Chemical, physical and morphological changes in weathered brine slurried coal fly ash

By

Sammy Mwasaha Nyale

B.Sc. Chemistry (Honours) - University of Nairobi

A thesis submitted in fulfilment of the requirements for the degree of Magister Scientiae in the Department of Chemistry, University of the Western Cape

Supervisor: Prof. Leslie F. Petrik

Co-supervisors: Dr. Richard O. Akinyeye

Dr. Wilson M. Gitari

November 2011

KEYWORDS

Fossil fuels

Coal

Coal combustion
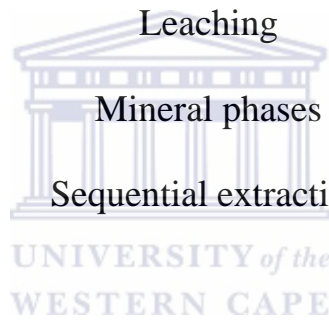
Coal gasification

Fly ash

Brine

Weathering

Leaching

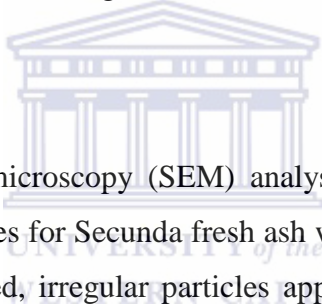Mineral phases

Sequential extraction

ABSTRACT

Energy production from coal comes with an environmental cost because of the toxic waste produced during coal combustion such as coal ash and brine which are potential water and soil pollutants. Coal ash and brine contain toxic elements which can leach and contaminate soils and ground water if not properly disposed.

This study investigated the mobility of species in coal fly ash co-disposed with brine at Sasol Secunda power station in order to establish if the ash dam could act as a salt sink. The ash was dumped as a slurry with 5:1 brine/ash ratio and the dam was in operation for 20 years. It was hypothesized that the disposed Secunda fly ash was capable of leaching toxic metal elements into the surrounding soils and ground water and therefore could not be used as a long term sustainable salt sink. Weathered fly ash samples were collected along a 51 m depth core at the Secunda ash dam by drilling and sampling the ash at 1.5 m depth intervals. A fresh fly ash sample was collected from the hoppers in the ash collection system at the power station. Characterization of both Secunda fresh ash and Secunda weathered ash core samples was done using X-ray diffraction (XRD) for mineralogy, X-ray fluorescence (XRF) for chemical composition and scanning electron microscopy (SEM) for morphology. Analysis of extracted pore water and moisture content determination of Secunda fresh ash and Secunda weathered ash core samples was done in order to evaluate the physico-chemical properties of the fly ash. The chemical partitioning and mobility of metal species in the ash dam was evaluated using the sequential extraction procedure.

The XRD spectra revealed quartz, mullite and calcite as the dominant mineral phases in the weathered Secunda ash core samples while Secunda fresh ash contained quartz, mullite and lime. The major oxides identified by XRF analysis for both Secunda fresh ash and Secunda weathered ash include: SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, Na_2O, TiO_2 and K_2O. The minor oxides identified for both Secunda fresh ash and Secunda weathered ash were P_2O_5, SO_3 and MnO. The trace elements identified for both Secunda fresh ash and Secunda weathered ash were As, Ba, Ce, Co, Nb, Ni, Pb, Rb, Sr, V, Y, Zr and Th. However, U was detected in

some of the Secunda weathered ash samples but not in Secunda fresh ash. Both Secunda fresh ash and Secunda weathered ash was classified as class F based on the sum of the oxides of silicon, aluminium and iron by mass and the CaO content as reported by XRF analysis, and further classified as sialic and ferrocalsialic type highlighting the significant levels of Si, Al, Ca and Fe in the fly ash based on XRF analysis. The XRF analysis further showed that brine codisposal on the ash may have been responsible for the slight enrichment of some species such as Na, SO_4^{2-}, Mg, K and V in the disposed Secunda weathered fly ash. However, there was no significant accumulation of these species in the disposed fly ash despite continuous addition of an estimated 117.65 billion litres of brine over the 20 year period that the dam existed. Furthermore, Secunda ash dam showed an overall total salt capture capacity of only -0.01 weight %, a strong indication that the ash dam was incapable of holding salts and would release elements to the environment over time.

The scanning electron microscopy (SEM) analysis revealed spherical particles with smooth outer surfaces for Secunda fresh ash while Secunda ash core samples consisted of agglomerated, irregular particles appearing to be encrusted, etched and corroded showing that weathering and leaching had occurred in the ash dam. A decrease in pH, electrical conductivity (EC) and total dissolved solids (TDS) was observed in Secunda ash core samples compared to Secunda fresh ash. While Secunda fresh ash (n = 3) had a pH of 12.38 ± 0.15, EC value of 4.98 ± 0.03 mS/cm and TDS value of 2.68 ± 0.03 g/L, the pH of Secunda ash core (n = 35) was 10.04 ± 0.50, the EC value was 1.08 ± 0.14 mS/cm and the TDS value was 0.64 ± 0.08 g/L. The lower pH in the ash dam created an environment conducive to the release of species through leaching, while the lower EC and TDS in the ash dam implied the loss of ionic species from the ash which resulted from leaching. The moisture content (MC) analysis indicated that Secunda ash dam was very damp with an average MC of 54.2 ± 12.66 % for Secunda ash core creating favourable conditions for leaching of species in the ash dam while Secunda fresh ash had MC of 1.8 ± 0.11 %. The bottom of Secunda ash dam appeared water logged which could cause slumping of the dam.

The sequential extraction procedure revealed that the major and trace elements contained in both Secunda fresh fly ash and Secunda weathered fly ash could leach upon exposure to different environmental conditions. The elements showed partitioning between five geochemical phases i.e. water soluble fraction, exchangeable fraction, carbonate fraction, Fe & Mn fraction and residual fraction. The labile phases consisted of the water soluble fraction, exchangeable fraction and carbonate fraction. The % leached out in the labile phases was expressed as a fraction of each element's total content e.g. Si (6.15 %) meant that 6.15 % of the total amount of Si in the ash was released in the labile phases. Na was the most labile among the major elements in the ash dam while Si and Al which form the major aluminosilicate ash matrix also showed significant lability. The % leached out in the labile phases for these major elements was as follows: for Secunda fresh ash: Si (6.15 %), Al (7.84 %), Na (11.31 %); for weathered Secunda ash core samples (n = 35): Si (7.53 %), Al (8.12 %), Na (11.63 %).

This study showed that the fly ash generated at Sasol Secunda power station could not be used as a long term sustainable salt sink. The wet disposal method used at Sasol Secunda power station poses a high risk of groundwater contamination due to the high liquid to solid ratio used to transport the ash for disposal, which may lead to rapid dissolution of all the soluble components in the fly ash. The large volumes of brine that pass through Secunda ash dam in the wet ash handling system present a greater environmental concern than the dry ash handling system which involves small amounts of brine entering the ash dump.

DECLARATION

I hereby declare that "*Chemical, physical and morphological changes in weathered brine slurried coal fly ash*" is my own work, that it has not been submitted for any degree or examination in any other University, and that all the sources I have used or quoted have been indicated and acknowledged by complete references

Sammy Mwasaha Nyale   November 2011

Signed…………………….

UNIVERSITY *of the*
WESTERN CAPE

ACKNOWLEDGEMENTS

UNIVERSITY *of the*
WESTERN CAPE

LIST OF ABBREVIATIONS

AAS - Atomic absorption spectrometry

AMD - Acid mine drainage

ASTM - American society for testing materials

CB - Carbonate fraction

CCBs - Coal combustion by products

CCD - Charge-coupled device detector

CCRs - Coal combustion residues

CEC - Cation exchange capacity

CG - Coal gasification

EC - Electrical conductivity

EDR - Electro dialysis reversal

EFC - Eutectic freeze crystallization

EPA - Environmental protection agency

ESP - Electrostatic precipitator

EX - Exchangeable fraction

FA - Fly ash

FBC - Fluidized-bed combustion

FBDB - Fixed bed dry bottom gasifier

Fe & Mn - Iron and manganese fraction

FGD - Flue gas desulfurization

FT - Fischer-tropsch process

GHG - Greenhouse gas emissions

HTFT - High temperature fischer-tropsch process

IC - Ion chromatography

ICP - Inductively coupled plasma

ICP-AES - Inductively coupled plasma-atomic emission spectrometry

ICP-MS - Inductively coupled plasma-mass spectroscopy

ICP-OES - Inductively coupled plasma-optical emission spectrometry

IGCC - Integrated gasification combined cycle

LCZ - Lower convective zone

LOI - Loss of ignition

MC - Moisture content

NCZ - Non-convective zone

PCC - Pulverized coal combustion system

RCRA - Resource conservation and recovery act

RED - Reversed electro dialysis

RES - Residual fraction

RO - Reverse osmosis

SA - Republic of south africa

SE - Sequential extraction

SEM - Scanning electron microscopy

SRO - Spiral reverse osmosis

TDS - Total dissolved solids

TMC - Total metal content

TPS - Thermo-electric power station

UCZ - Upper convective zone

USGS - United states geological survey

WEO - World energy outlook

WHO - World health organization

WS - Water soluble fraction

XRD - X-ray diffraction

XRF - X-ray fluorescence

ZLED - Zero liquid effluent discharge

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

UNIVERSITY *of the*

WESTERN CAPE

ACADEMIC OUTPUT

The proceedings outlined below are based on this study.

Oral Presentations

Nyale S.M., Akinyeye, R.O., Gitari, W.M., Petrik, L.F. Chemical and mineralogical analysis of coal fly ash co-disposed with brine at SASOL synfuels-Secunda power station in Mpumalanga province, South Africa. Presented at the UWC post graduate annual research open day, University of the Western Cape, Bellville on the 26th day of October, 2010.

Sammy M. Nyale, Richard O. Akinyeye, Wilson M. Gitari, Leslie F. Petrik. Investigation of the mineralogy, weathering patterns and chemical mobility in coal fly ash co-disposed with brine from a 20 year old ash dam at a coal fired power station in Mpumalanga Province, South Africa. The 15th Southern African conference on Coal, Carbon and Energy Technology, 17th - 18th November, 2010 at Glenhove Conference Centre, Rosebank, Johannesburg, South Africa.

Sammy M. Nyale, Richard O. Akinyeye, Wilson M. Gitari, Leslie F. Petrik. Chemical and mineralogical analysis of fine coal ash co-disposed with brine at a coal fired power station in Mpumalanga Province, South Africa. The International Conference on Analytical Sciences (Analitika 2010), University of Stellenbosch, 5th - 9th December, 2010.

Poster Presentation

Nyale, S.M, Gitari, W.M., Akinyeye, R.O., Petrik, L.F. Chemical composition and partitioning of species in weathered brine slurried coal fly ash. Presented at the UWC post graduate annual research open day, University of the Western Cape, 25th - 26th October, 2011.

DEDICATION

This work is dedicated to the almighty GOD, my creator, to my lovely wife Truphena Philip Otieno, for her perseverance during my absence from home in the duration of this study, and to my sons Joe Kiti Mwasaha and Philip Imani Mwasaha.

I love you all…

CHAPTER ONE

1. GENERAL INTRODUCTION

This chapter gives a general introduction of this research work. The aims and objectives are presented here.

1.1 BACKGROUND

The fossil fuels, coal, oil and gas account for approximately 80 % of the world's energy supplies (Goldemberg, 2006). Coal, compared with petroleum and natural gas, is the most abundant hydrocarbon fuel on the planet (Williams, 2001) and has many uses including generation of electricity, manufacture of synthetic petroleum and natural gas, manufacture of coal gas, coal tar, ammonia and coke, domestic fuel for cooking and heating, heating water in steam engines and boilers. Therefore, coal plays a major economic role in many countries globally. In order to meet increasing energy needs arising from population increase and higher standards of living, the Republic of South Africa (SA) uses coal to produce cheap electricity and fuels. SA relies heavily on the combustion of low grade brown coal to produce energy (Petrik et al., 2003).

Sasol is a South African company involved in coal mining and conversion of the coal into chemicals, liquid fuels and gas. The company has stations at Sasolburg and Secunda in SA and other operations in 38 countries around the globe creating employment for about 34,000 people (www.sasol.com). Sasol is the world's leader in commercial application of the coal gasification process having a total of 97 "Sasol-Lurgi Fixed Bed Dry Bottom" (FBDB) gasifiers: 17 at Sasolburg station and 80 at Secunda station (Dyk et al., 2006). Sasol also undertakes coal combustion to produce steam used to drive turbines for electricity generation. Approximately 28 million tons of coal is utilized per year by the gasification process at Sasol Sasolburg and Secunda stations leading to the release of about 7 million tons of gasification ash. Sasol uses 70 % of its total coal supplies for the gasification process while the remaining 30 % is used for steam production to drive turbines for electricity generation (Petrik et al., 2008). Sasol Secunda station

1

disposes fly ash produced from coal combustion in ash dams. The fly ash is mixed with brine to form a slurry which is pumped from the power plant to the ash dams.

Brines are waters saturated or nearly saturated with salts. Sasol Secunda station produces brines as a result of desalination procedures such as electrodialysis reversal (EDR) and spiral reverse osmosis (SRO) which are essential in the production of clean water for boiler feed and cooling purposes. Sasol Secunda station is operated in accordance with the zero liquid effluent discharge (ZLED) policy which dictates that apart from seepage water losses, no saline water is discharged to surface water resources (Petrik et al., 2008). The fly ash and brine contain toxic elements which may leach thereby potentially posing an environmental hazard to the surrounding soil and ground water.

This study involves the evaluation of the chemical, physical, morphological and mineralogical characteristics of brine impacted fly ash samples collected from Secunda ash dam at different depths in order to understand the weathering, leaching and mobility patterns of the major and trace species by depth in the ash dam. The sequential extraction procedure has been used in this study in order to shed light on the chemical partitioning of the metal species in the ash dam. In the sequential extraction procedure, the metal species show partitioning between five geochemical phases i.e. water soluble fraction, exchangeable fraction, carbonate fraction, Fe & Mn fraction and residual fraction.

1.2 STUDY AREA

Sasol Secunda power station, in the Mpumalanga province of the Republic of South Africa was chosen as the study area in this research. Secunda town is situated approximately 200 km south east of Pretoria. The location is shown on the map in Figure 1.
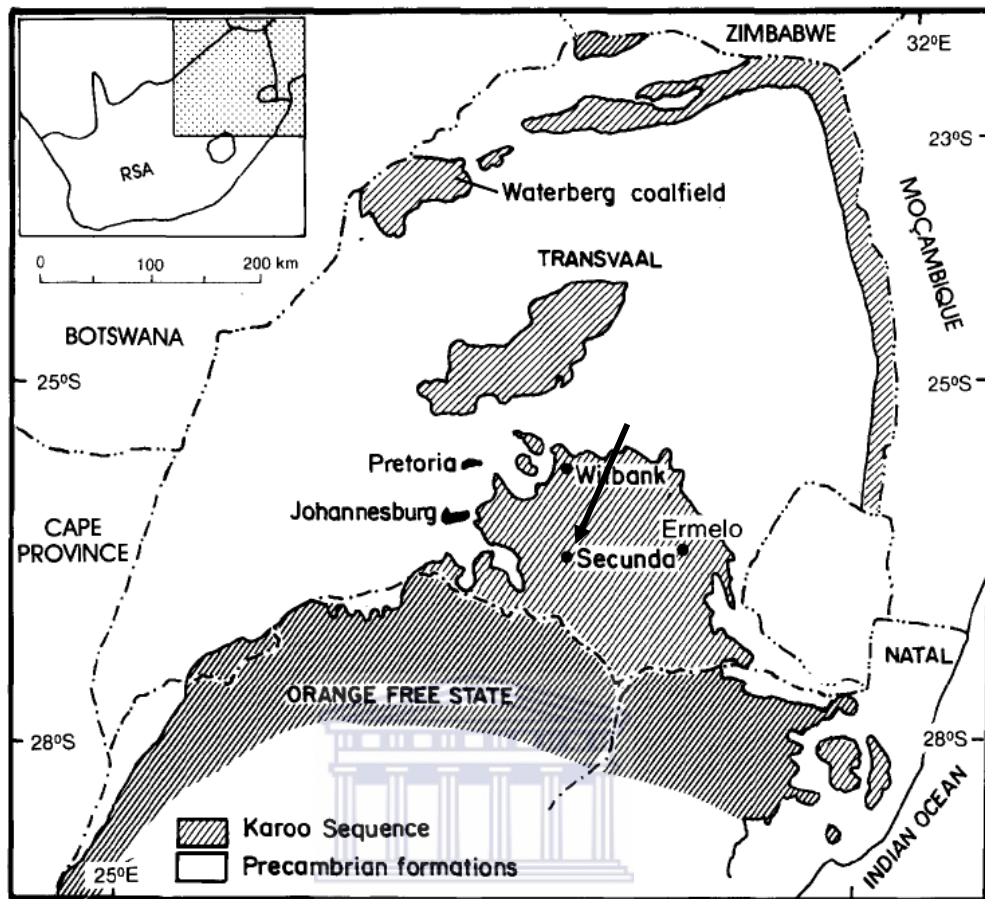
Figure 1: Location of South Africa's coal fields (Sourced from Snyman, 1989).

