above, sodium hydroxide consumption and electricity production had the decisive effect on the overall impact. The first strategy should be to use alternative neutralizing agents for pH adjustment, but this will depend on the availability and effectiveness of these substances. It has been reported that when lime used, excess calcium compounds can coat the pH sensors. Maintaining the pH at optimum value ensures selective separation in copper SX and preventing the conversion of sodium cyanide to hydrogen cyanide gas during cyanidation which is also harmful to the environment. Secondly, nitric acid consumption produces from ammonia in the solder leach and acid wash prior to cyanidation can be reduced by recovering the NOx gasses as nitric acid. Alternatively physical separation processes such as magnetic separation, eddy current etc. can be used to remove most of the base metals that are targeted by using nitric acid. The environmental impacts caused by the waste streams i.e. the waste water, off-gas treatment and the non-metals that are separated from metals during the different leaching steps are not considered. Collection and disassembly of waste printed circuit boards as well as the impact of transportation are also not considered. Heat integration technology can be applied at various points within the process plant. The energy consumption of the process units that are being operated at elevated temperatures can be reduced by recovering heat from hot waste/emission streams. This will reduce the environmental impact of the hot waste streams on the environment, and will also reduce the impact of the foreground process impacts.

6. CONCLUSION AND RECOMMENDATIONS

The conclusions and recommendation in this section are discussed in terms of the study objectives described in section 1.4.

This study developed a hydrometallurgical process plant with overall yields for copper and gold of 81% and 97% respectively. This was done by combining traditional metallurgical processes at conditions suitable for PCB processing. The analytical tools applied to the developed process yielded results from which quantified the environmental impact and resource intensity of the developed process.

There is scope for more work to be done on the subject of WPCB recycling as well as LCA and exergy analysis. The work done in this study is not a full bodied representation but rather a platform for further work. However, based on the findings of the LCA and exergy analysis the following conclusions can be drawn:

6.1   Overall Conclusions

- **Potential environmental impact associated with a hydrometallurgical process**

The LCA revealed that the gold elution, nitric acid washing stage and copper leach are the major contributors to the overall environmental impact. Their contribution respectively ranges from a minimum of 2.62% to 74.2%, 0.44% to 77.9% and 3.17% to 29.8% across the different impact categories. The main causes of impact are due to the use of sodium hydroxide and coal-based electricity. Therefore, the reduction of these process inputs within the plant will reduce the overall environmental burden. The latter was confirmed by replacing sodium hydroxide with hydrated lime in the copper leach and reducing the electricity and sodium hydroxide requirement. Both LCA and exergy analysis highlighted the roles of gold elution and copper leach as the foremost contributors to the overall process inefficiencies. Also, the total electric energy consumption can be reduced by recovering the thermal energy from waste streams or replacing the coal-based electrical energy with a cleaner source of energy.

- **Resource intensity associated with a process**

The exergy analysis showed that the copper and gold recovery processes are the most inefficient processes in the overall process chain. This was established by determining the exergy destruction of each process unit as well as its relative contribution to the overall exergy destruction. Copper and gold recovery processes contributed 39% and 37% respectively to the overall exergy destruction.

Unit process analysis showed that the copper leaching process and the gold elution process are the most inefficient process units within these two sections. Therefore, optimisation of these unit processes should be prioritised. The overall exergetic efficiency of the process was determined to be 0.85%. This was attributed to the fact that the desirable products, copper and gold, is recovered in relatively small quantities when compared to the overall process exergetic flow input needed to produce high quality products. The designed process is also relatively complicated in terms of the multi-step process technologies used and the large number of reactions required producing the desirable products. This increases the process irreversibility and thus reduces the exergetic efficiency. Analysis showed that various techniques can be employed to improve the exergetic efficiency. This can be done by recovering valuable products from the waste streams and re-integrating it into the process (i.e. recovering lost physical exergetic streams for heating purposes) or selling it as new desirable products. The suggestions for improvement may increase the exergetic efficiency but it can only be justified by performing an economic analysis.

6.2   Recommendations

- **Process optimization**

The study showed that exergy analysis and LCA tools can be used to quantify the resource intensity and the environmental impact of a given process quantitatively. The techniques are able to identify the hot spots in terms of resource intensity and environmental impact within the process hence enabling the assessment of the environmental sustainability of a process. However, these analytical tools only highlight the potential environmental impacts and pinpoint the process units with the greatest irreversibilities. Based on these findings suggestions can be made for possible improvement but clear steps of how to optimise the process are not derivable from these tools.

Goßling-Reisemann (2008) stated that the environmental profile of a process may be improved by reducing the losses caused by process irreversibilities (section 2.9.3). Considering that a conventional exergy analysis only pinpoints components with highest irreversibilities an advance exergy analysis can be performed which provides insights into the effect of the interconnectivity of process components on the process efficiency. Possible suggestions for improvement deduced from a conventional analysis may affect the thermodynamic performance of other system components and therefore the overall thermodynamic performance. Only by understanding the mutual interdependencies among system components will enable a realistic assessment of the potential for improvement. This assessment becomes possible in an advanced exergetic analysis, in which the

system component exergy destruction is split into exogenous, endogenous, avoidable and unavoidable exergy destruction parts. With the information received from an advanced exergy analysis an economic analysis will also be required to justify the findings.

- **Process comparison and selection for sustainability**

Recognising that the technological aspects of different recycling options have been investigated in detail in literature, an exergy analysis and LCA of different the process options can be compared to assist the selection of the best recycling routes for future studies. Processes that employ techniques from pyrometallurgy and biometallurgy may be of particular interest for comparison.

- **Empirical data and scalability**

The mass and energy balances were mainly constructed from experimental data for WPCBs or literature data that were based on copper and gold ores. Therefore, the results presented in this study are not a true representation of a full scale plant for e-waste recycling. The findings can be validated by future experimental work especially for gold recovery from cyanide.

- **Exergy analysis and LCA**

Exergy at a specified state is a function of both the conditions of the environment as well as the system's properties. It may be of interest to understand how the process irreversibility change in response to a change of environmental temperature i.e. the role of seasonal changes is considered. To improve the findings of the LCA, the impacts caused by the collection and dismantling stages as well as transport and waste treatment should be considered. Appendix D provides a brief discussion of the relevant legislation, type of waste produce by the process considered as well suggest possible process technologies that can be employed to treat these waste streams.

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APPENDIX A- *MATERIAL STREAMS, AND THEIR SIMULATION AND EXERGY RESULTS*

Table A-0-1: Base Case - Exergy Analysis Results

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
1	PCBs	4578.75	25	1	5372.11
2	PCBs-shredded	4578.75	25	1	
3	PCBs- dust	169.41	25	1	312.43
4	Crushed PCBs	4409.34	25	1	5061.85
W1	Electricity		25	1	40.00
W2	Electricity		25	1	120.00
Q1	Heat loss		25	1	0.00
Q2	Heat loss		25	1	0.00
4	Crushed PCBs	4409.34	25	1	5061.85
5	HNO3(aq)	7932.04	25	1	28.84
6	NOx(g)	125.73	25	1	15.26
7	Solder PLS	12215.65	25	1	5008.51
8	Fe,Pb-Nitrate Solution	8037.31	25	1	20.18
11	Solder residue	4178.34	25	1	4988.33
W3	Electricity		25	1	11.58
Q3	Heat loss		25	1	0.00
9	Cooling water	8673.64	25	1	27.42
10	Cooling water	8673.64	60	1	31.62
11	Solder residue	4178.34	25	1	4988.33
12	H2SO4-96wt%	1765.21	25	1	113.54
13	H2O2-30wt%	2503.99	25	1	135.68
21	Raff- recycle-57%	7710.30	25	1	66.62
14	Cu PLS	16157.83	25	1	5034.13
W4	Electricity		25	1	14.35
Q4	Heat loss		25	1	0.00
32	Cooling water	32104.36	25	1	101.51
33	Cooling water	32104.36	60	1	117.05
14	Cu PLS	16157.83	25	1	5034.13
15	NaOH-50%	1439.33	25	1	37.85
16	O2(g)	136.87	25	1	1.02
17	Cu PLS-pH adjusted	17460.30	25	1	4933.16
18	Cu residue	3361.79	25	1	4836.19
Q5	Heat loss		25	1	0.00
19	Cu PLS to SX	14098.51	25	1	96.97
20	Raffinate	13526.84	25	1	116.87

21	Raff- recycle-57%	7710.30	25	1	66.62
22	Raffinate- bleed waste-43%	5816.54	25	1	50.25
23	Advanced Electrolyte	47704.32	25	1	569.77
24	Spent Electrolyte	47132.65	25	1	596.04
25	Kerosene-makeup	569.22	25	1	1478.83
26	Hydrocarbons	569.22	25	1	1482.35
W5	Electricity		25	1	0.70
Q5	Heat loss		25	1	0.00
23	Advanced Electrolyte	47704.32	25	1	569.77
24-	Spent Electrolyte	46966.21	25	1	595.75
27	Advanced Electrolyte	47704.33	45	1	572.10
28	Spent Electrolyte	46966.22	45	1	597.51
W6	Electricity		45	1	3.93
27	Advanced Electrolyte	47704.33	45	1	572.10
28	Spent Electrolyte	46966.22	45	1	597.51
29	O2(g)	148.46	45	1	1.11
30	Cu-Cathode	589.65	45	1	74.65
W7	Electricity		45	1	253.49
Q7	Heat loss		45	1	0.83
34	Cooling water	13431.18	25	1	42.47
35	Cooling water	13431.18	60	1	48.97
24-	Spent Electrolyte	46966.21	25	1	595.75
24	Spent Electrolyte	47133.38	25	1	596.04
31	H2O-makeup	167.17	25	1	0.53
18	Cu residue	3361.79	25	1	4836.19
36	HNO3-60%	2570.15	25	1	7.11
37	H2O-dilution	233.65	25	1	0.74
38	NO2(g)	620.39	25	1	45.35
39	Nitrate salts+ solids	5545.20	25	1	4673.51
42	Nitrate salts	2290.92	25	1	-1.55
43	Washed residue	3254.28	25	1	4675.06
W8	Electricity		25	1	4.72
Q8	Heat loss		25	1	0.00
40	Cooling water	13191.21	25	1	41.71
41	Cooling water	13191.21	60	1	48.09
43	Washed residue	3254.28	25	1	4675.06
44	NaCN(aq)-30%-makeup	0.96	25	1	0.24
45	Ca(OH)2(s)	46.17	25	1	2.68
46	H2O-makeup	126.86	25	1	0.40
47	Au-slurry	6278.54	25	1	4687.29
54	CN recycle-95%	2850.27	25	1	9.07
Q9	Heat loss		25	1	0.00
47	Au-slurry	6278.54	25	1	4687.29