1.3 PROBLEM STATEMENT

South Africa (SA) was ranked seventh largest producer of coal globally in 2009. SA has the largest coal reserves in Africa at approximately 75 % of Africa's total coal reserves, mining between 245 Mt to 250 Mt of coal per year and exporting around 71.4 Mt which is approximately a third of the total annual production (BP, 2010; Wagner & Hlatshwayo, 2005; DME, 2006). With increasing energy demands each year, SA utilizes these huge coal deposits to produce electricity and fuels.

Sasol Secunda power station utilizes a low-rank bituminous coal for steam and synthetic gas production (Moitsheki et al., 2010) producing two kinds of coal ashes: gasification ash (from coal gasification process) consisting of coarse and fine particles and fly ash (from coal combustion process) which is made up of fine

particles. The gasification ash produced is then sieved to separate the coarse particles from fine particles. The coarse fraction is dumped separately via conveyer, while the fine gasification ash fraction together with fly ash from the coal combustion process is mixed with brine using an ash: brine ratio of 1:5 and is then transported as a slurry from the power station to ash dams hydraulically. The ash dam in this study consists of approximately 83 % fly ash from coal combustion boilers and 17 % fine ash from coal gasification chambers or gasifiers. About 40 million tons of coal is mined per annum at Sasol (www.sasol.com) and 70 % of this is consumed in the gasification process; the remaining 30 % is used for steam production to drive turbines for electricity generation. Approximately 28 million tons of coal is utilized per year by the gasification process producing about 7 million tons of gasification ash (Petrik et al., 2008). The fly ash and brine contain toxic elements which may leach upon contact with aqueous media such as infiltrating rain water at the dam site thus might pose an environmental hazard to the surrounding soil and ground water. The extent of the problem is unknown and unquantified. In safeguarding the environment, it is crucial to adopt best disposal methods that minimize weathering and subsequent leaching of major and trace elements from fly ash, or develop more utilization options for coal fly ash.

1.4 AIM OF STUDY

The aim of this study was to investigate and understand the chemical, physical, morphological and mineralogical characteristics of a 20 year old weathered fly ash co-disposed with brine at Sasol Secunda power station in a wet disposal method. This was to evaluate and quantify the weathering patterns and mobility of metal species in the ash dam in order to establish if the ash dam could act as a salt sink, ultimately shedding light on whether the ash disposal practice minimizes environmental impacts.

1.5 OBJECTIVES

The main objectives of this study are geared towards investigating and understanding the changes taking place due to weathering processes, mobility of

chemical species and mineralogical transformations in fly ash co-disposed with brine. This project addresses the answers to the following research questions;

i)   What is the chemical composition of fly ash from Sasol Secunda power station?

ii)   What are the morphological properties of the fly ash co-disposed with brine at Sasol Secunda power station?

iii)   What are the physico-chemical properties of the fly ash co-disposed with brine at Sasol Secunda power station?

iv)   What are the mineral phases likely to form during the fly ash/brine interaction in the ash dam at Sasol Secunda power station?

v)   How is the leaching process of metal species affected in the fly ash/brine dam with respect to different depths and mineralogical association?

vi)   What are the mobility patterns of different metal species down the fly ash/brine dam

1.6 RESEARCH APPROACH

The weathered fly ash samples were collected along a 51 m depth core at the ash dam by drilling and sampling the ash at different depth intervals. The fresh fly ash sample was collected from the hoppers in the ash collection system at the power station. The first set of experiments in this study involved characterization of the fresh and the weathered fly ash core samples using XRD, XRF and SEM for determining the mineralogy, chemical composition and morphology respectively. Physico-chemical properties of both fresh and the weathered fly ash were also determined using pore water analysis and moisture content determination. The first set of experiments was conducted in order to understand the weathering patterns in the ash dam. The second set of experiments was performed to determine elemental mobility patterns in the ash dam and their mineralogical phase associations using the sequential extraction procedure. The major and trace metal analysis of the different fractions at different depths was expected to show the movement of metal species down the core.

1.7 HYPOTHESIS

Co-disposing the fly ash and brine at Sasol Secunda ash dam does not result in a long term sustainable salt sink.

1.8 SCOPE AND DELIMITATIONS OF STUDY

In the past, the Environmental & Nano Sciences (ENS) Research Group in the Department of Chemistry, University of the Western Cape has carried out studies on South African fly ash. Akinyemi et al., (2011a) investigated the mineralogy and mobility patterns of chemical species in weathered South African fly ash obtained from an ash dump in a "dry disposal" system at Eskom while Fatoba (2007) studied the chemical composition and leaching behaviour of Sasol Secunda fresh fly ash. However, the characteristics of the weathered fly ash co-disposed with brine at the Sasol Secunda ash dam had not been studied. Therefore in this study, characterization of the weathered fly ash co-disposed with brine in comparison with fresh fly ash was done and sequential extraction experiments were conducted to shed light on the movement of metal species down the ash dam, in a wet ash handling system.

The disposal water at Sasol Secunda power station contains hydrocarbons. These organics have the potential to inhibit mineralization in the fly ash/brine dam. However, this study did not cover organics because of budgetary constraints.

1.9 OUTLINE OF THESIS CHAPTERS

The remaining chapters in this study will be set out as follows;

Chapter Two: This chapter will include the literature review on the origin of fly ash and brine as well as their disposal and environmental implication.

Chapter Three: This chapter will give the outline of the sampling, experimental and analytical methods used in meeting the objectives of this study.

Chapter Four: This chapter will discuss the first section of the results obtained in this study. The chapter will contain detailed discussions of chemical, mineralogical, morphological and extracted pore water analysis results. The mobility of species will be discussed. The risk of toxic and other species leaching to ground water will be brought out.

Chapter Five: This chapter will present the second section of the results obtained in this study which involved sequential fractionations of the core samples by depth. The chemical partitioning and species fractionation will be discussed.

Chapter Six: This chapter will outline the findings and general conclusions obtained from this study and the recommendations to the respective industry players.

CHAPTER TWO

2. LITERATURE REVIEW

This chapter includes the literature review on the origin of fly ash and brine as well as their disposal and environmental implications.

2.1 INTRODUCTION

Humans are always striving towards improving their standards of living and energy supplies play a crucial role in meeting this objective. Urbanization, modernization and population increase are responsible for rising global energy demands. Fossil fuels are the major source of energy today, and are expected to continue meeting about 84 % of world's energy demand until 2030. However, the use of fossil fuels faces environmental challenges including generation of toxic solid wastes, Greenhouse Gas emissions (GHG) among others (Asif & Muneer, 2007; WEO, 2007). Coal fired power plants generate huge amounts of fly ash as a post-combustion residue and brine effluents which arise from water treatment procedures. These wastes have the potential to impact negatively on the environment therefore, coal fired power plants are faced with the challenge of environmental remediation as well as high costs incurred in disposing these wastes safely.

In the Republic of South Africa (SA), Sasol and Eskom which are the major energy companies in SA produce huge quantities of fly ash of which only about 5 % is utilized. Today, Sasol Synfuels consumes over 45 million tons of coal per annum releasing over 4 million tons of fly ash. Sasol Secunda complex uses approximately 255 million litres of fresh water per day for steam generation and cooling purposes. The fresh feed water is produced using desalination procedures which generate brine in the process. Eskom uses the "dry dumping" system where the fly ash is dumped by conveyor in dry state while brine is used to condition the ash to reduce air pollution by avoiding particulate material being blown away by the wind. Sasol on the other hand uses the "wet dumping" system where the fly ash is mixed with brine and dumped in slurry form (Mahlaba et al, 2011a; Petrik

et al., 2008; Petrik et al., 2003). Understanding the origin, characteristics and properties of fly ash and brine, and their interaction chemistry is crucial in coming up with better disposal mechanisms and more utilization options for these wastes, hence protecting the environment and avoiding high disposal costs.

2.2 FOSSIL FUELS

Fossil fuels are non-renewable, combustible forms or compounds of carbon. They are crucial sources of energy in the world today. It is believed that millions of years ago, plants and animals died due to various natural calamities like cyclones, floods, forest fires, earthquakes etc. These dead plants and animals were buried under the earth and were subjected to high pressure, high temperature anaerobic bacterial decomposition in the absence of oxygen to form fossil fuels. Naturally, energy from the sun is trapped and stored in plants in the form of chemical energy. This energy is later transferred to animals when the plants are consumed as food. Therefore, on burning the fossil fuels, the chemical energy contained in the remnants of the buried plants and animal matter is then released in the form of heat and light energy. There are three types of fossil fuels: natural gas, coal and petroleum or oil (www.tutorvista.com/content/chemistry/chemistry-i/coal-petroleum/fossil-fuels.php).

The world's energy requirements are ever increasing, and are heavily dependent on fossil fuels. British Petroleum (BP, 2006) reported that the world primary energy consumption increased by 4.4 % in 2004 compared to the previous year while in 2005 consumption was higher than 2004, increasing by a 2.7 % margin. In 2009 however, global primary energy consumption fell by 1.1 %, the largest decline since 1980, due to the infamous global economic recession (BP, 2010). The world's energy market is estimated to be worth approximately 1.5 trillion dollars and is dominated by fossil fuels (Goldemberg, 2006). However, there is growing concern that these non-renewable sources of energy are diminishing thereby posing a risk of being completely depleted. This leads to the question, ''when will non-renewable energy sources get depleted?''. Shafiee & Topal (2009) presented a new formula for calculating when fossil fuel reserves are likely

to be depleted and concluded that reserves depletion time for oil is approximately 35 years, coal is 107 years and gas is 37 years. The findings showed that coal reserves will be available up to 2112, and will be the only fossil fuel remaining after 2042. However, no one can predict exactly when supplies of fossil fuels will get exhausted; therefore views differ on this subject. For example, according to Asif & Muneer (2007), coal reserves will get exhausted in Russia after 1034 years, followed by India, USA, and China after 315 years, 305 years and 83 years respectively. In 2009, the United States Geological Survey (USGS) reported previously undiscovered volumes of 3,844 million barrels of oil, 3,705 billion cubic feet of natural gas and 202 million barrels of natural gas liquids in three different regions in USA (USGS, 2009). Fossil fuels account for approximately 80 % of world's energy supplies, followed by traditional biomass at 9.3 % and nuclear energy at 6.9 %. Coal constitutes approximately 65 % of the fossil fuel reserves in the world, with the remaining 35 % being oil and gas (Goldemberg, 2006; Shafiee & Topal (2009). Hence, coal contributes approximately 52 % of the total world's energy supplies. Table 1 shows the distribution of fossil fuel reserves as at end of 2005.

Table 1: World's fossil fuel reserves as at end of 2005

Region	Oil		Natural Gas		Coal	
	Thousand million barrels	Percentage	Trillion cubic metres	Percentage	Thousand million tonnes	Percentage
Middle East	742.7	61.90 %	72.13	40.10 %	0.4	0.04 %
Europe & Eurasia	140.5	11.70 %	64.01	35.60 %	287.1	31.60 %
Africa	114.3	9.50 %	14.39	8.00 %	50.3	5.50 %
South & Central America	103.5	8.60 %	7.02	3.90 %	19.9	2.19 %
North America	59.5	5.00 %	7.46	4.10 %	254.4	27.99 %
Asia Pacific	40.2	3.40 %	14.84	8.30 %	296.9	32.70 %
Total	1200.7		179.83		909	

Source: BP (2006).

As seen on the table, the majority of the world's oil and gas supplies are in the Middle East followed by Europe and Eurasia regions. Coal supplies are abundant in Asia Pacific and North America. Africa has reasonable quantities of all the three fossil fuel resources coming at third in oil and fourth in natural gas and coal reserves. South Africa has the largest coal reserves in Africa, at approximately 75 % of Africa's total coal reserves (Wagner & Hlatshwayo, 2005) while Libya and Nigeria lead the African continent in oil reserves. As at 2005, Libya had 39.1 billion barrels in proven oil reserves while Nigeria had 35.9 billion barrels. The two African nations had more oil reserves than the United States and China which had 29.3 billion barrels and 16 billion barrels respectively (Frynas & Paulo, 2007).

2.3 COAL

Coal is a black combustible mineral consisting of a mixture of elemental carbon and compounds of carbon containing nitrogen, sulphur, hydrogen and oxygen. Coal is believed to have been formed through the carbonization process, which involved the slow conversion of vegetable matter over millions of years under the earth at high temperature and pressure, in the presence of anaerobic bacteria and in the absence of oxygen. Coal can be classified into four types based on the carbon content as shown in Table 2 below.

Table 2: Classification of coal

Coal type	Carbon content	Common name
Anthracite	96 %	Hard coal
Bituminous	65 %	Household coal
Lignite	38 %	Soft coal or Brown coal
Peat	11 %	

Source: www.tutorvista.com/content/chemistry/chemistry-i/coal-petroleum/coal.php.

Coal contains minerals or mineral matter, which can be defined as all inorganic non coal material present in coal. This refers to any other element in coal except for carbon, hydrogen, oxygen, sulphur and nitrogen. The commonly occurring

major minerals in coal are silicates, carbonates, sulphites and sulphates (Rao & Gluskoter, 1973). According to Vassilev & Vassileva (2007), approximately 316 minerals or mineral groups have been identified in coals. Coal is one, if not the most, complex of all natural occurring raw materials. To characterize a coal you need to consider several variables including moisture content, carbon, hydrogen, sulphur, nitrogen and oxygen content, vitrinite content among others (Snyman, 1989). Coal can be further classified in terms of grade, based on quantity of ash or inorganic material left after complete combustion; type, based on amounts of the constituent macerals (vitrinite, exinite or liptinite and inertinite); and rank, based on the degree of metamorphism, i.e., the properties of vitrinite in a particular coal (Snyman, 1989).

2.3.1 COAL COMBUSTION

Coal combustion involves the burning of coal to produce energy. One of the most common systems used in coal combustion today is the pulverized coal combustion system (PCC). Figure 2 illustrates all the stages typical in a PCC. In the first step, the coal is finely and evenly ground prior to the combustion process. The ground coal then enters the furnace where it is combusted producing fly ash (FA), bottom ash and boiler slag. FA is very fine and is usually carried along with the flue gases. Electrostatic precipitators (ESPs) collect the FA from flue gas before being released into the atmosphere, using a series of collection plates. The ESPs operate by introducing an electrostatic charge in the collection plates which creates an affinity for the FA (UND EERC, 2011).
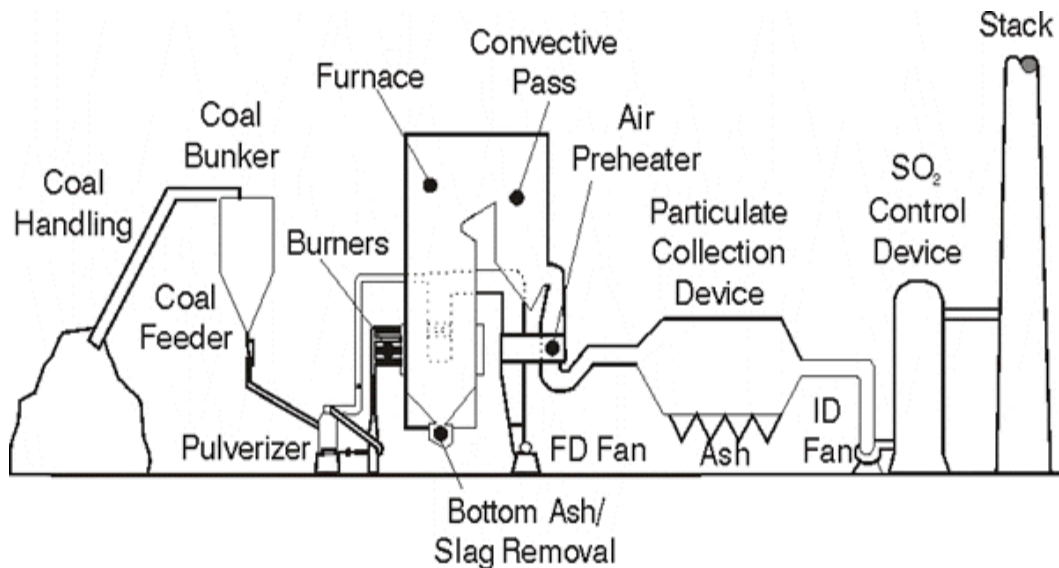
Figure 2: A schematic representation of a pulverized coal combustion system (Sourced from UND EERC, 2011).

The forced draft fan (FD fan) forces air into the furnace while the induced draft fan (ID fan) drives flue gases out of the furnace (Figure 2). Bottom ash and boiler slag are coarser than FA and are collected from the bottom of the furnace. The resulting sulphur gases are removed via the flue gas desulfurization (FGD) process. Here, calcium rich lime or limestone is used to specifically remove sulphur gases from the flue gas stream. Three common types of FGD processes used today include wet scrubbers, dry scrubbers, and sorbent injection.

Other coal combustion systems include cyclone firing, stoker firing and fluidized-bed combustion. In a cyclone firing system, coarsely pulverized coal is combusted in a cylindrical or cyclone burner producing a glassy slag while in a stoker firing system; the coal is combusted on a stationary or moving grate. In the fluidized-bed combustion (FBC) system, coal is mixed with a sorbent (e.g. limestone) or other bed material prior to combustion. The fluidized fuel and sorbent or bed material allows complete combustion and removal of sulphur gases during the combustion process (UND EERC, 2011).

2.3.2 COAL GASIFICATION

Gasification is the conversion of fossil fuels, biomass and wastes into chemicals or synthesis gas (syngas) for subsequent utilization. The major products obtained from the gasification process include ammonia, methanol, hydrogen and oxy-chemicals. Others are carbon dioxide, Fischer-Tropsch (FT) liquids and fuel gas. The gasification process can also be used for electricity generation. Coal gasification (CG) involves the conversion of coal into chemicals, fuel gases and subsequent power generation (Minchener, 2005, Gasification World Database, 2007). Figure 3 illustrates a typical coal gasification process employed at one of the Sasol power plants in South Africa.
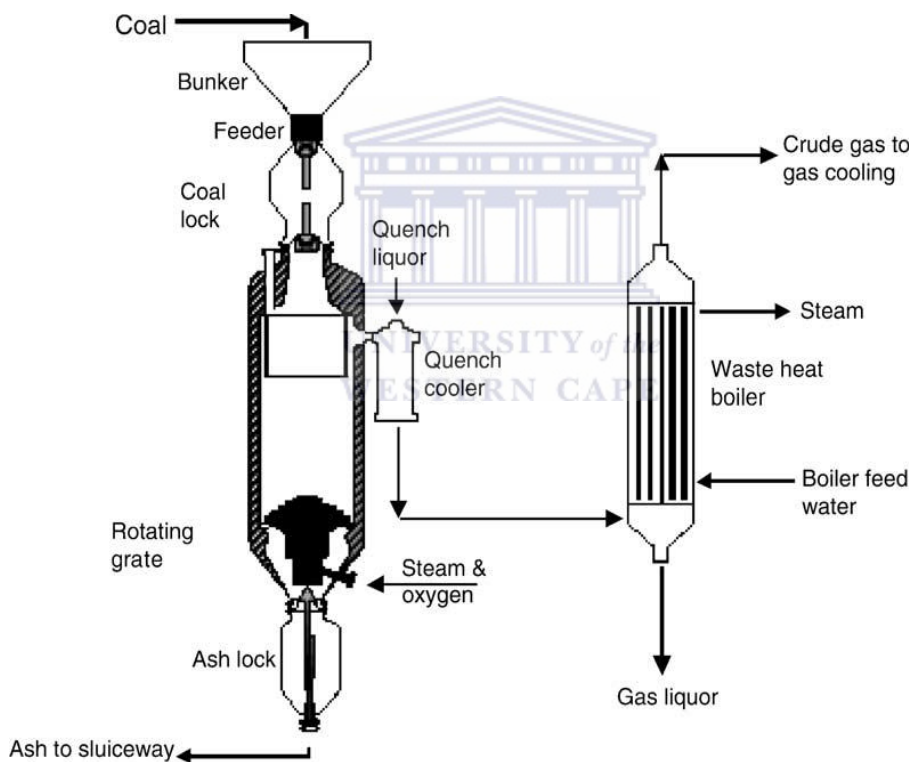
Figure 3: A schematic diagram of Sasol - Lurgi gasification process (Sourced from Dyk et al., 2006).

In the Sasol-Lurgi gasification process, coal is subjected to steam and oxygen under high pressure conditions to produce synthesis gas or crude gas which is composed of CO and H_2. The synthesis gas can be used for heating purposes in

urban areas and industrial processes, as a substitute for natural gas to compensate low natural gas supplies, or for production of petrol and diesel for automobiles using a High Temperature Fischer-Tropsch (HTFT) process from the Sasol advanced Synthol proprietary technology and generation of electricity by means of an Integrated Gasification Combined Cycle (IGCC). There are two modes of operation in the gasification process where the ash can either be removed in a dry state or as a molten slag from the gasifier. The most commercially proven for pressurized application is the Sasol-Lurgi fixed bed dry bottom gasifier which is also designed to process a variety of coal feedstock from different sources (Dyk et al., 2006).

The CG process involves very high temperatures which causes the melting of the mineral elements in the coal. This can lead to formation of new phases through transformation of the already existing mineral matter in the coal. The new mineral phases can then be collected at the bottom of the gasifier in molten state. Several power plants add basic oxides into the gasifier in order to decrease the ash melting temperature and reduce the viscosity of the molten slag (Ninomiya & Sato, 1997). CG is a "greener" technology compared to coal combustion in terms of emissions. However, there is some unburnt carbon (3 - 5 %) found in coarse gasification ash (Wagner et al., 2008).

2.4 COAL MINING AND PROCESSING

Coal mining and coal processing activities lead to production of by-products or wastes which raise human health and environmental concern. Both underground and open cast coal mining methods expose sulphide minerals to air and water forming acid mine drainage (AMD) which contains sulphuric acid (H_2SO_4) formed through pyrite (FeS_2) oxidation. Studies have shown that AMD has a typical pH of about 2 or even lower in some cases, and total dissolved solids (TDS) of around 4,000 - 5,000 mg/L. The low pH causes mobility of toxic metal species in form of anions and cations which may contaminate the environment. Coal gasification and coal combustion processes produce FA which is composed of all the inorganic materials or residues that are left behind after coal processing. These materials are commonly referred to as coal combustion residues (CCRs) or

coal combustion by-products (CCBs) which include fine sand (silica), unburnt carbon and some metals like arsenic, thorium, barium, strontium, cobalt, lead, nickel, vanadium, zirconium, cadmium, chromium, copper, mercury, selenium and zinc among others. CCRs vary in chemical composition, particle size and morphology among other properties (Petrik et al., 2003; EPA, 2009; Vassilev & Vassileva, 2007).

Sulphur emissions from coal combustion pose an environmental hazard, acting as a precursor to formation of acid rain causing soil acidification and forest degradation. Hence, to protect the environment and maintain good air quality, the installation of advanced flue gas desulphurization (FGD) systems was recommended in an effort to fight sulphur emissions in coal combustion power plants as per the US Clean Air Act Amendments of 1990. This was coupled with recommendations for power plants to switch from high-sulphur to low-sulphur coal or blending of the two (Singh & Paul, 2001; Álvarez-Ayuso et al., 2006). In the wake of the US Resource Conservation and Recovery Act (RCRA), coal ashes have gained several utilization options, including soil conditioning, land reclamation, mineral recovery, highway construction, cement mixtures and manufacturing, and special physical/chemical reagents. This assists many power plants which have to bear high costs in meeting safe disposal techniques of these by-products. However, the utilization of these by-products has to be followed up with an environmental evaluation in order to ensure that the by-products will not cause undesired human health and environmental effects (Piehler et al., 1982).

2.5 FLY ASH

2.5.1 Origin of fly ash

Fly ash (FA) is a fine solid residue produced from coal burning process. The name was probably coined to mean "very fine ash" which actually "flies around". FA is generated when pulverized coal is combusted at around 1200 to 1700 °C in a typical combustion chamber in a thermo-electric power station (TPS). It is estimated that the world generates approximately 500 million tons of FA per annum. FA accounts for approximately 70 % of the total residues arising from

pulverized coal combustion in TPSs and originates from the various inorganic and organic constituents in the parent or feed coal used. Other coal combustion by-products include bottom ash (10 - 12 %), boiler slag (4 - 6 %) and Flue Gas Desulphurization (FGD) material (10 - 12 %). Bottom ash is a coarse solid residue which collects at the bottom of the boiler with larger particles compared to those of FA. Boiler slag is a hard and glassy residue found in the bottom hoppers resulting from melted material in the boiler under high temperatures. FGD material is a solid residue produced in the flue gas scrubbers. This material results from the flue gas desulphurization process which is done to combat SO_2 gas by reacting slurried limestone or lime with the SO_2 gas to produce $CaSO_3$. FA can be collected via two ways; by the use of electrostatic precipitators (ESPs) or the use of baghouses which trap the ash within the flue gas stream to prevent escape into the atmosphere. Coal gasification produces fine ash which is also referred to as FA (Ahmaruzzaman, 2010; Bayat, 1998; Hui et al., 2005; Jala & Goyal, 2006; Vassilev & Vassileva, 2007). Sasol Synfuels utilizes over 45 million tons of coal per year producing over 4 million tons of FA annually. The ash dam at Sasol Secunda power station comprises of approximately 83 % FA from coal combustion and 17 % FA from the gasification chambers (i.e. from coal gasification) and fine bottom ash. The particle size of Sasol Secunda FA is <250 µm (Mahlaba et al., 2011a).

2.5.2 Chemical, mineralogical, physical and morphological characteristics of fly ash

Fly ash is mainly made up of inorganic matter present in the feed coal. Most fly ashes around the world are grey in colour, alkaline with an abrasive texture and having refractory properties. Coal fly ash particle size generally ranges from less than 1 µm to 150 µm (finer than Portland cement). The physical and chemical properties of fly ash largely depend on the coal type used which in turn is influenced by the geography of the region from which the coal was formed. Therefore, the chemical composition of fly ash is often similar to that of the parent coal from which it is derived. However, apart from the nature of the parent coal, the composition and properties of FA also depends on other factors such as combustion conditions and disposal methods employed at the power station

(Ahmaruzzaman, 2010; Jala & Goyal, 2006; Mishra & Das, 2010; Vassilev & Vassileva, 2007). Campbell (1999) noted that additives such as sulphur trioxide (SO_3), sodium carbonate, sodium sulphate, sodium bicarbonate and ammonia, which are added to improve the efficiency of electrostatic precipitators in ash collection systems may influence the composition of fly ash.

Coal fly ash contains elements and minerals in various quantities. Approximately 188 minerals or mineral groups have been identified in coal fly ashes. The most common major elements are silicon (Si), aluminium (Al) and iron (Fe) while calcium (Ca), potassium (K), sodium (Na) and titanium (Ti) are commonly found in minor quantities. The common minerals in coal fly ash are quartz (SiO_2), mullite ($Al_6Si_2O_{13}$), hematite (Fe_2O_3) and magnetite (Fe_3O_4) however $CaSO_4$, MgO and CaO also occur in coal fly ash (Petrik et al., 2003; Vassilev & Vassileva, 2007). Wang & Wu (2006) proposed an empirical formula for coal fly ash based on the dominance of certain key elements as shown below:

$$Si_{1.0}Al_{0.45}Ca_{0.51}Na_{0.047}Fe_{0.039}Mg_{0.020}K_{0.013}Ti_{0.011}$$

The presence of radioactive elements in coal fly ash has also been reported. Peppas et al., (2010) identified five radionuclides namely ^{238}U, ^{226}Ra, ^{232}Th, ^{210}Pb and ^{40}K in coal fly ashes from Greece and Denmark. The authors further showed that the concentration of radionuclides in coal fly ash varied among different size fractions. Therefore, it is possible to have fly ash sampled from different points in the same power station with varying radiological characteristics as a result of different size fractions.

Coal fly ash is classified into three classes based on the chemical composition as per the American Society for Testing and Materials (ASTM). The ASTM C618 specification classifies coal fly ash into class F, class C and class N. This classification system is based on the use of coal fly ash as a pozzolan or mineral admixture in concrete. Class F fly ash is obtained from the burning of anthracite and bituminous coals while class C fly ash is produced from the burning of lignite and sub-bituminous coals. Table 3 shows the chemical requirements for the

different classes of coal fly ash. In class F fly ash, the sum of the oxides of silicon, aluminium, and iron by mass is ≥70 % while in class C fly ash this sum is between 50 and 70 %. Class C fly ash has higher calcium oxide (CaO) or free lime content than class F. Both class F and C fly ashes are pozzolanic in nature however, class C fly ash has cementitious properties (self-hardening when reacted with water) unlike class F fly ash. Class N fly ash is composed of raw natural pozzolans such as calcined clays and shales; opalinecherts, and shales; tuffs, diatomaceous earths, volcanic ashes, and pumicites (ASTM C-618, 1993; Mishra & Das, 2010; UND EERC, 2011).

Table 3: Chemical specifications for the three different classes of coal fly ash

Chemical specifications	F	C	N
Silicon dioxide + aluminium oxide + iron oxide ($SiO_2 + Al_2O_3 + Fe_2O_3$), min %	70	50	70
Sulphur trioxide (SO_3), max %	5	5	4
Calcium oxide (CaO)	<10	>20	
Moisture content, max %	3	3	3
Loss of ignition (LOI), max %	6	6	10

Source: ASTM C-618 (1993).

Lignite and sub-bituminous coal fly ashes (class C) mostly have higher concentration of sulphate compounds compared to bituminous coal fly ashes (Class F). However, lignite and sub-bituminous coal fly ashes mostly have lower loss of ignition (LOI) than bituminous coal fly ashes (Ahmaruzzaman, 2010). Table 4 shows the normal range of the chemical composition of fly ashes from different coal types.