48	Compressed air	45.00	25	1	0.00
49	N2(g),O2(g)	44.98	25	1	0.01
50	Au PLS	6278.56	25	1	4687.27
51	Au-residue	3277.50	25	1	4677.52
52	Au-complex	3001.06	25	1	9.75
W9	Electricity		25	1	51.72
Q10	Heat loss		25	1	0.00
86	Cooling water	5242.13	25	1	16.57
87	Cooling water	5242.13	60	1	19.11
53	Barren solution	3000.29			9.54
54	CN recycle-95%	2850.27	25	1	9.07
55	CN bleed-5%	150.01	25	1	0.48
52	Au-complex	3001.06	25	1	9.75
56	Carbon makeup	35.84	25	1	59.76
57	Loaded Carbon	598.18	25	1	996.27
79	Recycled Carbon-cooled	561.56	25	1	936.31
W15	Electricity		25	1	5.80
Q11	Heat loss		25	1	0.00
58	HCl-3wt%	9053.56	25	1	46.57
59	HCl-3wt%	9053.56	90	1	60.55
W10	Electricity		25	1	148.50
61	Acid wash rinse water	1914.03	25	1	6.05
62	Acid wash rinse water	1914.03	110	2	11.05
W11	Electricity		25	1	41.42
57	Loaded Carbon	598.18	25	1	996.27
59	HCl-3wt%	9053.56	90	1	60.55
60	HCN(g)	0.08	89	1	0.12
62	Acid wash rinse water	1914.03	110	2	11.05
63	HCl solution discharge	9053.61	88.92	1	60.10
64	Wash water discharge	1914.03	108	1	10.86
65	Acid washed Carbon	598.05	110	2	996.67
66	NaCN/NaOH soak soln	6035.70	25	1	168.43
67	NaCN/NaOH soak soln	6035.70	110	2	183.22
W12	Electricity		25	1	124.15
68	Eluant	6035.70	25	1	19.08
69	Eluant	6035.70	110	2	34.84
W13	Electricity		25	1	130.62
65	Acid washed Carbon	598.05	110	2	996.67
67	NaCN/NaOH soak soln	6035.70	110	2	183.22
69	Eluant	6035.70	110	2	34.84
70	Final rinse water	6035.70	25	1	19.08
71	Pregnant Eluate	6036.48	110	2	35.04
72	Cooling rinse water	6035.69	26	1	19.09

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73	Pre-soak solution-discharge	6035.55	110	2	183.08
74	NH3(g)	0.04	110	2	0.02
76	H2O	398.27	25	1	1.26
77	Steam	398.27	600	1	25.39
W14	Electricity		25	1	87.04
75	Stripped Carbon	597.40	26	1	996.07
77	Steam	398.27	600	1	25.39
78	Recycled Carbon	561.56	136	1	937.11
79	Recycled Carbon-cooled	561.56	25	1	936.31
80	Combustion gases	426.99	136	1	79.29
Q12	Heat loss		25	1	0.00
Q13	Heat loss		136	1	0.61
71	Pregnant Eluate	6036.48	110	2	35.04
72	Cooling rinse water	6035.69	26	1	19.30
81	NaOH-50%	9.66	25	1	0.21
82	pH-adj Solution	12081.84	50	1	41.51
Q14	Heat loss		50	1	4.32
82	pH-adj Solution	12081.84	50	1	41.51
83	O2(g)/H2(g)	0.05	50	1	0.02
84	Au cathode	0.56	50	1	0.01
85	Barren gold solution	12081.22	50	1	41.51
W16	Electricity		50	1	2.23
Q15	Heat loss		50	1	0.02
88	Cooling water	245.76	25	1	0.78
89	Cooling water	245.76	60	1	0.90

Table A-0-2:10% Electricity Increase- Exergy Analysis Results

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
1	PCBs	4578,75	25	1	5372,11
2	PCBs-shredded	4578,75	25	1	
3	PCBs- dust	169,41	25	1	312,43
4	Crushed PCBs	4409,34	25	1	5061,85
W1	Electricity		25	1	44,00
W2	Electricity		25	1	132,00
Q1	Heat loss		25	1	0,00
Q2	Heat loss		25	1	0,00
4	Crushed PCBs	4409,34	25	1	5061,85
5	HNO3(aq)	7932,04	25	1	28,84
6	NOx(g)	125,73	25	1	15,26
7	Solder PLS	12215,65	25	1	5008,51
8	Fe,Pb-Nitrate Solution	8037,31	25	1	20,18
11	Solder residue	4178,34	25	1	4988,33
W3	Electricity		25	1	12,74
Q3	Heat loss		25	1	0,00
9	Cooling water	8790,98	25	1	27,80
10	Cooling water	8790,98	60	1	32,05
11	Solder residue	4178,34	25	1	4988,33
12	H2SO4-96wt%	1765,21	25	1	113,54
13	H2O2-30wt%	2503,99	25	1	135,68
21	Raff- recycle-57%	7710,30	25	1	66,62
14	Cu PLS	16157,83	25	1	5034,13
W4	Electricity		25	1	15,78
Q4	Heat loss		25	1	0,00
32	Cooling water	32249,71	25	1	101,97
33	Cooling water	32249,71	60	1	117,58
14	Cu PLS	16157,83	25	1	5034,13
15	NaOH-50%	1439,33	25	1	37,85
16	O2(g)	136,87	25	1	1,02
17	Cu PLS-pH adjusted	17460,30	25	1	4933,16
18	Cu residue	3361,79	25	1	4836,19
Q5	Heat loss		25	1	0,00
19	Cu PLS to SX	14098,51	25	1	96,97
20	Raffinate	13526,84	25	1	116,87
21	Raff- recycle-57%	7710,30	25	1	66,62
22	Raffinate- bleed waste-43%	5816,54	25	1	50,25
23	Advanced Electrolyte	47704,32	25	1	569,77
24	Spent Electrolyte	47132,65	25	1	596,04
25	Kerosene-makeup	569,22	25	1	1478,83
26	Hydrocarbons	569,22	25	1	1482,35
W5	Electricity		25	1	0,77
Q5	Heat loss		25	1	0,00
23	Advanced Electrolyte	47704,32	25	1	569,77
24-	Spent Electrolyte	46966,21	25	1	595,75

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
27	Advanced Electrolyte	47704,33	45	1	572,10
28	Spent Electrolyte	46966,22	45	1	597,51
W6	Electricity		45	1	3,93
27	Advanced Electrolyte	47704,33	45	1	572,10
28	Spent Electrolyte	46966,22	45	1	597,51
29	O2(g)	148,46	45	1	1,11
30	Cu-Cathode	589,65	45	1	74,65
W7	Electricity		45	1	278,84
Q7	Heat loss		45	1	0,99
24-	Spent Electrolyte	46966,21	25	1	595,75
24	Spent Electrolyte	47133,38	25	1	596,04
31	H2O-makeup	167,17	25	1	0,53
18	Cu residue	3361,79	25	1	4836,19
36	HNO3-60%	2570,15	25	1	7,11
37	H2O-dilution	233,65	25	1	0,74
38	NO2(g)	620,39	25	1	45,35
39	Nitrate salts+ solids	5545,20	25	1	4673,51
42	Nitrate salts	2290,92	25	1	-1,55
43	Washed residue	3254,28	25	1	4675,06
W8	Electricity		25	1	4,72
Q8	Heat loss		25	1	0,00
40	Cooling water	13191,21	25	1	41,71
41	Cooling water	13191,21	60	1	48,09
43	Washed residue	3254,28	25	1	4675,06
44	NaCN(aq)-30%-makeup	0,96	25	1	0,24
45	Ca(OH)2(s)	46,17	25	1	2,68
46	H2O-makeup	126,86	25	1	0,40
47	Au-slurry	6278,54	25	1	4687,29
54	CN recycle-95%	2850,27	25	1	9,07
Q9	Heat loss		25	1	0,00
47	Au-slurry	6278,54	25	1	4687,29
48	Compressed air	45,00	25	1	0,00
49	N2(g),O2(g)	44,98	25	1	0,01
50	Au PLS	6278,56	25	1	4687,27
51	Au-residue	3277,50	25	1	4677,52
52	Au-complex	3001,06	25	1	9,75
W9	Electricity		25	1	51,72
Q10	Heat loss		25	1	0,00
86	Cooling water	5242,13	25	1	16,57
87	Cooling water	5242,13	60	1	19,11
53	Barren solution	3000,29			9,54
54	CN recycle-95%	2850,27	25	1	9,07
55	CN bleed-5%	150,01	25	1	0,48
52	Au-complex	3001,06	25	1	9,75
56	Carbon makeup	35,84	25	1	59,76
57	Loaded Carbon	598,18	25	1	996,27
79	Recycled Carbon-cooled	561,56	25	1	936,31