Table 4: Normal range of chemical composition for fly ash produced from different coal types

Component (wt. %)	Bituminous	Sub-bituminous	Lignite
SiO_2	20 - 60	40 - 60	15 - 45
Al_2O_3	5 - 35	20 - 30	10 - 25
Fe_2O_3	10 - 40	4 - 10	4 - 15
CaO	1 - 12	5 - 30	15 - 40
MgO	0 - 5	1 - 6	3 - 10
SO_3	0 - 4	0 - 2	0 - 10
Na_2O	0 - 4	0 - 2	0 - 6
K_2O	0 - 3	0 - 4	0 - 4
LOI	0 - 15	0 - 3	0 - 5

Source: Ahmaruzzaman (2010).

Several studies on the morphology of coal fly ash have been done over the years. It has been found that coal fly ash is mainly composed of hollow spheres commonly known as "cenospheres" with the average size ranging between 45 μm and 150 μm (Ngu et al., 2007). The formation of cenospheres takes place at temperatures ranging approximately 1500 - 1650 °C (Anshits et al., 2010). Fly ash particles have smooth outer surfaces which are due to the presence of aluminosilicate structures that exist in the form of small spherical grains (Styszko-Grochowiak et al., 2004). According to Ward & French (2005), the aluminosilicate fraction forms the glassy matrix within the fly ash which is capable of adsorbing trace elements. The adsorbed elements are loosely held to the surfaces of the fly ash and can easily leach to the surrounding environment.

2.5.3 Disposal of fly ash

In the Republic of South Africa and many other countries around the world, coal fly ash is either "dry" dumped or hydraulically disposed as slurry in "wet" disposal method (Mahlaba et al., 2011a). The two major energy companies in South Africa, Sasol and Eskom, use different disposal methods with Sasol preferring the wet disposal method while Eskom employs the dry dumping method. At Sasol Secunda power station, the fly ash is collected then mixed with brine and stirred to form slurry using a 5:1 brine/ash ratio. The slurry is later pumped via pipes to the ash dam where it is left to settle. Excess disposal water is

then removed using a penstock. However, some of the saline water infiltrates through the dam and is later collected at the bottom of the ash dam using a toe drain. At Eskom Tutuka power station, the fly ash is collected and transported from the power station to the ash dump using conveyor belts (Akinyemi, 2011b). Prior to the transportation, the fly ash is conditioned with brine in order to moisten it. However, after disposal more brine is used to condition the fly ash at the ash dump in order to reduce the dust arising from wind-blown fly ash particulates. Figure 4 shows pictures taken at Sasol Secunda and Eskom Tutuka power stations highlighting the wet and dry disposal methods respectively.

Figure 4: Ash disposal methods (left: wet disposal, right: dry disposal).

Many countries around the world today dispose fly ash in landfills, ponds or lagoons while bottom ash is dumped in landfills or abandoned mine sites. These disposal mechanisms pose different challenges including high disposal costs, encroachment on agricultural land and general environmental degradation due to the leaching of toxic elements from the fly ash into surrounding soil or ground water (Ahmaruzzaman, 2010; Levandowski & Kalkreuth, 2009). There is also the danger of ash ponds or ash dams collapsing because of the high water content in them. The wet disposal method is more likely to encounter this scenario as opposed to the dry disposal method. Figure 5 shows the real magnitude of the danger posed when a coal ash retention pond breaks its walls.

Figure 5: A collapsed coal ash retention pond (Sourced from Safer environment, 2009).
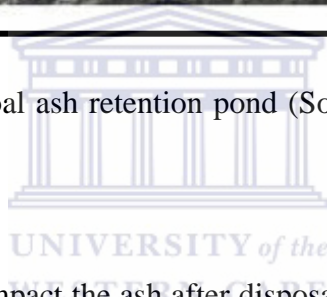
Some power stations compact the ash after disposal in order to create a hard layer which minimizes infiltration of aqueous materials reducing leaching. Others rehabilitate ash dams and dumps by planting vegetation on them after the dumping process stops so as to minimize leaching (Carlson & Adriano, 1993).

2.5.4 Environmental impact of fly ash after disposal

As mentioned earlier, coal fly ash has the potential to release toxic elements into the environment through leaching which may pollute both surface and ground water. Toxic trace metal elements from the flue gas condense on the fly ash particles making them potentially hazardous to the environment. Coal fly ash particles can also be blown by wind from the dump site to pollute the air. Inhalation of coal fly ash particles poses health risks to humans as these particles settle on the lung surface and may leach genotoxic compounds into the human body. Crystalline silica which is a major component in coal fly ash is classified as a genotoxic human carcinogen (Borm, 1997). Apart from the release of toxic

elements, ash dams and dumps may occupy fertile land which could otherwise be used for crop farming. According to Jones (1995), there is a high risk of groundwater contamination in wet disposal mechanisms than dry disposal methods due to the high liquid to solid ratios used in making the slurries before disposal, which leads to rapid dissolution of all the soluble components in the fly ash. Widespread research is being done around the world focusing on turning waste materials like coal fly ash into new useful products (Wang & Wu, 2006). More utilization options for coal fly ash would mean less threat to the environment as dumping of fly ash would be minimized or even stopped completely if all the fly ash around the world could be utilized.

2.5.5 Utilization options of fly ash

Approximately 16 % of the 500 million tons of fly ash produced per annum globally is utilized while the remaining 84 % (about 420 million tons) is disposed in ash dumps or dams (Ahmaruzzaman, 2010; Mahlaba et al., 2011b). Today's research should focus on utilization options for the fly ash rather than looking for better ways of disposing it. In order to come up with utilization options for fly ash, it is necessary to understand the chemical composition, mineralogy, surface chemistry and reactivity of the ash. Fly ash can be utilized as a form of fertilizer as it may contain some macronutrients and micronutrients such as P, K, Ca, Mg, Zn, Fe, Cu, Mn, B, and Mo which are crucial for plant growth. Fly ash can also be utilized in road and embankments construction and in structural filling as its geotechnical properties such as specific gravity, permeability, internal angular friction, and consolidation characteristics make it suitable for this purpose (Ahmaruzzaman, 2010). In India, where coal fired power plants contribute about two thirds towards meeting the power demands of the nation, coal fly ash is utilized in brick-making, land filling, construction purposes and soil amendment (Sarkar et al., 2006). Fly ash can be utilized in the manufacture of cement and concrete due to its lime binding capacity. Fly ash from pulverized coal combustion is categorized as a pozzolan. Pozzolans are aluminosilicate materials which exhibit cementitious properties upon contact with water and calcium hydroxide at room temperature. In Brazil, fly ash is utilized in the production of pozzolanic cement and paving (Levandowski & Kalkreuth, 2009) while in Greece,

most of the coal fly ash produced from power plants is utilized in cement manufacture (Skodras et al., 2007). Fly ash can also be utilized in zeolite synthesis due to its high percentage of silica (60 - 65 %), alumina (25 - 30 %), Fe_2O_3 (6 - 15 %) and magnetite or as an adsorbent due to its suitable physicochemical characteristics such as bulk density, particle size, porosity, water holding capacity, and surface area (Ahmaruzzaman, 2010). Other utilization options of fly ash include use as a low-cost adsorbent for flue gas cleaning, wastewater treatment for the removal of toxic ions or heavy metals and organic matters. By understanding the characteristics and properties of coal and fly ash, it is possible to come up with utilization options and environmental impact assessment after disposal. Mineralogical and geochemical studies are required to understand the inorganic matter contained in coal. This is crucial in coming up with utilization options and environmental impact evaluation (Ahmaruzzaman, 2010; Levandowski & Kalkreuth, 2009; Liu et al., 2005; Skodras et al., 2007; Sarkar et al., 2006). Wang & Wu (2006) considered fly ash as a resource that is so far insufficiently exploited rather than a waste material. The authors looked at the possible uses of fly ash based on some properties and factors such as chemical composition, size range, pozzolanic nature and abundance. Figure 6 shows some of the possible uses of this resource based on these properties and factors.
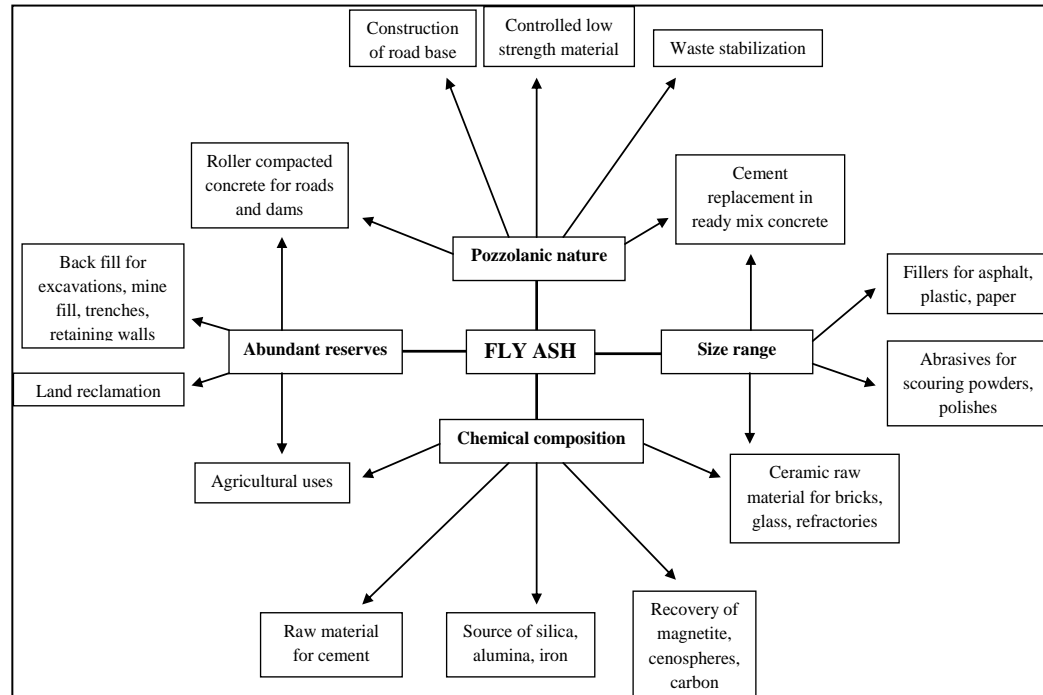
Figure 6: Possible uses of fly ash based on specific properties (Sourced from Wang & Wu, 2006).

Mishra & Das (2010) looked at the utilization option of coal fly ash in stowing or mine back filling of underground coal mines. The authors considered the physico-chemical and mineralogical characteristics of fly ash and concluded that pond ash was the better stowing material than fly ash based on particle size and permeability. However, fly ash too has a huge potential in stowing or mine backfilling which presents the opportunity of using it in bulk. Several factors must be considered in choosing the right stowing material for example, particle shape and size, density, permeability and water holding capacity are crucial in hydraulic stowing. Another important factor is that the material has to be chemically inert and free of any carbonaceous matter in order to avoid spontaneous heating. Montes-Hernandez et al., (2009) proposed the use of coal fly ash to sequester carbon dioxide by aqueous carbonation since most coal fly ashes contain a significant amount of lime (CaO) (about 4.1 wt. %). The carbonation process takes place in two steps as shown in the equations below which involve the hydration of lime (1) and carbonation of calcium hydroxide suspension (2).

$$CaO + H_2O \rightarrow Ca(OH)_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.(1)$$

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O \ldots\ldots\ldots\ldots\ldots\ldots.....(2)$$
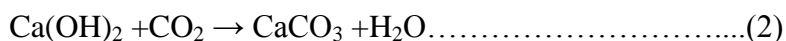
Nyambura et al., (2011) showed that brine impacted coal fly ash from SA could be used for CO_2 sequestration through mineral carbonation. Today, coal combustion by-products such as fly ash are being considered in several utilization options driven by the availability of mineral elements resembling earth's crust contained in these by-products, thus making them excellent replacements for natural materials. Some of the modern day applications for these by-products include use as substitute for Portland cement in the manufacturing of roofing tiles, use as structural fills, sheetrock, agricultural fertilizers and soil amendments. Fly ash contains almost all essential plant nutrients in ionic form and has an ameliorating effect on physical, chemical and microbial nature of soil making it a useful additive in crop production on degraded soils and waste lands (Ahmaruzzaman, 2010; Jala & Goyal, 2006; Vassilev & Vassileva, 2007).

Gitari et al., (2008) investigated the use of fly ash (FA) in the treatment of coal mines waste water, commonly referred to as acid mine drainage (AMD) and concluded that the removal of species such as Al, Fe and sulphates from AMD could be attained at a certain target pH depending on the FA: AMD ratio used and contact time of the two. Madzivire et al., (2010) showed that coal fly ash could be used for sulphate removal from circumneutral mine water at various pH through precipitation of gypsum and ettringite. In recent years, zeolite synthesis from coal fly ash has attracted a lot of interest. High cation exchange capacity (CEC) zeolites can be produced from coal fly ash and later utilised in waste water and AMD treatment (Somerset et al., 2005) and flue gas treatment (Querol et al., 2002). The zeolites can be used for the uptake of heavy metals such as Ni, Cd, Zn and Pb from AMD (Somerset et al., 2005) and ammonium from polluted waters (Querol et al., 2002). Coal fly ash zeolites can also be used as molecular sieves e.g. to adsorb water molecules from gas streams or in the capture of SO_2 and NH_3 from low water gaseous emissions (Querol et al., 2002). Babajide et al., (2010)

studied the use of coal fly ash as a catalyst in biodiesel production. The study showed that fly ash loaded with KNO_3 can be used in the conversion of sunflower oil to methyl esters and glycerol. The oil conversion increased with increased catalyst loading.

2.6 BRINE

2.6.1 Origin and composition of brine

Brine is water saturated or nearly saturated with salt(s). Brines occur naturally or as a result of industrial activities. The most common salt naturally present in brine is sodium chloride. However, brines may contain different kinds of salts depending on the conditions leading to their formation. Brines generally contain cations and anions such as sodium, potassium, calcium, magnesium, iron, ammonia, silica, sulphate, chloride, bromide, nitrate, bicarbonate, fluoride and trace elements. These ions are present in different quantities depending on the origin of the brine (Benitez et al., 2003; McKaveney et al., 1972). Brines are waters more concentrated in dissolved materials than sea water and can contain salt concentration more than five times greater than the average salt content of sea water. Natural brines exist deep inside the earth, however some are found on the surface of the earth with extremely high concentration of dissolved elements, ions and molecules (Water Encyclopedia, 2011). Fresh water is considered to have salinity levels < 200 mg/L while brackish water ranges 1000 - 15,000 mg/L. Saline water lies at > 15,000 mg/L while brine may have salinity levels > 50,000 mg/L (El-Manharawy & Hafez, 2001). Table 5 shows the composition of sea water from different regions. Pluta & Zuber (1995) classified fresh waters as having total dissolved solids (TDS) < 1 g/L while mixed or brackish waters and brines as having TDS 1 - 35 g/L and 35 - 230 g/L respectively. A previous study has shown that saturated brine is 26.4 % salt by weight at 15.5 ℃ (60 ℉) and 23.3 % salt by weight at 0 ℃ (32 ℉) (Petrik et al., 2007). Desalination plants are major sources of brine. Desalination processes involve the removal of salt constituents from saline waters to acceptable levels set by international watchdog institutions such as the World Health Organization (WHO). According to Tiwari et al., (2003), sea water has salinity levels ranging 35,000 - 45,000 ppm (mg/L) in the

form of total dissolved salts while most of the normal water on earth has levels up to 10,000 ppm (mg/L). WHO salinity limits are set at 500 ppm up to a maximum of 1,000 ppm for a few special cases.