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
W15	Electricity		25	1	5,80
Q11	Heat loss		25	1	0,00
58	HCl-3wt%	9053,56	25	1	46,57
59	HCl-3wt%	9053,56	90	1	60,55
W10	Electricity		25	1	148,50
61	Acid wash rinse water	1914,03	25	1	6,05
62	Acid wash rinse water	1914,03	110	2	11,05
W11	Electricity		25	1	41,42
57	Loaded Carbon	598,18	25	1	996,27
59	HCl-3wt%	9053,56	90	1	60,55
60	HCN(g)	0,08	89	1	0,12
62	Acid wash rinse water	1914,03	110	2	11,05
63	HCl solution discharge	9053,61	88,92	1	60,10
64	Wash water discharge	1914,03	108	1	10,86
65	Acid washed Carbon	598,05	110	2	996,67
66	NaCN/NaOH soak soln	6035,70	25	1	168,43
67	NaCN/NaOH soak soln	6035,70	110	2	183,22
W12	Electricity		25	1	124,15
68	Eluant	6035,70	25	1	19,08
69	Eluant	6035,70	110	2	34,84
W13	Electricity		25	1	130,62
65	Acid washed Carbon	598,05	110	2	996,67
67	NaCN/NaOH soak soln	6035,70	110	2	183,22
69	Eluant	6035,70	110	2	34,84
70	Final rinse water	6035,70	25	1	19,08
71	Pregnant Eluate	6036,48	110	2	35,04
72	Cooling rinse water	6035,69	26	1	19,30
73	Pre-soak solution-discharge	6035,55	110	2	183,08
74	NH3(g)	0,04	110	2	0,02
76	H2O	398,27	25	1	1,26
77	Steam	398,27	600	1	25,39
W14	Electricity		25	1	87,04
75	Stripped Carbon	597,40	26	1	996,07
77	Steam	398,27	600	1	25,39
78	Recycled Carbon	561,56	136	1	937,11
79	Recycled Carbon-cooled	561,56	25	1	936,31
80	Combustion gases	426,99	136	1	79,29
Q12	Heat loss		25	1	0,00
Q13	Heat loss		136	1	0,61
71	Pregnant Eluate	6036,48	110	2	35,04
72	Cooling rinse water	6035,69	26	1	19,30
81	NaOH-50%	9,66	25	1	0,21
82	pH-adj Solution	12081,84	50	1	41,51
Q14	Heat loss		50	1	4,32
82	pH-adj Solution	12081,84	50	1	41,51
83	O2(g)/H2(g)	0,05	50	1	0,02
84	Au cathode	0,56	50	1	0,01

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
85	Barren gold solution	12081,22	50	1	41,51
W16	Electricity		50	1	2,23
Q10	Heat loss		50	1	0,40
88	Cooling water	245,76	25	1	0,78
89	Cooling water	245,76	60	1	0,90

Table A-0-3: 10% Electricity Decrease - Exergy Analysis Results

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
1	PCBs	4578,75	25	1	5372,11
2	PCBs-shredded	4578,75	25	1	
3	PCBs- dust	169,41	25	1	312,43
4	Crushed PCBs	4409,34	25	1	5061,85
W1	Electricity		25	1	36,00
W2	Electricity		25	1	108,00
Q1	Heat loss		25	1	0,00
Q2	Heat loss		25	1	0,00
4	Crushed PCBs	4409,34	25	1	5061,85
5	HNO3(aq)	7932,04	25	1	28,84
6	NOx(g)	125,73	25	1	15,26
7	Solder PLS	12215,65	25	1	5008,51
8	Fe,Pb-Nitrate Solution	8037,31	25	1	20,18
11	Solder residue	4178,34	25	1	4988,33
W3	Electricity		25	1	10,43
Q3	Heat loss		25	1	0,00
9	Cooling water	8556,24	25	1	27,05
10	Cooling water	8556,24	60	1	31,20
11	Solder residue	4178,34	25	1	4988,33
12	H2SO4-96wt%	1765,21	25	1	113,54
13	H2O2-30wt%	2503,99	25	1	135,68
21	Raff- recycle-57%	7710,30	25	1	66,62
14	Cu PLS	16157,83	25	1	5034,13
W4	Electricity		25	1	12,91
Q4	Heat loss		25	1	0,00
32	Cooling water	31959,00	25	1	101,05
33	Cooling water	31959,00	60	1	116,52
14	Cu PLS	16157,83	25	1	5034,13
15	NaOH-50%	1439,33	25	1	37,85
16	O2(g)	136,87	25	1	1,02
17	Cu PLS-pH adjusted	17460,30	25	1	4933,16
18	Cu residue	3361,79	25	1	4836,19
Q5	Heat loss		25	1	0,00
19	Cu PLS to SX	14098,51	25	1	96,97
20	Raffinate	13526,84	25	1	116,87
21	Raff- recycle-57%	7710,30	25	1	66,62
22	Raffinate- bleed waste-43%	5816,54	25	1	50,25
23	Advanced Electrolyte	47704,32	25	1	569,77

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24	Spent Electrolyte	47132,65	25	1	596,04
25	Kerosene-makeup	569,22	25	1	1478,83
26	Hydrocarbons	569,22	25	1	1482,35
W5	Electricity		25	1	0,63
Q5	Heat loss		25	1	0,00
23	Advanced Electrolyte	47704,32	25	1	569,77
24-	Spent Electrolyte	46966,21	25	1	595,75
27	Advanced Electrolyte	47704,33	45	1	572,10
28	Spent Electrolyte	46966,22	45	1	597,51
W6	Electricity		45	1	3,93
27	Advanced Electrolyte	47704,33	45	1	572,10
28	Spent Electrolyte	46966,22	45	1	597,51
29	O2(g)	148,46	45	1	1,11
30	Cu-Cathode	589,65	45	1	74,65
W7	Electricity		45	1	228,14
Q7	Heat loss		45	1	0,67
24-	Spent Electrolyte	46966,21	25	1	595,75
24	Spent Electrolyte	47133,38	25	1	596,04
31	H2O-makeup	167,17	25	1	0,53
18	Cu residue	3361,79	25	1	4836,19
36	HNO3-60%	2570,15	25	1	7,11
37	H2O-dilution	233,65	25	1	0,74
38	NO2(g)	620,39	25	1	45,35
39	Nitrate salts+ solids	5545,20	25	1	4673,51
42	Nitrate salts	2290,92	25	1	-1,55
43	Washed residue	3254,28	25	1	4675,06
W8	Electricity		25	1	4,25
Q8	Heat loss		25	1	0,00
40	Cooling water	13147,46	25	1	41,57
41	Cooling water	13147,46	60	1	47,93
43	Washed residue	3254,28	25	1	4675,06
44	NaCN(aq)-30%-makeup	0,96	25	1	0,24
45	Ca(OH)2(s)	46,17	25	1	2,68
46	H2O-makeup	126,86	25	1	0,40
47	Au-slurry	6278,54	25	1	4687,29
54	CN recycle-95%	2850,27	25	1	9,07
Q9	Heat loss		25	1	0,00
47	Au-slurry	6278,54	25	1	4687,29
48	Compressed air	45,00	25	1	0,00
49	N2(g),O2(g)	44,98	25	1	0,01
50	Au PLS	6278,56	25	1	4687,27
51	Au-residue	3277,50	25	1	4677,52
52	Au-complex	3001,06	25	1	9,75
W9	Electricity		25	1	46,55
Q10	Heat loss		25	1	0,00
86	Cooling water	4718,12	25	1	14,92
87	Cooling water	4718,12	60	1	17,20
53	Barren solution	3000,29			9,54
54	CN recycle-95%	2850,27	25	1	9,07
55	CN bleed-5%	150,01	25	1	0,48
52	Au-complex	3001,06	25	1	9,75
56	Carbon makeup	35,84	25	1	59,76
57	Loaded Carbon	598,18	25	1	996,27
79	Recycled Carbon-	561,56	25	1	936,31

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	cooled				
W15	Electricity		25	1	5,22
Q11	Heat loss		25	1	0,00
58	HCl-3wt%	9053,56	25	1	46,57
59	HCl-3wt%	9053,56	90	1	60,55
W10	Electricity		25	1	133,65
61	Acid wash rinse water	1914,03	25	1	6,05
62	Acid wash rinse water	1914,03	110	2	11,05
W11	Electricity		25	1	37,28
57	Loaded Carbon	598,18	25	1	996,27
59	HCl-3wt%	9053,56	90	1	60,55
60	HCN(g)	0,08	89	1	0,12
62	Acid wash rinse water	1914,03	110	2	11,05
63	HCl solution discharge	9053,61	88,92	1	60,10
64	Wash water discharge	1914,03	108	1	10,86
65	Acid washed Carbon	598,05	110	2	996,67
66	NaCN/NaOH soak soln	6035,70	25	1	168,43
67	NaCN/NaOH soak soln	6035,70	110	2	183,22
W12	Electricity		25	1	111,74
68	Eluant	6035,70	25	1	19,08
69	Eluant	6035,70	110	2	34,84
W13	Electricity		25	1	117,56
65	Acid washed Carbon	598,05	110	2	996,67
67	NaCN/NaOH soak soln	6035,70	110	2	183,22
69	Eluant	6035,70	110	2	34,84
70	Final rinse water	6035,70	25	1	19,08
71	Pregnant Eluate	6036,48	110	2	35,04
72	Cooling rinse water	6035,69	26	1	19,30
73	Pre-soak solution-discharge	6035,55	110	2	183,08
74	NH3(g)	0,04	110	2	0,02
76	H2O	398,27	25	1	1,26
77	Steam	398,27	600	1	25,39
W14	Electricity		25	1	78,34
75	Stripped Carbon	597,40	26	1	996,07
77	Steam	398,27	600	1	25,39
78	Recycled Carbon	561,56	136	1	937,11
79	Recycled Carbon-cooled	561,56	25	1	936,31
80	Combustion gases	426,99	136	1	79,29
Q12	Heat loss		25	1	0,00
Q13	Heat loss		136	1	0,61
71	Pregnant Eluate	6036,48	110	2	35,04
72	Cooling rinse water	6035,69	26	1	19,30
81	NaOH-50%	9,66	25	1	0,21
82	pH-adj Solution	12081,84	50	1	41,51
Q14	Heat loss		50	1	4,32
82	pH-adj Solution	12081,84	50	1	41,51
83	O2(g)/H2(g)	0,05	50	1	0,02
84	Au cathode	0,56	50	1	0,01
85	Barren gold solution	12081,22	50	1	41,51

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W16	Electricity		50	1	2,01
Q10	Heat loss		50	1	0,36
88	Cooling water	198,55	25	1	0,63
89	Cooling water	198,55	60	1	0,72

Table A-0-4: 10% Gold Increase - Exergy Analysis Results

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
1	PCBs	4578,75	25	1	5372,11
2	PCBs-shredded	4578,75	25	1	
3	PCBs- dust	169,41	25	1	312,43
4	Crushed PCBs	4409,34	25	1	5061,85
W1	Electricity		25	1	40,00
W2	Electricity		25	1	120,00
Q1	Heat loss		25	1	0,00
Q2	Heat loss		25	1	0,00
4	Crushed PCBs	4409,34	25	1	5061,85
5	HNO3(aq)	7932,04	25	1	28,84
6	NOx(g)	125,73	25	1	15,26
7	Solder PLS	12215,65	25	1	5008,51
8	Fe,Pb-Nitrate Solution	8037,31	25	1	20,18
11	Solder residue	4178,35	25	1	4988,33
W3	Electricity		25	1	11,58
Q3	Heat loss		25	1	0,00
9	Cooling water	8673,64	25	1	27,42
10	Cooling water	8673,64	60	1	31,62
11	Solder residue	4178,35	25	1	4988,33
12	H2SO4-96wt%	1765,15	25	1	113,54
13	H2O2-30wt%	2503,88	25	1	135,67
21	Raff- recycle-57%	7710,06	25	1	66,62
14	Cu PLS	16157,44	25	1	5034,13
W4	Electricity		25	1	14,35
Q4	Heat loss		25	1	0,00
32	Cooling water	32104,36	25	1	101,51
33	Cooling water	32104,36	60	1	117,05
14	Cu PLS	16157,44	25	1	5034,13
15	NaOH-50%	1439,33	25	1	37,85
16	O2(g)	136,86	25	1	1,02
17	Cu PLS-pH adjusted	17459,91	25	1	4933,16
18	Cu residue	3361,84	25	1	4836,19
Q5	Heat loss		25	1	0,00
19	Cu PLS to SX	14098,07	25	1	96,97
20	Raffinate	13526,42	25	1	116,87
21	Raff- recycle-57%	7710,06	25	1	66,62
22	Raffinate- bleed waste-43%	5816,36	25	1	50,25
23	Advanced Electrolyte	47703,66	25	1	569,77
24	Spent Electrolyte	47132,02	25	1	596,04
25	Kerosene-makeup	569,20	25	1	1478,77
26	Hydrocarbons	569,20	25	1	1482,28
W5	Electricity		25	1	0,70
Q5	Heat loss		25	1	0,00
23	Advanced Electrolyte	47703,66	25	1	569,77
24-	Spent Electrolyte	46965,58	25	1	595,75

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
27	Advanced Electrolyte	47703,67	45	1	572,10
28	Spent Electrolyte	46965,60	45	1	597,51
W6	Electricity		45	1	3,93
27	Advanced Electrolyte	47703,67	45	1	572,10
28	Spent Electrolyte	46965,60	45	1	597,51
29	O2(g)	148,45	45	1	1,11
30	Cu-Cathode	589,62	45	1	74,65
W7	Electricity		45	1	253,48
Q7	Heat loss		45	1	0,83
24-	Spent Electrolyte	46965,58	25	1	595,75
24	Spent Electrolyte	47132,74	25	1	596,04
31	H2O-makeup	167,16	25	1	0,53
18	Cu residue	3361,84	25	1	4836,19
36	HNO3-60%	2570,07	25	1	7,11
37	H2O-dilution	233,64	25	1	0,74
38	NO2(g)	620,36	25	1	45,35
39	Nitrate salts+ solids	5545,18	25	1	4673,51
42	Nitrate salts	2290,85	25	1	-1,55
43	Washed residue	3254,33	25	1	4675,06
W8	Electricity		25	1	4,72
Q8	Heat loss		25	1	0,00
40	Cooling water	13194,69	25	1	41,72
41	Cooling water	13194,69	60	1	48,11
43	Washed residue	3254,33	25	1	4675,06
44	NaCN(aq)-30%-makeup	1,05	25	1	0,24
45	Ca(OH)2(s)	46,16	25	1	2,68
46	H2O-makeup	126,80	25	1	0,40
47	Au-slurry	6278,60	25	1	4687,29
54	CN recycle-95%	2850,26	25	1	9,07
Q9	Heat loss		25	1	0,00
47	Au-slurry	6278,60	25	1	4687,29
48	Compressed air	45,00	25	1	0,00
49	N2(g),O2(g)	44,97	25	1	0,01
50	Au PLS	6278,62	25	1	4687,27
51	Au-residue	3277,49	25	1	4677,52
52	Au-complex	3001,13	25	1	9,75
W9	Electricity		25	1	51,72
Q10	Heat loss		25	1	0,00
86	Cooling water	5242,33	25	1	16,58
87	Cooling water	5242,33	60	1	19,11
53	Barren solution	3000,27			9,54
54	CN recycle-95%	2850,26	25	1	9,07
55	CN bleed-5%	150,01	25	1	0,48
52	Au-complex	3001,13	25	1	9,75
56	Carbon makeup	35,84	25	1	59,76
57	Loaded Carbon	593,28	25	1	987,96
79	Recycled Carbon-cooled	556,58	25	1	928,00

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
W15	Electricity		25	1	5,80
Q11	Heat loss		25	1	0,00
58	HCl-3wt%	9053,54	25	1	46,57
59	HCl-3wt%	9053,54	90	1	60,55
W10	Electricity		25	1	148,50
61	Acid wash rinse water	1914,03	25	1	6,05
62	Acid wash rinse water	1914,03	110	2	11,05
W11	Electricity		25	1	41,42
57	Loaded Carbon	593,28	25	1	987,96
59	HCl-3wt%	9053,54	90	1	60,55
60	HCN(g)	0,09	89	1	0,12
62	Acid wash rinse water	1914,03	110	2	11,05
63	HCl solution discharge	9053,60	88,92	1	60,10
64	Wash water discharge	1914,03	108	1	10,86
65	Acid washed Carbon	593,13	110	2	988,36
66	NaCN/NaOH soak soln	6035,69	25	1	168,43
67	NaCN/NaOH soak soln	6035,69	110	2	183,22
W12	Electricity		25	1	124,15
68	Eluant	6035,69	25	1	19,08
69	Eluant	6035,69	110	2	34,84
W13	Electricity		25	1	130,62
65	Acid washed Carbon	593,13	110	2	988,36
67	NaCN/NaOH soak soln	6035,69	110	2	183,22
69	Eluant	6035,69	110	2	34,84
70	Final rinse water	6035,69	25	1	19,08
71	Pregnant Eluate	6036,55	110	2	35,04
72	Cooling rinse water	6035,68	26	1	19,09
73	Pre-soak solution-discharge	6035,52	110	2	183,08
74	NH3(g)	0,04	110	2	0,02
76	H2O	394,74	25	1	1,25
77	Steam	394,74	600	1	25,16
W14	Electricity		25	1	85,93
75	Stripped Carbon	592,11	26	1	987,76
77	Steam	394,74	600	1	25,16
78	Recycled Carbon	556,58	136	1	928,80
79	Recycled Carbon-cooled	556,58	25	1	928,00
80	Combustion gases	422,98	136	1	79,29
Q12	Heat loss		25	1	0,00
Q13	Heat loss		136	1	0,61
71	Pregnant Eluate	6036,55	110	2	35,04
72	Cooling rinse water	6035,68	26	1	19,30
81	NaOH-50%	9,66	25	1	0,21
82	pH-adj Solution	12081,89	50	1	41,51
Q14	Heat loss		50	1	4,28
82	pH-adj Solution	12081,89	50	1	41,51
83	O2(g)/H2(g)	0,05	50	1	0,02
84	Au cathode	0,62	50	1	0,01

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
85	Barren gold solution	12081,22	50	1	41,51
W16	Electricity		50	1	2,46
Q10	Heat loss		50	1	3,60
88	Cooling water	243,29	25	1	0,77
89	Cooling water	243,29	60	1	0,89

Table A-0-5: 10% Gold Decrease- Exergy Analysis Results

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
1	PCBs	4578,75	25	1	5372,11
2	PCBs-shredded	4578,75	25	1	
3	PCBs- dust	169,41	25	1	312,43
4	Crushed PCBs	4409,34	25	1	5061,85
W1	Electricity		25	1	40,00
W2	Electricity		25	1	120,00
Q1	Heat loss		25	1	0,00
Q2	Heat loss		25	1	0,00
4	Crushed PCBs	4409,34	25	1	5061,85
5	HNO3(aq)	7932,04	25	1	28,84
6	NOx(g)	125,74	25	1	15,26
7	Solder PLS	12215,64	25	1	5008,51
8	Fe,Pb-Nitrate Solution	8037,32	25	1	20,18
11	Solder residue	4178,33	25	1	4988,33
W3	Electricity		25	1	11,58
Q3	Heat loss		25	1	0,00
9	Cooling water	8673,64	25	1	27,42
10	Cooling water	8673,64	60	1	31,62
11	Solder residue	4178,33	25	1	4988,33
12	H2SO4-96wt%	1765,26	25	1	113,55
13	H2O2-30wt%	2504,11	25	1	135,68
21	Raff- recycle-57%	7710,53	25	1	66,62
14	Cu PLS	16158,23	25	1	5034,13
W4	Electricity		25	1	14,35
Q4	Heat loss		25	1	0,00
32	Cooling water	32104,36	25	1	101,51
33	Cooling water	32104,36	60	1	117,05
14	Cu PLS	16158,23	25	1	5034,13
15	NaOH-50%	1439,33	25	1	37,85
16	O2(g)	136,87	25	1	1,02
17	Cu PLS-pH adjusted	17460,69	25	1	4933,16
18	Cu residue	3361,74	25	1	4836,19
Q5	Heat loss		25	1	0,00
19	Cu PLS to SX	14098,94	25	1	96,97
20	Raffinate	13527,25	25	1	116,87
21	Raff- recycle-57%	7710,53	25	1	66,62
22	Raffinate- bleed waste-	5816,72	25	1	50,25