Table 5: Composition of sea water in mg/L from different regions showing the major ions present

mg/L	Typical sea water	Eastern Mediterranean	Arabian Gulf (Kuwait)	Red Sea (Jeddah)	Cape Town
Chloride (Cl^-)	18980	21200	23000	22219	19833
Sodium (Na^+)	10556	11800	15850	14255	10168
Sulphate (SO_4^{2-})	2649	2950	3200	3078	2733
Magnesium (Mg^{2+})	1262	1403	1765	742	1234
Calcium (Ca^{2+})	400	423	500	225	394
Potassium (K^+)	380	463	460	210	397
Bicarbonate (HCO_3^{3-})	140		142	146	
Strontium (Sr^{2+})	13				8
Bromide (Br^-)	65	155	80	72	
Borate (BO_3^{3-})	26	72			
Fluoride (F^-)	1				
Silicate (SiO_3^{2-})	1		1.5		
Iodide (I^-)	<1	2			
TDS	34483	38600	45000	41000	34800

Source: Lenntech (2011)

Desalination plants use water treatment procedures which lead to the production of effluents. One of the most common procedures used in desalination is reverse osmosis (RO). This procedure offers advantages in terms of cost effectiveness due to its low energy consumption and low membrane cost and its flexibility within the different demand areas like industry, agriculture and population supply. However, RO produces brine which is a concentrated effluent with potential hazardous consequences to the environment (Pluta & Zuber, 1995). Sasol Secunda power station uses RO technology in the desalination procedures which are essential in providing clean feed waters for steam generation and cooling purposes. Table 6 shows the concentrations of the major ions present in brine samples taken from Sasol Secunda power station.

Table 6: Concentrations in mg/L of the major ions in brine samples taken from Sasol Secunda power station

Ion	Concentration (mg/L)
Ca	699.09
Mg	8.46
Na	2355.53
Cl	1643.98
SO_4	4364.88
pH	5.76

Source: Nyamhingura (2009)

Nyamhingura (2009) showed that the concentrations of the ions in Secunda brine varied at different points in the plant. At Sasol Secunda power station, the saline effluents generated from water treatment procedures are used in the hydraulic transport of fly ash during disposal. The excess water collected from the ash dams after disposal is put together with other waste waters produced from the power plant. The resulting mixture is then treated using reverse osmosis (RO) and electro dialysis reversal (EDR), generating a different set of saline effluent which is again used for hydraulic transport of more fly ash produced, and the cycle continues.

2.6.2 Brine disposal mechanisms and environmental implications

In choosing a disposal method for high saline waste, several factors are considered, which include: the physical and geographical location of the discharge point, the volume of concentrate, the quality of concentrate, capital and operational costs involved among others (Arnal et al., 2005). The cost of disposing saline effluents depends on factors such as the location of the plant. Inland plants pose a greater challenge towards brine disposal compared to plants located along a coastline (i.e. near the sea) where the effluent is discharged into the sea and quickly gets diluted to non-hazardous levels. Several disposal methods have been used for plants located inland such as the use of evaporation ponds, deep well injection, irrigation of high salinity tolerant plants, disposal into surface water bodies, disposal to municipal sewers and concentration (i.e. by evaporation) into solids salts (Sethi et al., 2006). Previous studies have shown that concentrating the brine into a solid waste would be the best option since handling

a solid is much easier than a liquid or a thick effluent. However, most desalination plants today use conventional evaporation techniques which require thermal energy production hence making them non-economical (Pluta & Zuber, 1995). Arnal et al., (2005) suggested the application of evaporation under natural environmental conditions in order to reduce energy consumption. The brine can first be concentrated up to the RO operational limit of around 70 g/L of salinity. Then the resulting concentrated effluent can be crystallized by evaporation into a solid waste, which can later be reused.

The Deep Well Injection brine disposal method (Svensson, 2005) involves injecting the brine deep into aquifers containing waters that are deemed unfit for human consumption. However, this method has some drawbacks, first is the high cost of the injection exercise and second is the uncertainty of the injected brine having a negative impact on the surrounding environment. Another method used in brine disposal is Aquifer Re-injection. Here, the brine is re-injected back into the same source from which the desalination plant feed water came from. The intake point and the re-injection point are supposed to be considerably apart so as not to compromise feed water quality (Svensson, 2005). As mentioned in chapter one (section 1.3), Sasol Secunda power station practices a policy of brine disposal known as Zero Liquid Effluent Discharge (ZLED) policy. The Zero Liquid Discharge method involves a combination of several treatment and concentration steps followed by a thermal process (Johannsen et al., 2006) to produce a concentrated dry solid waste without disposing any liquid waste into the surrounding environment. The dry solid waste is then disposed into the sea, in mines or into designated salt sinks.

For many years, evaporation ponds have been used in salt recovery. This same method is applied in brine disposal whereby the saline waste is exposed to high temperature conditions leading to evaporation and subsequent recovery of a dry solid waste. One of the main challenges facing this method is the availability and the cost of acquiring land to establish the ponds. The ponds also need close monitoring to avoid downward seepage of the liquid waste into the ground which

means lining of the walls of the ponds is necessary. Other brine disposal methods used include discharge to wastewater treatment plants, disposal in coastal desalination sites and discharge to open land (Ahmed et al., 2000).

Brines from desalinations plants have the potential to impact negatively on the environment upon disposal. Some of the areas of concern include human and animal life, marine life and plant life (Al-Agha & Mortaja, 2005). Metals species such as Cd, Sr, Ni and Cr commonly contained in brines have been found to be carcinogenic. As is one of the most poisonous elements contained in brine and is capable of affecting lungs, skin, white and red blood cells, causing brain damage and even DNA damage. B, Pb, V and Cu can cause liver and kidney damage. Mo causes gout and liver dysfunction while Zn can cause pancreas damage (Lenntech, 2011). Through surface and ground water contamination, the elements mentioned above may end up being ingested by humans and animals. Marine life is often affected by the disharmony in salinity levels brought about by the disposal of brine into the sea since marine life depends on a certain osmotic balance with the surrounding environment (Svensson, 2005) which is crucial for their survival. It has been reported that disposed brine increases the temperature of sea water causing a reduction in dissolved oxygen in the water (Qdais, 1999). Although one of the uses of brine today is irrigation, it is important to note that not all plant life is tolerant to high salinity exposure. According to (Svensson, 2005), high salt tolerant species include sugar cane, sugar beet and cotton while less salt tolerant species include carrots, onions, beans, strawberries and almonds. According to Al-Faifi et al., (2010), disposed reject brine has the potential to impact negatively on soils, altering their chemical composition thus leading to undesirable effects such as lower permeability and poor aeration in the soils.

2.6.3 Uses of brine

Saline effluents have for a long time been considered as waste material. It is important to change this perception and actually view them as a resource. Several utilization options have been considered including use in agriculture and mineral production among others. Over the years, natural brines have attracted commercial interest due to the high concentration of dissolved components such

as Na and Mg in them. Saline water bodies such as the Great Salt Lake in Utah, USA, the Dead Sea in Israel, and the Salton Sea in California, USA are natural sources of brine which can be used in the production of table salt (Petrik et al., 2007). Brines from coal mines can also be utilized in table salt production through evaporation and crystallization processes. However, coal mine brines may contain less concentration of sodium chloride (NaCl) compared to natural saturated brines or brines obtained from leaching salt beds. Hence, to enable the process of table salt production from coal mine brines, the brines have to be pre concentrated to obtain NaCl concentration of 305 - 315 g/L to make them an ideal source of sodium chloride (Turek et al., 2008b, Turek, 2004). Coal mine brines can also be utilized in chlorine production (Turek et al., 1995). Turek et al., (2008a) proposed the production of electric energy from coal mine brine using reversed electro dialysis (RED) by mixing coal mine brine with low salinity water. An electro dialytic unit equipped with alternatively arranged cation and anion exchange membranes mounted in between two Pt-coated electrodes was used.

The SAL-PROC process is used in the production of chemicals through extraction of these chemicals from inorganic saline waters. The extraction is done through multiple evaporation and/or cooling together with mineral and chemical processing. The major advantage of this process is the "zero liquid discharge to the environment" aspect (Ahmed et al., 2003).

The Eutectic Freeze Crystallization (EFC) is a novel separation technique used for salt recovery from hyper saline brines (Lewis et al., 2010). The authors used the EFC technique to treat South African hyper saline brines and produced a number of pure salts such as sodium sulphate, magnesium sulphate and pure ice. The crystallizer was operated at eutectic conditions.

As mentioned earlier, saline effluents can be used for agricultural purposes such as the irrigation of high salt tolerant crops as mentioned in section 2.6.2, fish farming, algae and shrimp production. Some of the species of fish that can tolerate high salinity include tilapia, red snapper, barramundi, black bream, milk fish and

mullet. Saline effluents can also be used for electricity and heat generation. Solar ponds store energy from the sun and can be a source of thermal energy which can be utilized in electricity and heat generation (Ahmed et al., 2001; Svennson 2005; Walton et al., 2001). Figure 7 shows a schematic representation of a solar pond.
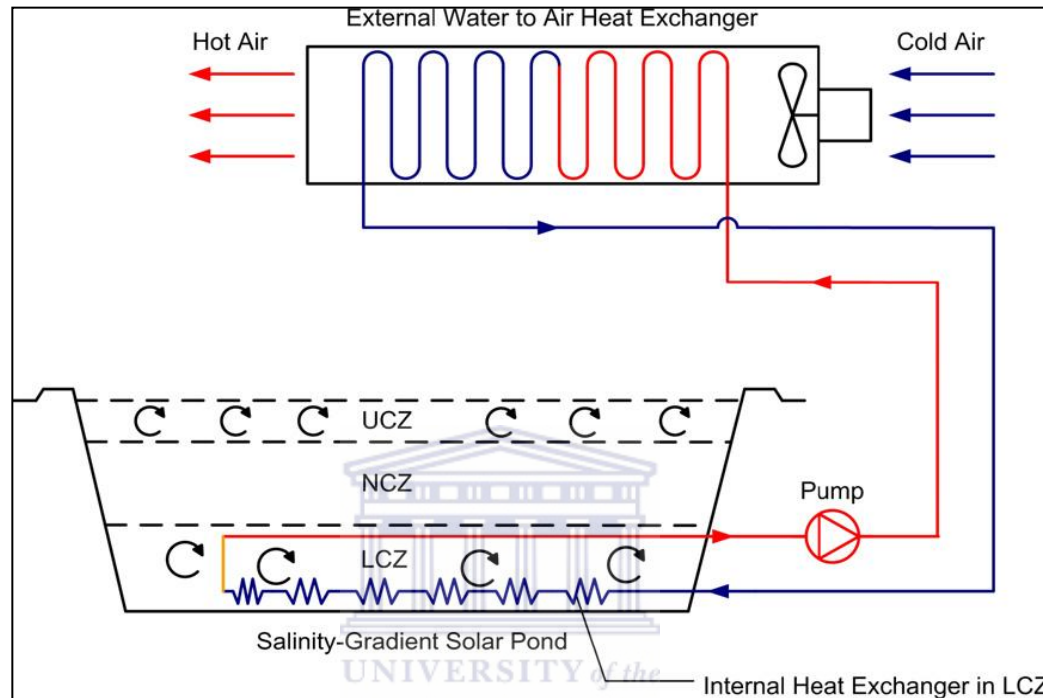
Figure 7: A schematic representation of a salinity-gradient solar pond (Sourced from Leblanc et al., 2010).

The pond has three zones namely upper convective zone (UCZ) or surface zone, non-convective zone (NCZ) or gradient layer and lower convective zone (LCZ) or storage zone. Heat is extracted from the LCZ using a heat exchanger located within the LCZ. A heat transfer fluid circulates in a closed cycle through the internal heat exchanger and transfers its thermal energy through an external heat exchanger (Leblanc et al., 2010).

2.7 THE CHEMISTRY OF FLY ASH AND BRINE INTERACTIONS

It is crucial to understand the chemistry that takes place when coal fly ash interacts with brine as these two are often co-disposed together. This understanding will make it possible to come up with better solutions to avoid environmental degradation by adopting better disposal methods and finding

utilization options for these wastes. Previous studies have suggested that brine species may be retained in coal fly ash minerals upon contact of the two (Ecke et al., 2003) which may lead to an environmentally friendly disposal technique. Lime (CaO) contained in fly ash can interact with brine species such as sulphates to form gypsum ($CaSO_4$) at certain pH conditions (Ecke et al., 2003; Mooketsi et al., 2007). Mahlaba et al., (2011b) investigated the behaviour of pastes (for use in paste backfilling) composed of mixtures of brine and two types of fly ashes. Brine composition was varied during the mixing. The authors revealed that the fly ash characteristics had more influence than the brine chemistry in paste formation. The fly ash seemed to stabilize the contaminants in the paste. However, other studies have shown that when brine and fly ash interact, the brine introduces some species into the fly ash but also the fly ash releases many species into the brine (Fatoba, 2010). Furthermore, fly ash has the tendency to continuously release species upon contact with aqueous media (Pandian, 2004) therefore the ability of fly ash to trap and retain species from brine for an extended period of time remains to be proved.

2.8 CHARACTERIZATION OF FLY ASH

2.8.1 Bulk chemical analysis by X-Ray Fluorescence (XRF)

X-ray fluorescence spectrometry (XRF) is an analytical technique that identifies and determines the concentrations of elements contained in solids, powders and liquids. XRF offers a major advantage in that it is non-destructive and can analyse many elements in the periodic table ranging from beryllium (Be) with atomic number 4 to uranium (U) with atomic number 92 at trace levels (Czichos et al., 2006). The XRF spectrometer works on the principle of bombarding atoms with X-rays which knock out inner shell electrons thus creating vacancies. These vacancies are then filled up when outer shell electrons fall back from higher energy levels. This phenomenon emits fluorescence energy and wavelength spectra, which are characteristic of atoms of specific elements thus enabling the estimation of their relative abundances (Weltje & Tjallingii, 2008). XRF technique can analyse elements from ppm to percent levels (EPA, 2004).

2.8.2 Mineralogical analysis by X-Ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive analytical technique that can determine the chemical composition and crystallographic structure of natural and manufactured materials (Vijay, 2007). The most commonly applied area in XRD is powder diffraction in determining the mineralogy of solids. In this technique, a powdered sample is placed on a holder and then bombarded with fixed wavelength X-rays. A goniometer then measures and records the intensity of the reflected radiation which is later stored into a database. The resulting data provides the reflection angles which are used to calculate the inter-atomic spacing or D spacing (measured in Angstrom units i.e. 10^{-8} cm). The D spacings are characteristic of specific mineral phases which aids in identifying the mineral phase by matching with database information (USGS, 1997).

2.8.3 Morphological analysis by Scanning Electron Microscopy (SEM)

Scanning electron microscopy (SEM) is an analytical technique used to investigate the surface morphology of substances. This technique uses a special kind of microscope known as the scanning electron microscope that uses electrons to form an image as opposed to the conventional microscope that uses light for imaging. The use of electrons for imaging rather than light offers many advantages including greater resolution due to higher magnification and larger depth of focus. The large depth of field allows the microscope to focus on a large part of the sample at one time while the high resolution makes it possible to investigate small features of the sample at high magnification (Goldstein et al., 2003). In SEM, an electron beam with energy up to 40 keV from an electron gun in the instrument bombards the sample and the images are formed using secondary electrons emitted from the sample (Bogner et al., 2007). Tungsten is commonly used for electron emission (Kowarik et al., 2009) in the electron gun.

2.8.4 Pore water analysis

Pore water or interstitial water refers to the water trapped in the small spaces between the grains of sediment (EPA, 2001). Figure 8 illustrates how pore spaces fill with water.
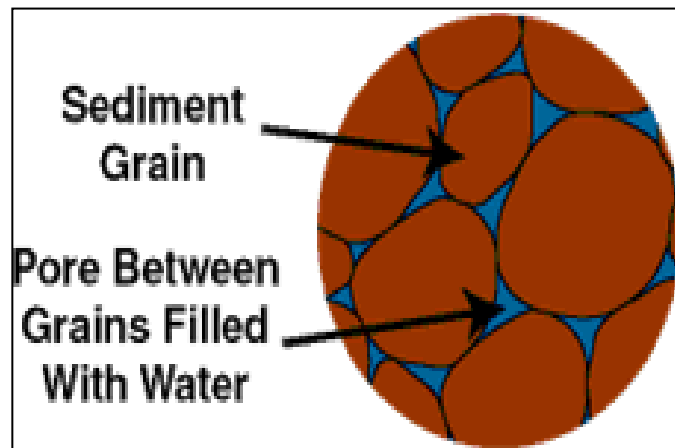
Figure 8: An illustration showing a microscopic cross section of sediment with pore spaces filled with water (Sourced from USGS, 2011).