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
	43%				
23	Advanced Electrolyte	47704,84	25	1	569,77
24	Spent Electrolyte	47133,14	25	1	596,04
25	Kerosene-makeup	569,25	25	1	1478,90
26	Hydrocarbons	569,25	25	1	1482,42
W5	Electricity		25	1	0,70
Q5	Heat loss		25	1	0,00
23	Advanced Electrolyte	47704,84	25	1	569,77
24-	Spent Electrolyte	46966,69	25	1	595,75
27	Advanced Electrolyte	47704,85	45	1	572,10
28	Spent Electrolyte	46966,71	45	1	597,51
W6	Electricity		45	1	3,93
27	Advanced Electrolyte	47704,85	45	1	572,10
28	Spent Electrolyte	46966,71	45	1	597,51
29	O2(g)	148,47	45	1	1,11
30	Cu-Cathode	589,68	45	1	74,66
W7	Electricity		45	1	253,50
Q7	Heat loss		45	1	0,83
24-	Spent Electrolyte	46966,69	25	1	595,75
24	Spent Electrolyte	47133,87	25	1	596,04
31	H2O-makeup	167,17	25	1	0,53
18	Cu residue	3361,74	25	1	4836,19
36	HNO3-60%	2570,27	25	1	7,11
37	H2O-dilution	233,66	25	1	0,74
38	NO2(g)	620,42	25	1	45,35
39	Nitrate salts+ solids	5545,25	25	1	4673,51
42	Nitrate salts	2291,02	25	1	-1,55
43	Washed residue	3254,23	25	1	4675,06
W8	Electricity		25	1	4,72
Q8	Heat loss		25	1	0,00
40	Cooling water	13196,15	25	1	41,72
41	Cooling water	13196,15	60	1	48,11
43	Washed residue	3254,23	25	1	4675,06
44	NaCN(aq)-30%-makeup	0,87	25	1	0,24
45	Ca(OH)2(s)	46,18	25	1	2,68
46	H2O-makeup	126,92	25	1	0,40
47	Au-slurry	6278,47	25	1	4687,29
54	CN recycle-95%	2850,28	25	1	9,07
Q9	Heat loss		25	1	0,00
47	Au-slurry	6278,47	25	1	4687,29
48	Compressed air	45,00	25	1	0,00
49	N2(g),O2(g)	44,98	25	1	0,01
50	Au PLS	6278,49	25	1	4687,27
51	Au-residue	3277,50	25	1	4677,52
52	Au-complex	3000,99	25	1	9,75
W9	Electricity		25	1	51,72
Q10	Heat loss		25	1	0,00

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
86	Cooling water	5241,92	25	1	16,57
87	Cooling water	5241,92	60	1	19,11
53	Barren solution	3000,29			9,54
54	CN recycle-95%	2850,28	25	1	9,07
55	CN bleed-5%	150,01	25	1	0,48
52	Au-complex	3000,99	25	1	9,75
56	Carbon makeup	35,85	25	1	59,77
57	Loaded Carbon	597,68	25	1	995,56
79	Recycled Carbon-cooled	561,13	25	1	935,59
W15	Electricity		25	1	5,80
Q11	Heat loss		25	1	0,00
58	HCl-3wt%	9053,57	25	1	46,57
59	HCl-3wt%	9053,57	90	1	60,55
W10	Electricity		25	1	148,50
61	Acid wash rinse water	1914,04	25	1	6,05
62	Acid wash rinse water	1914,04	110	2	11,05
W11	Electricity		25	1	41,42
57	Loaded Carbon	597,68	25	1	995,56
59	HCl-3wt%	9053,57	90	1	60,55
60	HCN(g)	0,07	89	1	0,12
62	Acid wash rinse water	1914,04	110	2	11,05
63	HCl solution discharge	9053,62	88,92	1	60,10
64	Wash water discharge	1914,04	108	1	10,86
65	Acid washed Carbon	597,56	110	2	995,96
66	NaCN/NaOH soak soln	6035,71	25	1	168,43
67	NaCN/NaOH soak soln	6035,71	110	2	183,22
W12	Electricity		25	1	124,16
68	Eluant	6035,71	25	1	19,08
69	Eluant	6035,71	110	2	34,84
W13	Electricity		25	1	130,62
65	Acid washed Carbon	597,56	110	2	995,96
67	NaCN/NaOH soak soln	6035,71	110	2	183,22
69	Eluant	6035,71	110	2	34,84
70	Final rinse water	6035,71	25	1	19,08
71	Pregnant Eluate	6036,41	110	2	35,04
72	Cooling rinse water	6035,70	26	1	19,09
73	Pre-soak solution-discharge	6035,57	110	2	183,08
74	NH3(g)	0,04	110	2	0,02
76	H2O	397,97	25	1	1,26
77	Steam	397,97	600	1	25,37
W14	Electricity		25	1	86,87
75	Stripped Carbon	596,95	26	1	995,36
77	Steam	397,97	600	1	25,37
78	Recycled Carbon	561,13	136	1	936,40
79	Recycled Carbon-cooled	561,13	25	1	935,59
80	Combustion gases	426,65	136	1	79,29
Q12	Heat loss		25	1	0,00

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
Q13	Heat loss		136	1	0,61
71	Pregnant Eluate	6036,41	110	2	35,04
72	Cooling rinse water	6035,70	26	1	19,30
81	NaOH-50%	9,66	25	1	0,21
82	pH-adj Solution	12081,78	50	1	41,51
Q14	Heat loss		50	1	4,29
82	pH-adj Solution	12081,78	50	1	41,51
83	O2(g)/H2(g)	0,04	50	1	0,02
84	Au cathode	0,51	50	1	0,01
85	Barren gold solution	12081,23	50	1	41,51
W16	Electricity		50	1	2,01
Q10	Heat loss		50	1	0,40
88	Cooling water	199,07	25	1	0,63
89	Cooling water	199,07	60	1	0,73

Table A-0-6: 10% Copper Concentration Increase- Exergy Analysis Results

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
1	PCBs	4578,75	25	1	5372,11
2	PCBs-shredded	4578,75	25	1	
3	PCBs- dust	169,41	25	1	312,43
4	Crushed PCBs	4409,34	25	1	5061,85
W1	Electricity		25	1	40,00
W2	Electricity		25	1	120,00
Q1	Heat loss		25	1	0,00
Q2	Heat loss		25	1	0,00
4	Crushed PCBs	4409,34	25	1	5061,85
5	HNO3(aq)	7486,55	25	1	28,84
6	NOx(g)	118,74	25	1	14,38
7	Solder PLS	11777,15	25	1	5008,51
8	Fe,Pb-Nitrate Solution	7586,04	25	1	20,18
11	Solder residue	4191,11	25	1	4988,33
W3	Electricity		25	1	11,34
Q3	Heat loss		25	1	0,00
9	Cooling water	8673,64	25	1	27,42
10	Cooling water	8673,64	60	1	31,62
11	Solder residue	4191,11	25	1	4988,33
12	H2SO4-96wt%	1745,67	25	1	112,28
13	H2O2-30wt%	2520,71	25	1	136,66
21	Raff- recycle-57.3%	7748,80	25	1	66,62
14	Cu PLS	16206,29	25	1	5034,13
W4	Electricity		25	1	14,38
Q4	Heat loss		25	1	0,00
32	Cooling water	32465,67	25	1	102,65
33	Cooling water	32465,67	60	1	118,37
14	Cu PLS	16206,29	25	1	5034,13
15	NaOH-50%	1399,37	25	1	37,85
16	O2(g)	134,26	25	1	1,00
17	Cu PLS-pH adjusted	17471,40	25	1	4933,16
18	Cu residue	3352,42	25	1	4836,19
Q5	Heat loss		25	1	0,00
19	Cu PLS to SX	14118,98	25	1	96,97
20	Raffinate	13523,22	25	1	116,87
21	Raff- recycle-57.3%	7748,80	25	1	66,62
22	Raffinate- bleed waste-43%	5774,41	25	1	50,25
23	Advanced Electrolyte	48194,11	25	1	569,77
24	Spent Electrolyte	47598,35	25	1	596,04
25	Kerosene-makeup	593,22	25	1	1541,17
26	Hydrocarbons	593,22	25	1	1544,83
W5	Electricity		25	1	0,72
Q5	Heat loss		25	1	0,00
23	Advanced Electrolyte	48194,11	25	1	569,77
24-	Spent Electrolyte	47424,89	25	1	595,75

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
27	Advanced Electrolyte	48194,13	45	1	572,10
28	Spent Electrolyte	47424,91	45	1	597,51
W6	Electricity		45	1	4,10
27	Advanced Electrolyte	48194,13	45	1	572,10
28	Spent Electrolyte	47424,91	45	1	597,51
29	O2(g)	154,72	45	1	1,16
30	Cu-Cathode	614,51	45	1	77,80
W7	Electricity		45	1	264,18
Q7	Heat loss		45	1	0,87
24-	Spent Electrolyte	47424,89	25	1	595,75
24	Spent Electrolyte	47599,10	25	1	596,04
31	H2O-makeup	174,21	25	1	0,55
18	Cu residue	3352,42	25	1	4836,19
36	HNO3-60%	2442,46	25	1	7,11
37	H2O-dilution	222,04	25	1	0,70
38	NO2(g)	589,32	25	1	43,08
39	Nitrate salts+ solids	5427,60	25	1	4673,51
42	Nitrate salts	2179,04	25	1	-1,55
43	Washed residue	3248,56	25	1	4675,06
W8	Electricity		25	1	4,63
Q8	Heat loss		25	1	0,00
40	Cooling water	13194,69	25	1	41,72
41	Cooling water	13194,69	60	1	48,11
43	Washed residue	3248,56	25	1	4675,06
44	NaCN(aq)-30%-makeup	0,91	25	1	0,24
45	Ca(OH)2(s)	43,68	25	1	2,54
46	H2O-makeup	128,10	25	1	0,41
47	Au-slurry	6271,55	25	1	4687,29
54	CN recycle-95%	2850,30	25	1	9,07
Q9	Heat loss		25	1	0,00
47	Au-slurry	6271,55	25	1	4687,29
48	Compressed air	45,00	25	1	0,00
49	N2(g),O2(g)	44,98	25	1	0,01
50	Au PLS	6271,57	25	1	4687,27
51	Au-residue	3270,52	25	1	4677,52
52	Au-complex	3001,05	25	1	9,75
W9	Electricity		25	1	51,72
Q10	Heat loss		25	1	0,00
86	Cooling water	5242,02	25	1	16,57
87	Cooling water	5242,02	60	1	19,11
53	Barren solution	3000,32			9,54
54	CN recycle-95%	2850,30	25	1	9,07
55	CN bleed-5%	150,02	25	1	0,48
52	Au-complex	3001,05	25	1	9,75
56	Carbon makeup	35,67	25	1	59,48
57	Loaded Carbon	595,30	25	1	991,53
79	Recycled Carbon-cooled	558,89	25	1	931,85

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
W15	Electricity		25	1	5,80
Q11	Heat loss		25	1	0,00
58	HCl-3wt%	9050,98	25	1	46,57
59	HCl-3wt%	9050,98	90	1	60,55
W10	Electricity		25	1	148,45
61	Acid wash rinse water	1913,49	25	1	6,05
62	Acid wash rinse water	1913,49	110	2	11,05
W11	Electricity		25	1	41,41
57	Loaded Carbon	595,30	25	1	991,53
59	HCl-3wt%	9050,98	90	1	60,55
60	HCN(g)	0,07	89	1	0,12
62	Acid wash rinse water	1913,49	110	2	11,05
63	HCl solution discharge	9051,03	88,92	1	60,10
64	Wash water discharge	1913,49	108	1	10,86
65	Acid washed Carbon	595,17	110	2	991,93
66	NaCN/NaOH soak soln	6033,98	25	1	168,43
67	NaCN/NaOH soak soln	6033,98	110	2	183,22
W12	Electricity		25	1	124,12
68	Eluant	6033,98	25	1	19,08
69	Eluant	6033,98	110	2	34,83
W13	Electricity		25	1	130,58
65	Acid washed Carbon	595,17	110	2	991,93
67	NaCN/NaOH soak soln	6033,98	110	2	183,22
69	Eluant	6033,98	110	2	34,83
70	Final rinse water	6033,98	25	1	19,08
71	Pregnant Eluate	6034,72	110	2	35,04
72	Cooling rinse water	6033,97	26	1	19,08
73	Pre-soak solution-discharge	6033,83	110	2	183,08
74	NH3(g)	0,04	110	2	0,02
76	H2O	396,37	25	1	1,25
77	Steam	396,37	600	1	25,27
W14	Electricity		25	1	86,63
75	Stripped Carbon	594,56	26	1	991,33
77	Steam	396,37	600	1	25,27
78	Recycled Carbon	558,89	136	1	932,65
79	Recycled Carbon-cooled	558,89	25	1	931,85
80	Combustion gases	424,96	136	1	79,29
Q12	Heat loss		25	1	0,00
Q13	Heat loss		136	1	0,61
71	Pregnant Eluate	6034,72	110	2	35,04
72	Cooling rinse water	6033,97	26	1	19,30
81	NaOH-50%	9,66	25	1	0,21
82	pH-adj Solution	12078,35	50	1	41,51
Q14	Heat loss		50	1	4,29
82	pH-adj Solution	12078,35	50	1	41,51
83	O2(g)/H2(g)	0,05	50	1	0,02
84	Au cathode	0,53	50	1	0,01

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
85	Barren gold solution	12077,77	50	1	41,51
W16	Electricity		50	1	2,11
Q10	Heat loss		50	1	0,40
88	Cooling water	209,27	25	1	0,66
89	Cooling water	209,27	60	1	0,76

Table A-0-7: 10% Copper Concentration Decrease- Exergy Analysis Results

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
1	PCBs	4578,75	25	1	5372,11
2	PCBs-shredded	4578,75	25	1	
3	PCBs- dust	169,41	25	1	312,43
4	Crushed PCBs	4409,34	25	1	5061,85
W1	Electricity		25	1	40,00
W2	Electricity		25	1	120,00
Q1	Heat loss		25	1	0,00
Q2	Heat loss		25	1	0,00
4	Crushed PCBs	4409,34	25	1	5061,85
5	HNO3(aq)	8432,29	25	1	28,84
6	NOx(g)	133,58	25	1	16,24
7	Solder PLS	12708,06	25	1	5008,51
8	Fe,Pb-Nitrate Solution	8544,04	25	1	20,18
11	Solder residue	4164,02	25	1	4988,33
W3	Electricity		25	1	11,85
Q3	Heat loss		25	1	0,00
9	Cooling water	8224,70	25	1	26,00
10	Cooling water	8224,70	60	1	29,99
11	Solder residue	4164,02	25	1	4988,33
12	H2SO4-96wt%	1786,37	25	1	114,91
13	H2O2-30wt%	2485,26	25	1	134,57
21	Raff- recycle-56.7%	7677,25	25	1	66,62
14	Cu PLS	16112,89	25	1	5034,13
W4	Electricity		25	1	14,32
Q4	Heat loss		25	1	0,00
32	Cooling water	31701,22	25	1	100,23
33	Cooling water	31701,22	60	1	115,58
14	Cu PLS	16112,89	25	1	5034,13
15	NaOH-50%	1484,11	25	1	37,85
16	O2(g)	139,79	25	1	1,04
17	Cu PLS-pH adjusted	17457,22	25	1	4933,16
18	Cu residue	3372,30	25	1	4836,19
Q5	Heat loss		25	1	0,00
19	Cu PLS to SX	14084,92	25	1	96,97
20	Raffinate	13540,13	25	1	116,87
21	Raff- recycle-56.7%	7677,25	25	1	66,62
22	Raffinate- bleed waste-43.3%	5862,87	25	1	50,25
23	Advanced Electrolyte	47151,25	25	1	569,77
24	Spent Electrolyte	46606,46	25	1	596,04
25	Kerosene-makeup	542,46	25	1	1409,32
26	Hydrocarbons	542,46	25	1	1412,67
W5	Electricity		25	1	0,67
Q5	Heat loss		25	1	0,00
23	Advanced Electrolyte	47151,25	25	1	569,77
24-	Spent Electrolyte	46447,83	25	1	595,75

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Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
27	Advanced Electrolyte	47151,23	45	1	572,10
28	Spent Electrolyte	46447,82	45	1	597,51
W6	Electricity		45	1	3,75
27	Advanced Electrolyte	47151,23	45	1	572,10
28	Spent Electrolyte	46447,82	45	1	597,51
29	O2(g)	141,48	45	1	1,06
30	Cu-Cathode	561,93	45	1	71,14
W7	Electricity		45	1	241,57
Q7	Heat loss		45	1	0,79
24-	Spent Electrolyte	46447,83	25	1	595,75
24	Spent Electrolyte	46607,14	25	1	596,04
31	H2O-makeup	159,31	25	1	0,50
18	Cu residue	3372,30	25	1	4836,19
36	HNO3-60%	2713,25	25	1	7,11
37	H2O-dilution	246,66	25	1	0,78
38	NO2(g)	655,22	25	1	47,89
39	Nitrate salts+ solids	5677,00	25	1	4673,51
42	Nitrate salts	2416,30	25	1	-1,55
43	Washed residue	3260,69	25	1	4675,06
W8	Electricity		25	1	4,83
Q8	Heat loss		25	1	0,00
40	Cooling water	13985,93	25	1	44,22
41	Cooling water	13985,93	60	1	50,99
43	Washed residue	3260,69	25	1	4675,06
44	NaCN(aq)-30%-makeup	1,01	25	1	0,24
45	Ca(OH)2(s)	48,97	25	1	2,84
46	H2O-makeup	125,46	25	1	0,40
47	Au-slurry	6286,40	25	1	4687,29
54	CN recycle-95%	2850,27	25	1	9,07
Q9	Heat loss		25	1	0,00
47	Au-slurry	6286,40	25	1	4687,29
48	Compressed air	45,00	25	1	0,00
49	N2(g),O2(g)	44,98	25	1	0,01
50	Au PLS	6286,42	25	1	4687,27
51	Au-residue	3285,31	25	1	4677,52
52	Au-complex	3001,11	25	1	9,75
W9	Electricity		25	1	51,72
Q10	Heat loss		25	1	0,00
86	Cooling water	5242,25	25	1	16,58
87	Cooling water	5242,25	60	1	19,11
53	Barren solution	3000,28			9,54
54	CN recycle-95%	2850,27	25	1	9,07
55	CN bleed-5%	150,01	25	1	0,48
52	Au-complex	3001,11	25	1	9,75
56	Carbon makeup	36,04	25	1	60,08
57	Loaded Carbon	601,47	25	1	1001,67
79	Recycled Carbon-cooled	564,61	25	1	941,39

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
W15	Electricity		25	1	5,80
Q11	Heat loss		25	1	0,00
58	HCl-3wt%	9056,46	25	1	46,57
59	HCl-3wt%	9056,46	90	1	60,55
W10	Electricity		25	1	148,54
61	Acid wash rinse water	1914,65	25	1	6,06
62	Acid wash rinse water	1914,65	110	2	11,05
W11	Electricity		25	1	41,44
57	Loaded Carbon	601,47	25	1	1001,67
59	HCl-3wt%	9056,46	90	1	60,55
60	HCN(g)	0,08	89	1	0,12
62	Acid wash rinse water	1914,65	110	2	11,05
63	HCl solution discharge	9056,52	88,92	1	60,10
64	Wash water discharge	1914,65	108	1	10,86
65	Acid washed Carbon	601,33	110	2	1002,07
66	NaCN/NaOH soak soln	6037,64	25	1	168,43
67	NaCN/NaOH soak soln	6037,64	110	2	183,22
W12	Electricity		25	1	124,19
68	Eluant	6037,64	25	1	19,09
69	Eluant	6037,64	110	2	34,85
W13	Electricity		25	1	130,66
65	Acid washed Carbon	601,33	110	2	1002,07
67	NaCN/NaOH soak soln	6037,64	110	2	183,22
69	Eluant	6037,64	110	2	34,85
70	Final rinse water	6037,64	25	1	19,09
71	Pregnant Eluate	6038,46	110	2	35,04
72	Cooling rinse water	6037,63	26	1	19,09
73	Pre-soak solution-discharge	6037,47	110	2	183,08
74	NH3(g)	0,04	110	2	0,02
76	H2O	400,43	25	1	1,27
77	Steam	400,43	600	1	25,52
W14	Electricity		25	1	87,52
75	Stripped Carbon	600,65	26	1	1001,47
77	Steam	400,43	600	1	25,52
78	Recycled Carbon	564,61	136	1	942,20
79	Recycled Carbon-cooled	564,61	25	1	941,39
80	Combustion gases	429,31	136	1	79,29
Q12	Heat loss		25	1	0,00
Q13	Heat loss		136	1	0,61
71	Pregnant Eluate	6038,46	110	2	35,04
72	Cooling rinse water	6037,63	26	1	19,30
81	NaOH-50%	9,66	25	1	0,21
82	pH-adj Solution	12085,76	50	1	41,51
Q14	Heat loss		50	1	4,29
82	pH-adj Solution	12085,76	50	1	41,51
83	O2(g)/H2(g)	0,05	50	1	0,02
84	Au cathode	0,60	50	1	0,01

Stream nr	Component	Flow (kg/hr)	Temp (deg C)	Pressure (atm)	Total Exergy (KWh/ton)
85	Barren gold solution	12085,11	50	1	41,51
W16	Electricity		50	1	2,37
Q10	Heat loss		50	1	3,60
88	Cooling water	234,53	25	1	0,74
89	Cooling water	234,53	60	1	0,86

APPENDIX B- *SAMPLE CALCULATIONS*

This section illustrates how the exergy is calculated of some species that were not available in HSC-Chemistry.