Pore water analysis is done in order to determine several parameters or characteristics associated with the water contained in the pore spaces of the material of concern. According to Bufflap & Allen (1994), pore water analysis may be used for toxicity identification, sediment quality assessment and diagenetic studies. Pore water analysis is necessary in coal fly ash studies since the pore water contained in disposed fly ash may contain environmentally hazardous constituents such as arsenic and boron (Kolbe et al., 2011).

2.8.5 Moisture content determination

Moisture content (MC) refers to the quantity of water in a material e.g. soil or sludge. MC is expressed as percentage by weight of water in the mass of the material. MC determination is done using thermo gravimetric and drying techniques (May et al., 1982). The MC of a substance can influence the physical properties such as appearance and morphology of that particular substance (Tahir et al., 2007). The level of MC in fly ash is of concern since high MC in disposed fly ash may exacerbate the leaching of soluble species in the fly ash. The "wet" fly ash disposal method is characterized by high MC in the fly ash dam which leads to high water content in the disposed ash that may cause the collapse of the ash dam with time as shown in section 2.5.3 (Figure 5).

2.8.6 Ion Chromatography (IC)

Ion chromatography or ion-exchange chromatography (IC) comprises of liquid chromatographic techniques used to separate, identify and quantify inorganic cations, anions and low molecular weight water soluble organic acids and bases. Common anions identified by IC include chloride, fluoride, nitrate, nitrite and sulphate while cations include sodium, potassium, lithium and ammonium. The technique works on a principle that uses ion-exchange resins to separate ions contained in aqueous samples since the affinity of ion-exchange resins varies for different metal ions. In IC analysis, a mobile phase which is an ionic liquid passes through a solid stationary phase made up of uniformly packed polymeric particles in a cylindrical column. Then a known amount of sample containing analytes of interest is introduced at the top of the cylindrical column using an injector while the mobile phase continues to run through the cylindrical column. In the process, the ions of the mobile phase and sample ions displace fixed ions and exchangeable counter-ions contained in the solid stationary phase. A detector fixed at the end of the column monitors the flow rate of the sample analytes which pass through the column at different rates depending on the affinity of the sample ions for the fixed ion exchange sites, the ionic strength of the mobile phase and the ion exchange groups attached to the column particles. The sample ions therefore reach the detector at the end of the column at different times hence resulting in separation (Fritz, 1977; Shaw & Haddad, 2004). Other analytical techniques used to quantify metal ions in samples of wide ranging composition include atomic spectroscopy, or more specifically atomic absorption spectrometry (AAS), inductively coupled plasma mass spectrometry (ICP-MS) and atomic emission spectrometry (ICP-AES) (Shaw & Haddad, 2004). However, a major advantage of IC over these techniques is that apart from analysing samples in parts-per-million (ppm), IC is the only technique able to quantitatively analyse anions at parts-per-billion (ppb) level (New Mexico State University, 2006).

2.8.7 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES)

Inductively coupled plasma-optical emission spectroscopy (ICP-OES) is one of the Inductively Coupled Plasma (ICP) spectroscopic techniques that are used to determine concentrations of elements in solution. In these techniques, samples are introduced into the instruments in liquid form. The samples and calibration standards are pumped in the form of a spray into the argon plasma generated by the instrument. The inductively coupled plasma-optical emission spectrometer is equipped with a torch which generates the plasma of argon gas reaching to temperatures of about 10,000 K (9,727 °C) (Karbasi et al., 2009). The elements in the samples and standards become thermally excited emitting light which is characteristic of their wavelengths. A spectrometer in the instrument collects the light which then passes through a diffraction grating that converts the light into a spectrum of its constituent wavelengths. The spectrum is amplified producing an intensity measurement which is finally converted to an elemental concentration by comparison with the calibration standards (Thomas, 2001). One of the major advantages of ICP-OES compared to older techniques such as AAS is that it has very low detection limits for most metals (Lunderberg et al., 2008). Furthermore, the high temperature plasma in ICP-OES atomizes and excites even the most refractory elements such as vanadium, zirconium and molybdenum which are difficult to analyse using AAS (Karbasi et al., 2009). According to Olesik et al., (1994), the precision of ICP-OES ranges 0.2 - 0.5 % for liquid samples or dissolved solids while accuracy ranges from 10 % using simple, pure aqueous standards, to 0.5 % using more elaborate calibration techniques. The sensitivity of ICP-OES ranges from sub-ppb to 100 ppb (Holloway & Vaidyanathan, 2009).

2.8.8 Sequential extraction

Sequential extraction (SE) is a procedure used to selectively leach out metal species from soil, sludge and sediment samples. Specific metal fractions dissolve in certain solutions under various environmental conditions. In SE, several reagents are used which exhibit selectivity towards specific geochemical phases. The specific metal fractions are then extracted selectively by using appropriate

reagents. The selectivity of the reagents used enables the extraction of metal species in the specific geochemical phases such as carbonates, sulphides, oxyhydroxides of iron, aluminium and manganese, phyllosilicate minerals and organic material. The accuracy of this method is evaluated by comparing the total metal concentrations with the sum of the specific individual fractions, i.e. mass balance. SE is capable of giving information concerning the mode of occurrence, bioavailability, the origin and mobility trends of metal species in materials such as soil, sludge and sediment (Filgueiras et al., 2002; Tessier et al., 1979). Jegadesaan et al., (2008) used SE in the partitioning of metal species in coal fly ash. SE aids in the investigation of biological and geochemical processes since it gives information about the 'solid-speciation' of chemical elements in soils and in suspended and deposited sediments (Martin et al., 1987).

Tessier et al., (1979) looked at the chemical behaviour of elements in river sediment samples based on five specific fractions namely exchangeable, bound to carbonates, bound to Fe & Mn oxides, bound to organic matter and residual fractions. The authors observed that metals extracted in the exchangeable fraction were released due to a change in the ionic strength of the medium while metal species bound to carbonates could be released as pH decreased as they were pH sensitive. As for the metal species bound to Fe & Mn oxides and organic matter, the authors observed that these could be released due to increasing oxidising or reducing conditions in the environment. The metal species within the residual fraction such as silicates showed resistance to release in solution signifying that these would stay locked up in this fraction for quite a long time under normal conditions in nature (Tessier et al., 1979). SE is however not without its limitations. Absolute selectivity of various extractants for metals in specific phases is not guaranteed (Martin et al., 1987). Shannon & White (1991) performed sequential extraction procedure on lake sediments and noted that sediment handling and treatment before or during extraction could alter the sediment chemistry causing repartitioning of metal phases into various sediment fractions.

2.9 SECTION SUMMARY

This literature review section considered the body of knowledge on the origin, characteristics, interaction chemistry and environmental implications of fly ash and brine, which informed the choice of the main objective of this study, which was to understand the changes taking place in the disposed ash from a wet ash handling system due to weathering processes. The mobility patterns of chemical species in the disposed ash is of importance in order to evaluate the salt holding capacity of the ash dam. The experimental and analytical methods used in this study are discussed in the next chapter.

UNIVERSITY *of the*

WESTERN CAPE

CHAPTER THREE

3. EXPERIMENTAL AND ANALYTICAL METHODS

This chapter gives the outline of the experimental and analytical methods employed in meeting the objectives of this study.

3.1 MATERIALS AND METHODOLOGY

The weathered fly ash from Secunda used in this study is made up of approximately 83 % fly ash from the combustion of pulverized coal to produce steam and electric power and 17 % comprising of fine ash from the gasification process and fine bottom ash. The fly ash has a particle size of <250 μm (Mahlaba et al, 2011a). The ash was pumped as slurry of 5:1 brine/ash ratio using the high saline stream that was generated from the water treatment processes in the plant. Table 7 below shows a list of the chemicals and reagents used in this study.

Table 7: Summary of chemicals and reagents

Chemical	Supplier	Purity
Ammonium acetate (CH_3COONH_4)	Kimix	98 %
Acetic acid (CH_3COOH)	Kimix	99.8 %
Nitric acid (HNO_3)	Kimix	55 %
Hydroxylamine hydrochloride ($H_3NO^{.}HCl$)	Kimix	99 %
Hydrofluoric acid (HF)	Kimix	40 %
Perchloric acid ($HClO_4$)	Merck	60 %
Boric acid (H_3BO_3)	B&M Scientific	99.5 %
Ammonia solution ($NH_{3(aq)}$)	Kimix	25 %

3.2 SAMPLING

3.2.1 Sample history

Sasol Secunda power station has disposed fly ash from coal gasification and power generation in dams over a period of 20 years. The ash dam from which the

samples used in this study were collected started operation in 1989 and ash dumping stopped in 2009. The oldest layer at the bottom of the ash dam was 20 years old and the youngest layer at the top of the ash dam was 1 year old. As earlier mentioned in chapter one, the fly ash was mixed with brine and disposed in slurry form.

3.2.2 Sample collection and storage

The weathered ash samples used in this study were collected using a drill. A geophysics electrical resistivity survey profile aided in choosing the drilling spot. The area was selected as shown in Figure 9. This study was conducted using ash samples obtained from Secunda core S2 (51 m).
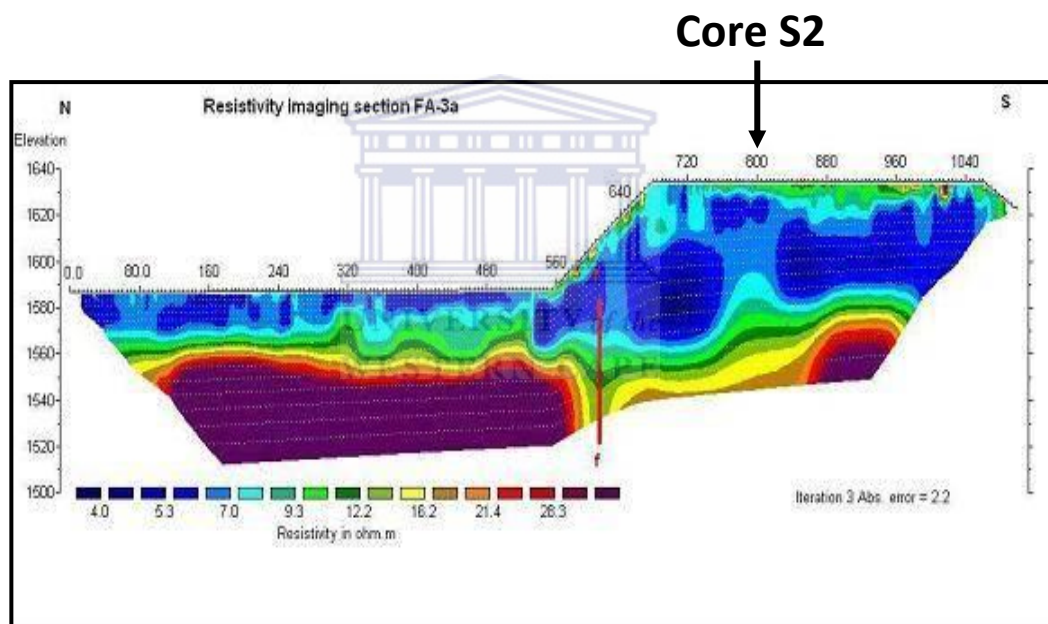
Figure 9: Resistivity mapping of Sasol Secunda ash dam showing the site for core S2.

Core S2 was drilled at 800 m (Lat 26.559099, long 29.119039). Figure 10 below shows photos of the drilling process at Secunda ash dam. A combination of air flush coring and standard percussion drilling was used to drill the cores at the ash dam.

Figure 10: Drilling process at Sasol Secunda ash dam.

An initial starter hole was drilled (215 mm diameter) using air percussion drilling through the top layer of the ash dam. The air flush coring technique was then used to drill to the bottom of the ash dam. Large diameter vertical boreholes were drilled in the ash dam to extract samples for evaluation. The drilling technique produced 165 mm diameter cores from which approximately 100 - 200 gram of fly ash sample was taken from the inside of the air flush core barrel at 1.5 m sampling intervals. The samples of ash were extracted from the core and secured in zip-lock plastic bags and degassed for preservation before analysis. The drilled holes were completed with small concrete rings with shallow (30 cm) sanitary seals, and equipped with special tall standing lockable caps. All the completed drilled holes were clearly numbered according to the existing numbering system at the site. Coring for S2 stopped at 51 m. After sampling, the ash samples were then stored in air tight sealed containers to prevent moisture loss and interaction with CO_2 and O_2 from the atmosphere (see Figure 11). The sample containers were stored in a dark cool cupboard to avoid temperature fluctuations. The ash samples were later milled into a homogeneous fraction before characterization (see Figure 11).

Figure 11: Sample storage and milling (left: storage in air tight containers, right: milled samples ready for analysis).

The fresh fly ash sample used in this study was collected from the hoppers inside the ash collection system at Sasol Secunda power station. The sample was also stored in an air tight sealed container, and in a dark cool cupboard to prevent contamination and temperature fluctuations.

3.3 ANALYTICAL METHODS

3.3.1 Scanning Electron microscopy (SEM)

Scanning electron microscopy was conducted in order to understand the changing morphology of the fly ash as age increased. One fresh fly ash sample and three samples of the weathered fly ash taken from the surface, 24 m (middle of core S2 of the Secunda ash dam) and 51 m (bottom of core S2 of the Secunda ash dam) were analysed. The ash samples were oven-dried at 105 $^{\circ}$C for 12 hours to remove any adsorbed moisture. A portion of each of the four dry samples was then spread onto specimen holders using special glue mixed with carbon graphite. The analysis was carried out with a Nova NanoSEM 230 series, equipped with an Oxford X-max detector, at low voltage and high contrast mode using the backscattered electrons detector.

3.3.2 X-ray Diffraction (XRD)

The mineralogical composition of the fresh fly ash and the weathered fly ash was investigated using XRD. One sample of fresh fly ash and ten weathered fly ash samples taken from different depths down core S2 of the Secunda ash dam were analysed; surface, 6 m, 12 m, 18 m, 24 m, 30 m, 36 m, 42 m, 48 m and 51 m. A portion of the fly ash samples were oven-dried at 105 °C for 12 hours to remove adsorbed water prior to XRD analysis. Two grams of each of the samples mentioned above were pressed into rectangular aluminium sample holders using an alcohol wiped spatula and then clipped into the instrument sample holder. A Philips PANalytical instrument with a pw3830 X-ray generator operated at 40 kV and 25 mA was used. The samples were step-scanned from 5 to 85 degrees 2 theta scale at intervals of 0.02 degrees and counted for 0.5 seconds per step.

3.3.3 X-ray Fluorescence (XRF)

The bulk chemical composition of the solid fresh fly ash and the samples of weathered fly ash from core S2 were determined by XRF. One fresh fly ash sample and 35 samples of the weathered fly ash taken at 1.5 m depth intervals down core S2 of the Secunda ash dam were analysed. A portion of the fly ash samples were oven-dried at 105 °C for 12 hours to remove adsorbed water and then milled to a fine powder. 10 grams of each of the samples mentioned above were used for this procedure. A Phillips PANalytical pw1480 X-ray fluorescence spectrometer using a rhodium tube as the X-ray source was used. The technique reports concentration as % oxides for major elements and ppm for minor elements. Elements reported as % oxides were converted to % elements by dividing the molecular weight of the element with that of its respective oxide, then multiplying the result by the reported % oxide value as shown below:

Elemental concentration (weight %) = <u>Molecular weight of the element</u>   x Reported value
                                     Molecular weight of the oxide

3.3.4 Pore water analysis

Pore water was extracted using a solid: water ratio of 1:10. This procedure was done in duplicates for the fresh fly ash and each of the 35 samples of the

weathered fly ash taken at 1.5 m depth intervals down core S2 of the Secunda ash dam. 5 grams of the fresh fly ash sample and 5 grams of each of the 35 core samples as obtained from core S2 were weighed and put in a sample bottle. 50 ml of ultra pure water was added and the mixture was then thoroughly agitated for 1 hour using a mechanical shaker, and allowed to settle for 15 minutes. The pH, electrical conductivity (EC), and total dissolved solids (TDS) of the supernatant were recorded at room temperature. A portable, waterproof Hanna pH meter series HI 991301N with a pH/EC/TDS/Temperature probe was used. The meter reports EC in mS/cm and TDS in ppt (g/L). pH calibration was done in accordance with the instruction manual using buffer solutions of pH 4 and 7 before the measurements were taken.