Exergy of activated carbon

The standard Gibbs free energy of activated carbon (AC) were not available in literature, therefore Equation 0-1 and Equation 0-2 were used to calculated the chemical and physical exergy respectively:

$$E_{chemical} = LHV\left(1.0401 + 0.1728\left(\frac{x_H}{x_C}\right) + 0.0432\left(\frac{x_O}{x_C}\right) + 0.2169\left(\frac{x_S}{x_C}\right)\left(1 - 2.0628\frac{x_H}{x_C}\right)\right)$$

Equation 0-1

$$E_{Physical} = c\left((T - T^0) - T^0 ln\left(\frac{T}{T^0}\right) + v_m \cdot (P - P^0)\right)$$

Equation 0-2

The higher heating value on a dry ash free basis was calculated using the **Modified-Dulong** equation (Kuleape, et al., 2014):

$$HHV_{kJ/kg} = (337C + 1419(H_2 - 0.125 O_2) + 93S + 23N$$

Equation 0-3

Where, C, H, O, S and N are the wt. % of elemental carbon, hydrogen, oxygen, sulphur and nitrogen. By substituting the AC composition given in Table A-1 and the mass of the carbon make-up stream given in Appendix A the chemical exergy becomes:

HHV   =   (337*0.801 + 1419*(0.0236- 0.125*0.1635) + 93*0.0006 +23*0.011

       =   27483.45 kJ/kg

LHV   ≈   HHV- m_{H2O}*Hvap,$_{,H2O}$

       =   (27483.45*35.84- (0.0236*35.84)*(2260))/1000

       =   983.095 MJ/hr

E $_{chemical}$ = 983.095* (1.0401+ 0.1728 * (0.0236/0.801) + 0.0432*(0.1635/0.801) +

0.2169* (0.0006/0.801) * (1- 2.0628 0.0236/0.801))

= 1035.935 MJ/hr

= 287.7596571 kWh/hr

= 62.84670911 kWh/ton PCBs

Exergy of Hydrocarbons

The hydrocarbons are formed due to the high volatility of kerosene. The chemical exergy of the hydrocarbons is therefore the chemical exergy of kerosene plus the exergy of the heat supplied to vaporise the kerosene. The specific chemical exergy, heat of vaporization (H_{vap}) and boiling point temperature of kerosene is taken from literature and are presented below (Hader, Darabseh and Alothman, 2011). The mass of hydrocarbons are given in Appendix A.

H $_{vap}$ = 250 kJ/kg

T $_{boilling\ point}$ = 503.15 ^{o}C

e $_{chemical}$ = 42.824 MJ/kg

The exergy of the heat supplied can be calculated as follows where Q is the H $_{vap}$.

$$E_Q = Q\left(1 - \frac{T^0}{T}\right)$$

Equation 0-4

The standard chemical exergy of the hydrocarbons is calculated as follows:

E $_{chemical,hydrocarbons}$ = (569.22* [42.824 + 250*(1-298.15/503.15)])/3.6

= 6787.32 kWh/hr

Chemical exergy of aqueous species

Complete dissociation of the aqueous species into its individual ions was assumed. HSC-Chemistry only calculates the chemical exergy of the stable species. Wall (2009) presented the standard chemical exergy for some aqueous species in the stable and dissociated state. By assuming complete dissociation, the standard chemical exergy of aqueous are calculated as follows:

$$E_{chemical,aqueous\ specie} = \Delta G_{i(+)} + \Delta G_{i(-)} + \sum v_k * E_k{}^0 \qquad \textbf{Equation 0-5}$$

Where $\Delta G_{i(+)}$ and $\Delta G_{i(-)}$ are the Gibbs free energy of the cation and anion of the aqueous specie i; E_k is the standard chemical exergy of the elemental reference species k in substance i and v_k is the stoichiometric coefficient of the elemental reference species. The calculation of specific chemical exergy for HNO3(aq) is demonstrated below:

Stable state: $0.5H_2(g) + 0.5N_2(g) + 1.5O_2(g) = HNO_3(aq)$
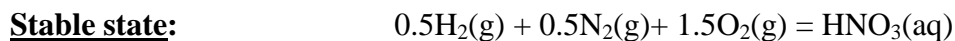
$\Delta G_{HNO3(a)}$ = -103.468   kJ/mol

$e_{,H2(g)}$ = 236.12   kJ/mol

$e_{,N2(g)}$ = 0.67   kJ/mol

$e_{,O2(g)}$ = 3.92   kJ/mol

$e_{,HNO3(aq)}$ = (-103.468 + (0.5*236.12+0.5*0.67+1.5*3.92))

          = **20.81 kJ/mol**

Dissociated: $0.5H_2(g) + 0.5N_2(g) + 1.5O_2(g) = H(+a) + NO_3(-a)$
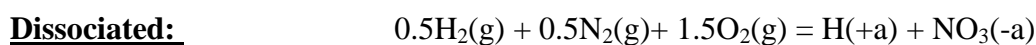
$\Delta G_{H(+a)}$ = 0   kJ/mol

$\Delta G_{NO3(-a)}$ = -110.828   kJ/mol

$e_{,H2(g)}$ = 236.12   kJ/mol

$e_{,N2(g)}$ = 0.67   kJ/mol

$e_{,O2(g)}$ = 3.92   kJ/mol

$e_{,HNO3(aq)}$ = (-110.828 + (0.5*236.12+0.5*0.67+1.5*3.92))

          = **13.447 kJ/mol**

Chemical exergy of non-ideal mixtures

The mixing of non-ideal solutions requires that the activities should be used instead of mole fractions. The Aqu-mode, a built-in feature in HSC Chemistry allows the calculation of activities of aqueous solutions. It can also be used to calculate the osmotic pressure, pH, boiling point

temperature etc. of aqueous solutions. The activity coefficient of the ionic species and water are calculated by equations given below (Ideas, 2006). The Pitzer-equations was used to calculate the activity coefficients of the ionic species. As an example, stream 39 (Appendix A) was selected to demonstrate the basis of the activity calculation.

$$a_{i(-)} = m_{(i-)} * \lambda_{(i+)}$$

$$a_{i(+)} = m_{(i+)} * \lambda_{(i+)}$$

$$a_{H2O} = x_{H2O} * \Upsilon_{H2O}$$

where m and $\lambda_{(i+)}$ are the molality and molal activity coefficients of ionic species i; x_{H2O} and Υ_{H2O} are the mole fraction and mole fraction activity coefficient. Figure B-1 present the results from the Aqua-mode in HSC Chemistry. The following equation can be used to calculate the standard chemical exergy of the mixture.

$$E_{chemical\,.mixture} = \sum_i x_i E_{chemical.i}{}^0 + RT^0 \sum_i x_i ln a_i$$

Equation 0-6

HNO3(aq) specie

$e_{,HNO3(aq)}$	$=$ 13.447 kJ/mol
$x_{H(+a)}$	$=$ 1.28E-08
$x_{NO3(-a)}$	$=$ 1.28E-08
$m_{H(+a)}$	$=$ 8.37E-07 mol/kg
$m_{NO3(-a)}$	$=$ 8.37E-07 mol/kg
$\lambda_{(H+)}$	$=$ 0.25
$\lambda_{(NO3-)}$	$=$ 2.94
$n_{HNO3(aq)}$	$=$ 1.23E-06 kmol/hr
$E_{,HNO3(aq)}$	$=$ 13.447*1.23E-06 + 8.314*273.15*1.28E-08*(ln(8.37E-07*0.25)+ *ln(8.37E-07 *2.94)
	$=$ **1.57E-02 kJ/hr**

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Figure 0-1: Activity coefficients of stream 39

APPENDIX C- *ASSUMPTIONS*

Feed capacity and composition:

- The feed material is disassembled and stripped from all relevant components such as capacitors, casing etc. before it enters the plant boundaries.

- There is no significant variation in the feed concentration or metal component ratios, i.e. copper/gold, will remain stable.

- Total processing capacity was taken to be 30 000 tonnes PCBs/annum.

- Plant Availability is 92%.

- Total plant operating days are 312 days.

- Plant operating hours/day is 21 hrs.

Comminution:

- All energy associated with ancillary equipment, i.e. conveyers and pumps were negligible when compared to the major equipment and are therefore ignored.

- All electrical work inputs are lost in the form of heat.

- During crushing the local temperature of the PCBs can increase to over 250°C due to impacting, resulting in pyrolytic cleavage of chemical bonds in the matrix that produces brominated and non-brominated phenols and aromatic/aliphatic ethers (Luda, 2011). This phenomenon was not considered.

- Oxidisation of metals during the comminution process was not considered.

- 3.7% of the feed to the circuit was considered to be lost as dust. The dust generated are assumed tol be collected by a bag-house system where 1% was assumed to be lost from this system to the environment (Wang *et al.*, 2015).

- The material is completely liberated at the size fraction smaller than 2mm.

- Bond work index was assumed to be 21.2 kWh/ton. This value was determined for metals entrapped in spent furnace linings used in the non-ferrous metal industry (Krishna and Raghavendra, 2008).

- Specific energy requirement for the shredder is 40 kWh/ton PCBs; values of 38.05 kWh/ton PCBs and 28 - 36 kWh/ton have been reported for a shredder of hammer mill type (Commission, 2001; Johansson and Björklund, 2010).

Solder removal process:

- The solid liquid separation step is 100% i.e. no moisture is trapped in solid phase and no solid slippage to the liquid phase was assumed.

- 10% of the total heat energy is lost to the atmosphere.

- All energy associated with ancillary equipment, i.e. pumps was ignored.

- Similar extent of reactions are assumed as reported by Rossouw, (2015).

- Operating conditions: 1.5M HNO_3, 25ºC and 1atm.

- Cooling water outlet temperature was taken to be 60ºC.

- Reaction time is 8hrs.

Copper recovery process:

- The solid liquid separation step yields perfect separation- no moisture trapped in solid phase and no solid slippage to the liquid phase.

- 10% of the heat energy is lost to the atmosphere.

- All reagents are supplied to the system in excess of 25% of the stoichiometric requirements.

- The neutralisation process i.e. pH adjustment step, loses all of the heat generated in the exothermic reaction to the atmosphere.

- No crud formation in solvent extraction process unit.

- No physical entrainment in solvent extraction process unit.

- Operating conditions: 2.5M H_2SO_4, 30wt. % H_2O_2, 25ºC and 1atm.

- Reaction time is 8hrs.

- 50wt. % NaOH is used for neutralisations.

- pH of PLS is adjusted to 1.8.

- Cooling water outlet temperature was taken to be 60ºC

- 70% extraction efficiency and 100% efficiency for stripping in SX.

- net transfer rate = 0.35 g/ℓ

- Extractant concentration is 32 vol.% and kerosene as diluent.

- The AE and SE copper concentrations were assumed to be 35 g/ℓ and 45 g/ℓ respectively.

- Sulphuric acid in SE is 180 g/ℓ.

- Electrowinning temperature is 45ºC and extent of reaction is 30%.

- No acid mist formation.

- Operating conditions for EW: CE was assumed as 90%, overall potential is 2V, 45ºC and extent of reaction is 30%.

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Precious metal recovery

- Solid- liquid separation is 100% efficient -no moisture trapped in solid phase and no solid slippage to the liquid phase.

- 10% of the heat energy is lost to the atmosphere.

- All energy associated with ancillary equipment, i.e. pumps were ignored.

- It was assumed that nitric acid wash removes 100% of the base metals and that no precious metals will be co-extracted in the circuit.

- NaCN concentration is 120 mg/ℓ and fed in excess of 25%.

- The gold complex is adsorbed as a neutral component as $Ca(Au(CN)_2)_2$.

- Leaching of gold may occur during adsorption is considered negligible.

- Ammonia production catalysed by activated carbon is not considered.

- Cyanide decomposes on contact with activated carbon at elevated temperatures, (adsorption process is exothermic). The increase in system temperature was assumed to have a negligible effect on cyanide decomposition.

- Carbon losses due to attrition within the process were assumed to be negligible.

- 6% of the carbon will be lost as carbon dioxide during carbon regeneration.

- 99% of the gold in solution is assumed to deposit on cathodes.

- Specific energy of 5.8 kWh/ton was assumed for the adsorption units.

APPENDIX D- *WASTE MANAGEMENT*

The recovery of metals from PCBs can assist with reducing the harmful waste load in general waste landfill sites in South Africa and the processing of the waste has the potential to create various economic and work opportunities. By extracting the valuable metals via hydrometallurgical processes creates a range of potential environmental risk. The processing of the PCBs will create dust, the leaching processes will create acidic metal rich solutions and various gasses will be generated during the processing.

The downstream management of these systems does not have to comply with the limits as discussed in Section 4(1) (b) of NEM:WA (*see section 2.4.3 for more information*). The waste generated from metallurgical plants is controlled by Department of Minerals and Resources, Department of Environmental Affairs and the Department of Water Affairs. The allowable discharge and storage toxicity limits given by these authorities are in line with the NEMA acts, because the metallurgical processing waste can lead to hydrogeological disruptions, acidification of the natural environment and breakdowns in the environment's nutrient cycles (Department of Environmental Affairs, 2018).

It is thus of critical importance to include waste management strategies when creating any metallurgical process, because it might have a net-negative effect on the environment.

- **Waste Generated from Process**

The process developed for this thesis generated a range of solid, liquid and gas waste streams. Each stream will be evaluated by comparing it with the relevant South African legislation. If it is determined that a stream is hazardous, then the various treatment options and their stream quality outputs will be discussed. The feasibility of the various processes will have to be determined by an economic study.

All waste generated in South Africa is classified according to a SANS 10234 national standard. The true impact and the specific discharge limits for each processing plant or mining activity is determined by the South African DMR, DEA and DWA. This is dependent on the area of operation and the impact that the discharge will have on the physical environment.

- **Solid Waste**

The process design assumed perfect solid liquid separation. The solid waste generated in process is thus free of any liquid and stable- i.e. it cannot be leached into the environment if it is not exposed to an acidic medium or any leach promoting environment.

Table D-0-1: Solid Waste Stream Composition

Component	Streams	
	3	51
Total Flow-kg/hr	169,41	3148,35
Cu	4,72	
Al	4,69	
Fe	8,04	
Sn	0,25	
Ni	0,12	
Zn	1,34	
Pb	1,87	
Au		0,01
Ag	0,02	0,00
C_2H_4	56,57	775,32
C_3H_6	27,43	375,91
$C_{10}H_8O_4$	27,43	375,91
$C_{15}H_{12}Br_4O_2$	5,77	397,57
C_2H_3Cl	1,21	200,46
SiO_2	21,92	563,14
Al_2O_3	3,52	230,50
CaO	4,50	229,52

- **Environmental Impact**

The solid waste is still leachable and can negatively impact the water system and the soil of the area where it is stored.

- **Treatment Options**

Solid waste is traditionally sent to a tailings storage facility close to the treatment area. Due to the high leachable concentration of the metals the facility should be lined to avoid leaching into the aquafers and the surrounding soil. The stored solid waste can be processed with additional

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downstream processes for metal recovery or plastic recycling because there still exist commercial value in the waste in terms of metal and plastic content.

- **Liquid Waste**

Liquid waste is generated at various points throughout the process. Due to the high acid consumed at various points within the system, the liquid waste is discharged at an acid pH, pH less than 7.

Table D-0-2: Liquid Waste Composition

Component	Streams							
	8	22	42	55	63	64	73	85
Total Flow-kg/hr	8037,31	5816,54	2290,64	150,01	9053,56	1914,03	6035,55	12081,22
H_2O	7345,0	3508,8	1470,6	150,0	8782,0	1914,0	5733,91	12076,22
$HNO_3(aq)$	0,04		0,0					
$Pb(NO_3)_2(aq)$	202,3		4,3					
$Ni(NO_3)_2(aq)$	18,6		15,5					
$Zn(NO_3)_2(aq)$	4,8		18,3					
$AgNO_3(aq)$	0,04		2,6					
$Al(NO_3)_3(aq)$	137,9		622,8					
$Fe(NO_3)_3(aq)$	312,9		81,8					
$Cu(NO_3)_2(aq)$	4,3		74,8					
$Sn(NO_3)_2(aq)$	11,5							
$CuSO_4(aq)$		272,9						
$Al_2(SO_4)_3(aq)$		112,8						
$FeSO_4(aq)$		10,0						
$NiSO_4(aq)$		18,0						
$ZnSO_4(aq)$		220,2						
$Ag_2SO_4(aq)$		0,2						
$SnSO_4(aq)$		1,1						
$Ca(OH)_2(aq)$								
$H_2O_2(aq)$								
$H_2SO_4(aq)$		394,6						
$NaAu(CN)_2(aq)$								0,01
$NaOH(aq)$				0,01			120,7	4,72
$NaCN(aq)$							180,9	0,28

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| HCl(aq) | | | | 271,6 | | | |
| Na₂SO₄(aq) | | 1277,9 | | | | | |

- **Environmental Impact**

The acidity and the high metal content prevent the streams in Table D-0-2 from being discharged into the environment. The streams will poison the surrounding water bodies and be detrimental to the surrounding soil.

- **Treatment Options**

The first step in managing the liquid waste streams is to recycle as much as possible back into the process plant. A fit-for-purpose water management strategy, where the water is used at a specific quality at various points within the system.

The water in the discharge streams still contains various metals with commercial value and various water treatment techniques can be utilised for recovery before discharge:

a. Desalination
b. Nano-filtration
c. Ion exchange
d. Evaporative crystallisation
e. Eutectic freeze point crystallization techniques

- **Gas Waste**

Various process units generate gas and dust within the process plant.

Table D-0-3: Gas Stream Compositions

Component	Streams									
	6	16	26	29	38	49	60	74	80	83
Total-kg/hr	125,73	136,87	2846,11	148,46	620,67	44,98	0,08	0,04	422,08	0,05
$NO_2(g)$	65,6				620,4					
$NO(g)$	60,2									
$O_2(g)$		136,9		148,5		9,0				0,05
$N_2(g)$						36,0			131,34	
$CO_2(g)$								0,03		
$NH_3(g)$								0,01		
$HCN(g)$							0,08		290,74	
$H_2O(g)$					0,3					
Hydrocarbons			2846,1							

- **Environmental Impact**

The gas generated within the system can be detrimental to human health and the environment in general. It has the potential to generate localised acid rain and can be seen as carcinogenic.

- **Treatment Options**

Industry generally manages the harmful gas streams with scrubbing processes. The benefits of these processes are that it can have an added benefit of generating useful products that can be recycled within the system. Nitric acid can be generated from the NO_x streams. The general management of hydrogen and carbon monoxide gas is to burn it in the presence of the air.