3.3.4.1 Anion analysis

Ion chromatography (IC) was used in the identification and quantification of the anions present in the extracted pore water after leaching the fly ash with ultrapure water. The aqueous extracts from the pore water procedure were then filtered through a 0.45 μm pore membrane to remove suspended solids. The aqueous samples used in this procedure had electrical conductivity (EC) range of between 0.85 mS/cm and 4.98 mS/cm hence 1000x dilution factor was used. In the dilution, 0.01 ml of sample was diluted with 9.99 ml of ultra-pure water. The samples were analysed using a Dionex DX-120 ion chromatograph with an Ion Pac AS14A column and AG14-4 mm guard column.

3.3.5 Moisture content determination

The procedure involved weighing the moist samples as obtained from core S2 prior to drying. The fly ash samples were then oven dried for 24 hours at 105 °C. After drying, the dry sample weight was noted. The percentage moisture content was calculated by dividing the weight difference between the moist and dry ash (amount of water removed) with that of the dry ash as shown below:

% Moisture content = <u>Weight of moist sample – Weight of dry sample</u> x 100

Weight of dry sample

This procedure was done for the fresh fly ash and each of the 35 samples of the weathered fly ash taken at 1.5 m depth intervals down core S2 of the Secunda ash dam.

3.3.6 Sequential extraction

The sequential extraction procedure was used to investigate the chemical partitioning and mobility of the metal species in the weathered coal fly ash from Secunda ash dam, that had been in contact with brine. The sequential extraction procedure used in this study was a modification of the method proposed by Tessier et al., (1979) which included the exchangeable fraction, carbonate fraction, Fe & Mn fraction and residual fraction. In this study, the water soluble fraction was added as the first extraction step followed by exchangeable fraction extraction, carbonate fraction extraction, Fe & Mn fraction extraction and residual fraction. The modification was necessitated by the fact that this study involved coal fly ash while the original method proposed by Tessier et al., (1979) was adopted mainly for analysis of soils. The water soluble fraction was considered in order to simulate what happens naturally at the ash dam where rain falls, causing potential leaching of elements. The major, minor and trace elements in the leachates obtained from the fresh Secunda ash as well as the extracted weathered ash were identified using ICP-OES. The aqueous leachate samples were filtered through a 0.45 µm pore membrane to remove suspended solids and then acidified to stabilize the cations. 1000x dilution factor was used in diluting the aqueous leachate samples prior to ICP-OES analysis where 0.01 ml of extracted leachate from each fraction was diluted with 9.99 ml of 2 % HNO_3. The major, minor and trace element analysis was done using a Varian 710-ES series spectrometer equipped with a CCD detector, axially-viewed plasma, a cooled cone interface, and ICP Expert II software.

3.3.6.1 Water soluble fraction

1 g of each of the 35 weathered fly ash samples taken at 1.5 m depth intervals from the surface to the bottom of core S2 of the Secunda ash dam was weighed into 50 mL centrifuge tubes and 45 mL of ultrapure water was added. 1 g of the

fresh fly ash taken from the hoppers was also weighed into a 50 mL centrifuge tube and 45 mL of ultrapure water added. This procedure was done in triplicates. The samples were then shaken at room temperature for 1 hour with a mechanical shaker. The solution was allowed to settle down for 1 hour. The mixture was centrifuged at 6000 rpm for 20 minutes and the supernatant carefully filtered through a 0.45 µm nucleopore membrane into a 100 mL clear plastic sample bottle while minimizing weight loss. The filtered supernatant recovered was set aside for analysis of major and trace species with ICP-OES. Following ICP analysis, the dry weight concentration of the analytes for this sequential extraction step was calculated (i.e. from mg/L to mg/kg) using the dilution factor and the original weight of the sample. The solid residues left in the centrifuge tubes after filtration were kept in a refrigerated condition ready for the next extraction step.

3.3.6.2 Exchangeable fraction

45 mL of 1M ammonium acetate buffer solution at pH 7 was added to the solid residue recovered from the water soluble fraction. The solution was shaken for 1 hour at room temperature, and then allowed to settle for 1 hour. This procedure was done in triplicates. The mixture was then centrifuged at 6000 rpm for 20 minutes and carefully filtered through a 0.45 µm nucleopore membrane into a 100 mL clear plastic sample bottle while minimizing weight loss. The filtered supernatant recovered was set aside for analysis of major and trace species with ICP-OES. The dry weight concentration of the analytes for this step was calculated (i.e. from mg/L to mg/kg) using the dilution factor and the weight of the residue from step 3.3.6.1 (i.e. the difference between the mass of analytes that came out from water soluble fraction and the original weight of the ash sample). The residue recovered from this step was kept in a refrigerated condition ready for the next extraction step.

3.3.6.3 Carbonate fraction

45 mL of 1M ammonium acetate buffer solution at pH 5 was added to the solid residue recovered from the exchangeable fraction. The solution was shaken for 1 hour at room temperature. The solution was allowed to settle for 1 hour, and then centrifuged at 6000 rpm for 20 minutes and then filtered through a 0.45 µm

nucleopore membrane into a 100 mL clear plastic sample bottle while minimizing weight loss. The filtered supernatant recovered was set aside for analysis of major and trace species with ICP-OES. This procedure was done in triplicates. The dry weight concentration of the analytes for this step was calculated (i.e. from mg/L to mg/kg) using the dilution factor and the weight of the residue from step 3.3.6.2 (i.e. the difference between the mass of analytes that came out from the exchangeable fraction and the initial weight of the solid residue from the exchangeable fraction). The residue recovered from this step was kept in a refrigerated condition ready for the next extraction step.

3.3.6.4 Iron and manganese (Fe & Mn) fraction

45 mL of 1 M hydroxylamine hydrochloride in 0.025 M nitric acid solution was added to the solid residue from the carbonate fraction. The solution was shaken for 1 hour at room temperature. The solution was allowed to settle down for 1 hour, centrifuged at 6000 rpm for 20 minutes and then filtered through a 0.45 μm nucleopore membrane into a 100 mL clear plastic sample bottle while minimizing weight loss. The filtered supernatant recovered was set aside for analysis of major and trace species with ICP-OES. This procedure was done in triplicates. Following ICP analysis, the dry weight concentration of the analytes for this step was calculated (i.e. from mg/L to mg/kg) using the dilution factor and the weight of the residue from step 3.3.6.3 (i.e. the difference between the mass of analytes that came out from the carbonate fraction and the initial weight of the solid residue from the carbonate fraction). The solid residue recovered from this extraction step was kept in a refrigerated condition ready for the next step.

3.3.6.5 Residual fraction

The solid residue recovered from the Fe & Mn fraction was rinsed with ultrapure water and quantitatively transferred into a crucible, oven dried at 105 ℃ for 2 hours and weighed. Approximately 0.90 g of dried sample was recovered and then carefully transferred into the Teflon of a Parr bomb. 14 mL of combined acids Perchloric acid: Hydrofluoric acid: Nitric acid ($HClO_4$: HF: HNO_3) mixed in the ratio of 3:3:1 respectively, was added and the Teflon cup placed in the Parr bomb, sealed and heated to 180 °C for 3 hours in an oven. The Parr bomb was then

removed from the oven and allowed to cool down. After cooling, the solution was diluted with 70 mL of supersaturated boric acid (H_3BO_3) and then filtered through a 42 μm nucleopore membrane. The solution obtained was further diluted with ultrapure water to 100 mL volume and set aside for analysis of major and trace species with ICP-OES. The dry weight concentration of the analytes for this step was calculated (i.e. from mg/L to mg/kg) using the dilution factor and the weight of the solid residue recovered. This procedure was done in triplicates.

3.3.6.6 Total metal content determination

0.5 g of each of the 35 weathered fly ash samples taken at 1.5 m depth intervals from the surface to the bottom of core S2 of the Secunda ash dam was weighed into a Teflon cup. 0.5 g of the fresh fly ash taken from the Secunda fly ash hoppers was also weighed into a Teflon cup. 7 mL of combined acids Perchloric acid: Hydrofluoric acid: Nitric acid ($HClO_4$: HF: HNO_3) mixed in the ratio of 3:3:1 respectively was added. The Teflon cup was placed in the Parr bomb and then the Parr bomb was sealed and heated to 180 °C for 3 hours in an oven. It was then removed from the oven and allowed to cool down. After cooling, the solution was diluted with 35 mL of supersaturated boric acid (H_3BO_3) and then filtered through a 42 μm nucleopore membrane. The solution obtained was further diluted with ultrapure water to 100 mL volume and set aside for analysis of major and trace species with ICP-OES. The dry weight concentration of the analytes for this step was calculated (i.e. from mg/L to mg/kg) using the dilution factor and the weight of the sample. This procedure was done in triplicates.

3.3.6.7 Mass balance

The calculations of the dry weight concentration of the analytes for each sequential extraction step provided the dry weight concentration per element per fraction. In order to confirm the accuracy of the sequential extraction procedure, the concentrations obtained from the water soluble, exchangeable, carbonate, Fe & Mn and residual fractions for each element were summed up and compared with the total concentration of that particular element obtained from the total metal content (TMC) determination step i.e. for example, the mass balance for sodium (Na) was calculated as follows:

(WS+EX+CB+FE+RES) = TMC

Where; **WS:** Dry weight concentration of Na from water soluble fraction.

EX: Dry weight concentration of Na from exchangeable fraction.

CB: Dry weight concentration of Na from carbonate fraction.

FE: Dry weight concentration of Na from Fe& Mn fraction.

RES: Dry weight concentration of Na from residual fraction.

TMC: Total dry weight concentration of Na.

The error margin used was (WS+EX+CB+FE+RES) $\leq$ 10 % TMC.

3.4 SECTION SUMMARY

Chapter three has given an overall overview of the analytical procedures used in this study. Chapters four and five will give detailed discussions of the results obtained as follows; chapter four will discuss the characterization of Secunda fresh fly ash and core S2 samples while chapter five will discuss the results obtained from the sequential extraction procedure performed on these samples.

CHAPTER FOUR

RESULTS AND DISCUSSION (I)

4. CHEMICAL, PHYSICAL, MINERALOGICAL AND MORPHOLOGICAL CHARACTERISTICS OF SASOL SECUNDA COAL FLY ASH

This chapter presents and discusses the first section of the results obtained in this study. The chapter contains detailed discussions of the mineralogy, chemical composition, morphology and physical characteristics of fresh Secunda fly ash and the weathered fly ash core S2 obtained from the Secunda ash dam. The analytical techniques and methods used include scanning electron microscopy (SEM), X-ray diffraction (XRD), X-ray fluorescence (XRF), pore water analysis, Ion chromatography (IC) and moisture content determination which have been described in chapter three in sections 3.3.1, 3.3.2, 3.3.3, 3.3.4, 3.3.4.1 and 3.3.5 respectively. The fresh Secunda fly ash and the weathered fly ash core samples obtained from Secunda ash dam were later used for the sequential extraction procedure and subsequent analysis using Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-OES) which will be discussed in chapter five.

4.1 MINERALOGICAL ANALYSIS BY X-RAY DIFFRACTION (XRD)

The XRD technique was used to investigate the mineralogical composition of Secunda fresh fly ash and the weathered Secunda fly ash core as described in chapter three (section 3.3.2). The XRD patterns for the fresh Secunda ash and the weathered core S2 samples are presented in Figure 12.
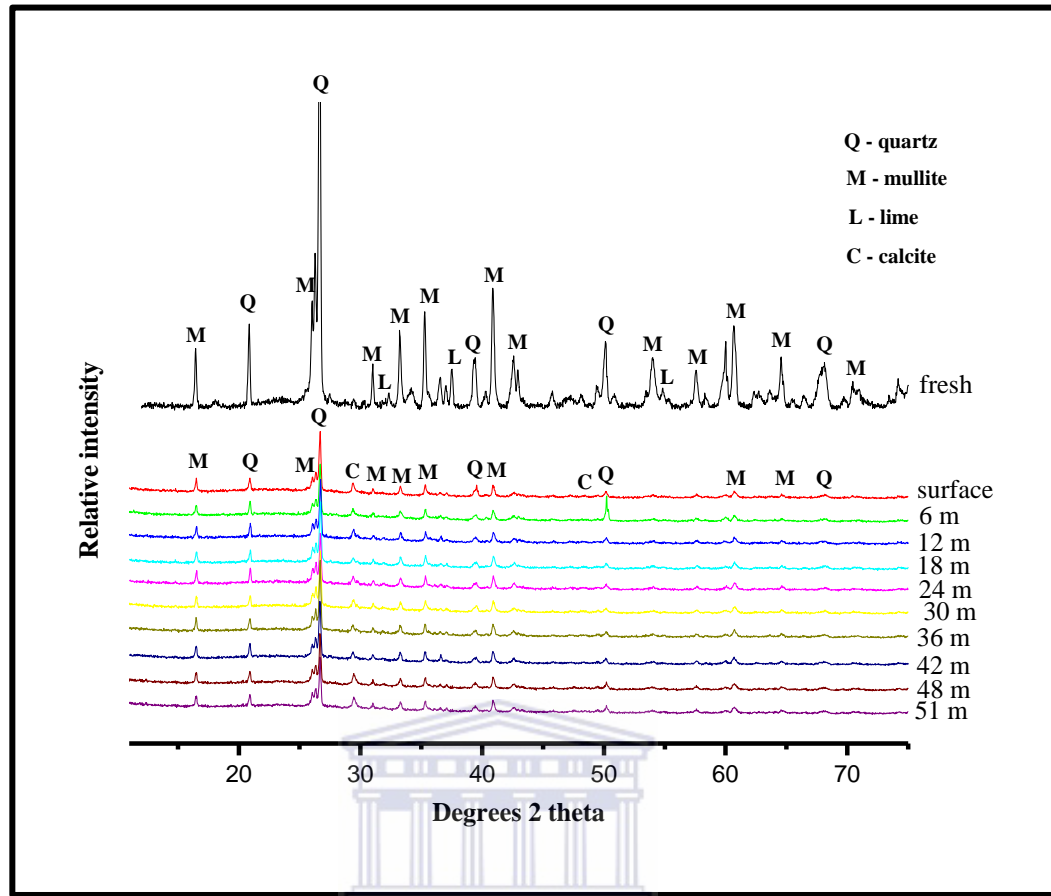
Figure 12: XRD patterns for Secunda fresh fly ash and Secunda weathered fly ash core S2 samples at different depths (surface, 6 m, 12 m, 18 m, 24 m, 30 m, 36 m, 42 m, 48 m and 51 m) showing the different mineral phases.

Three crystalline mineral phases were identified in the fresh fly ash namely quartz, mullite and lime. Three crystalline mineral phases were identified in the weathered fly ash namely quartz, mullite and calcite. These are common mineral phases found in fresh or weathered coal fly ash (Rao & Gluskoter, 1973). The XRD patterns showed a similar trend from the surface sample, down the core to the bottom of the ash dam. The three crystalline mineral phases identified in the weathered fly ash remained consistent at every sampling depth (Figure 12). According to Thompson & Argent (1999), mullite ($3Al_2O_3 2SiO_2$ or $Si_2Al_6O_{13}$) is formed when kaolinite [$Al_2Si_2O_5(OH)_4$] found in the parent coal undergoes phase transformation under the high temperatures (1200 - 1400 °C) typical in coal combustion processes as shown in the equations below:

53

2 $Al_2Si_2O_5(OH)_4$ —Heat ➤ 2 $Al_2Si_2O_7$ + 4 H_2O…..(a) formation of disordered metakaolin from kaolinite

2 $Al_2Si_2O_7$ —Heat ➤ $Si_3Al_4O_{12}$ + SiO_2……(b) oxolation of the metakaolin into aluminium-silicon spinel

3 $Si_3Al_4O_{12}$ ——Heat ➤2 $Si_2Al_6O_{13}$ + 5 SiO_2…..(c) formation of mullite from aluminium-silicon spinel.

Quartz (SiO_2) from parent coal survives the combustion conditions hence it is found unchanged in fly ash (Bandopadhyay, 2010). Lime (CaO) present in the fresh fly ash may have originated from the thermal decomposition of calcite ($CaCO_3$) (Navarro et al., 2009) contained in the parent coal during coal combustion as shown in the equation below:

$CaCO_3(s)$ —— Heat ——➤ $CaO(s) + CO_2(g)$
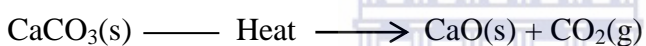
The calcite ($CaCO_3$) identified in the weathered fly ash may have been formed via the aqueous carbonation process involving contact of lime (CaO) contained in the fresh fly ash with ingressed CO_2 and water present in the ash dam (Nyambura et al., 2011) as shown in the equations below:

$CaO + H_2O \rightarrow Ca(OH)_2$……………..(a) hydration of lime into calcium hydroxide suspension

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$……(b) carbonation of calcium hydroxide suspension to form calcite

All the mineral phases detected by XRD corresponded to the significant levels of Si, Al and Ca contained in the fresh fly ash and the weathered fly ash as reported by XRF analysis which will be discussed in section 4.4, while much lower levels of elements like Fe and Mg, for example, may have made it difficult to detect by XRD any mineral phases associated with them such as hematite (Fe_2O_3) and enstatite ($Mg_2Si_2O_6$). However, other mineral phases present in the ash dam were

not detected by XRD probably because they were in a transition/amorphous state, or present in very low thus undetectable levels.

In conclusion, it can be seen from the XRD analysis that the weathered fly ash samples obtained from core S2, in a wet ash handling system involving codisposal of the fly ash with brine as a slurry, did not show mineralogical inhomogeneity but rather gave a consistent trend from the top of the ash dam, along the core down to the bottom. This mineralogical consistency shown by XRD however probably points to the limitation of XRD as an analytical tool in that it can only detect relatively abundant crystalline mineral phases, and not detect amorphous material or minerals present in low concentration.

4.2 MORPHOLOGICAL ANALYSIS BY SCANNING ELECTRON MICROSCOPY (SEM)

The SEM was conducted as described in chapter three (section 3.3.1) in order to understand the morphological changes of Secunda fly ash as the age of the ash increased down the ash core. The morphologies of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples are shown in Figure 13 where 13A shows the morphology of Secunda fresh fly ash sample and 13B, 13C and 13D show the morphologies of Secunda weathered fly ash core samples for surface (1 year old), 24 m (approx. 10 years old) and 51 m (20 years old) respectively.
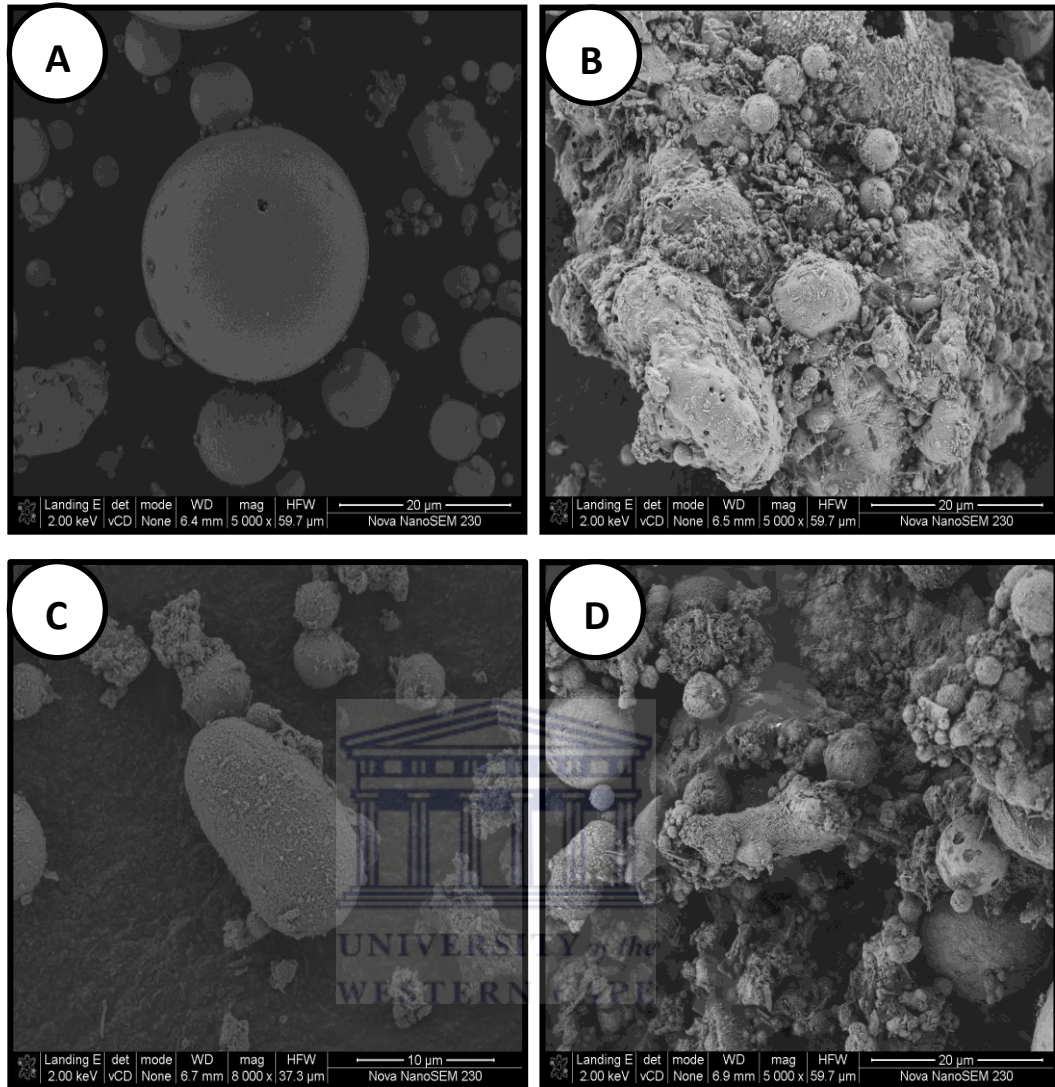
Figure 13: SEM micrographs of Secunda fly ash samples: (A) Secunda fresh fly ash; (B, C and D) Secunda weathered fly ash from core S2 for surface (1 year old), 24 m (approx. 10 years old) and 51 m (20 years old) respectively.

The changes in surface morphology between the fresh fly ash and the weathered fly ash are evident from the SEM micrographs. The fresh fly ash mainly consists of spherical particles with smooth outer surfaces (Fig. 13A) while the 1 year old weathered fly ash (Fig. 13B) is made up of agglomerated, irregular particles beginning to show signs of aging due to weathering causing the formation or deposition of secondary material on the outer surfaces of the previously smooth particles (Fig. 13B). However, spherical particles can still be observed in the 1 year old fly ash (Fig. 13B). The fly ash collected from 24 m which is at the middle

of the ash dam and approximately 10 years old (Fig. 13C) shows signs of agglomeration with irregular particles, though some spherical particles are still present. The 20 year old weathered fly ash (Fig. 13D) appears to be encrusted, etched and corroded. There is evidence of agglomeration and perforations on the outer surfaces of the spherical particles present (Fig. 13D). The spherical shaped particles in the SEM micrographs have diameter sizes ranging from less than 5 μm to 30 μm while the agglomerated particles' diameter sizes range from 10 μm to 40 μm.

According to Anshits et al., (2010), fresh coal fly ash consists of cenospheres which are formed as a result of thermochemical transformations of mineral particles during coal combustion process, where the minerals melt to form small droplets which upon sudden cooling and action of surface tension forces adopt the spherical shape. The average temperature for cenosphere formation is approximately 1500 - 1650 °C. The smooth outer surfaces of the fresh fly ash particles can be attributed to the presence of aluminosilicate structures which normally occur in the form of small spherical grains (Styszko-Grochowiak et al., 2004) while the agglomeration, encrustations, etchings and corrosion observed in the weathered fly ash (1 year, 10 year and 20 year old) may be as a result of weathering and leaching processes leading to dissolution and transformation of existing material and subsequent precipitation of secondary mineral phases such as amorphous aluminosilicate in the fly ash (Akinyemi et al., 2011a). The SEM shows heterogeneity not observed by XRD.

It can be concluded that weathering and leaching are responsible for the changes in morphology of the disposed Secunda fly ash within the ash dam as age increases.

4.3 PORE WATER ANALYSIS AND MOISTURE CONTENT DETERMINATION

The physico-chemical properties of fresh Secunda fly ash and the weathered fly ash from Secunda core S2 were investigated as described in chapter three section

3.3.4 for the pH, EC and TDS, section 3.3.4.1 for the distribution of anionic species and section 3.3.5 for the moisture content determination. The raw data generated and used for the results presented in this section are presented in Appendix 1. A detailed discussion of the results obtained is given below. The data was replicated for accuracy purposes.

4.3.1 The pH profile of Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples

The pH profile of the pore water extracted from Secunda fresh fly ash and Secunda weathered fly ash as a function of depth is presented in Figure 14.
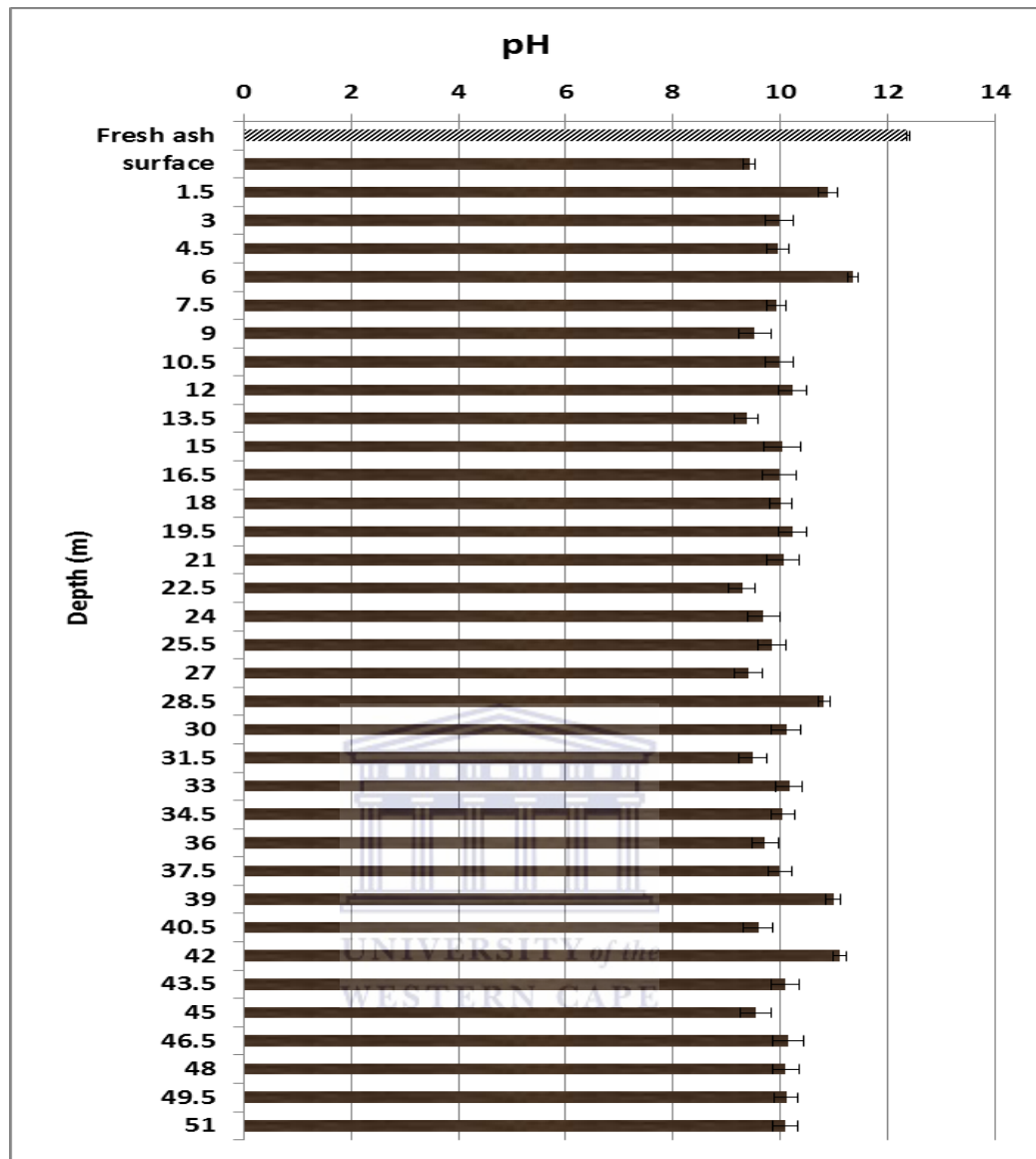
Figure 14: pH profile of Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples with respect to depth.

The fresh fly ash had a pH of 12.38 ± 0.03 while the mean pH for the weathered fly ash core S2 was 10.04 ± 0.50 (Figure 14) showing significant weathering and loss of alkalinity over time. The pH for the weathered fly ash core ranged between 9.29 at 22.5 m and 11.36 at 6 m. The pH values obtained from the extracted pore water for both fresh fly ash and the weathered fly ash affirm that the fly ash is alkaline. This is due to the presence of alkaline earth metals' oxides such as CaO and MgO which are the greatest contributors towards the alkalinity of the fly ash upon contact with water (Choi et al., 2002; Grisafe et al., 1988). The decrease in

pH from 12.38 in the fresh fly ash to a mean of 10.04 in the weathered fly ash can be attributed to chemical interactions of the fly ash with brine, atmospheric O_2, CO_2 and percolating rain water, leading to the dissolution and consequent reduction of the alkaline materials present in the fly ash as shown in the example equations below showing the conversion of CaO into soluble calcium bicarbonate.

$CaO + H_2O \rightarrow Ca(OH)_2$………………..(a) hydration of lime in the fly ash into calcium hydroxide suspension as a result of brine and infiltrating rain water in the ash dam

$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$………(b) carbonation of calcium hydroxide, by ingressed carbon dioxide in the ash dam, into calcium carbonate

$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2$…..(c) reaction of calcium carbonate with water and carbon dioxide in the ash dam to form soluble calcium bicarbonate

The pH variations would affect the mobility of the chemical species in the fly ash effectively dictating the element mobility patterns within the ash dam (Petrik et al., 2010; Ward et al., 2009). According to Dutta et al., (2009), pH is the major factor affecting element mobility and leaching patterns in fly ash, for most elements there is higher element release (more leaching) at low pH and vice versa. Other factors that may play a role in element mobility and leaching patterns in fly ash include ash and water contact time and solid-liquid ratio.

4.3.2 The electrical conductivity (EC) profile of Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples

The EC profile of the pore water extracted from Secunda fresh fly ash and Secunda weathered fly ash as a function of depth is presented in Figure 15.
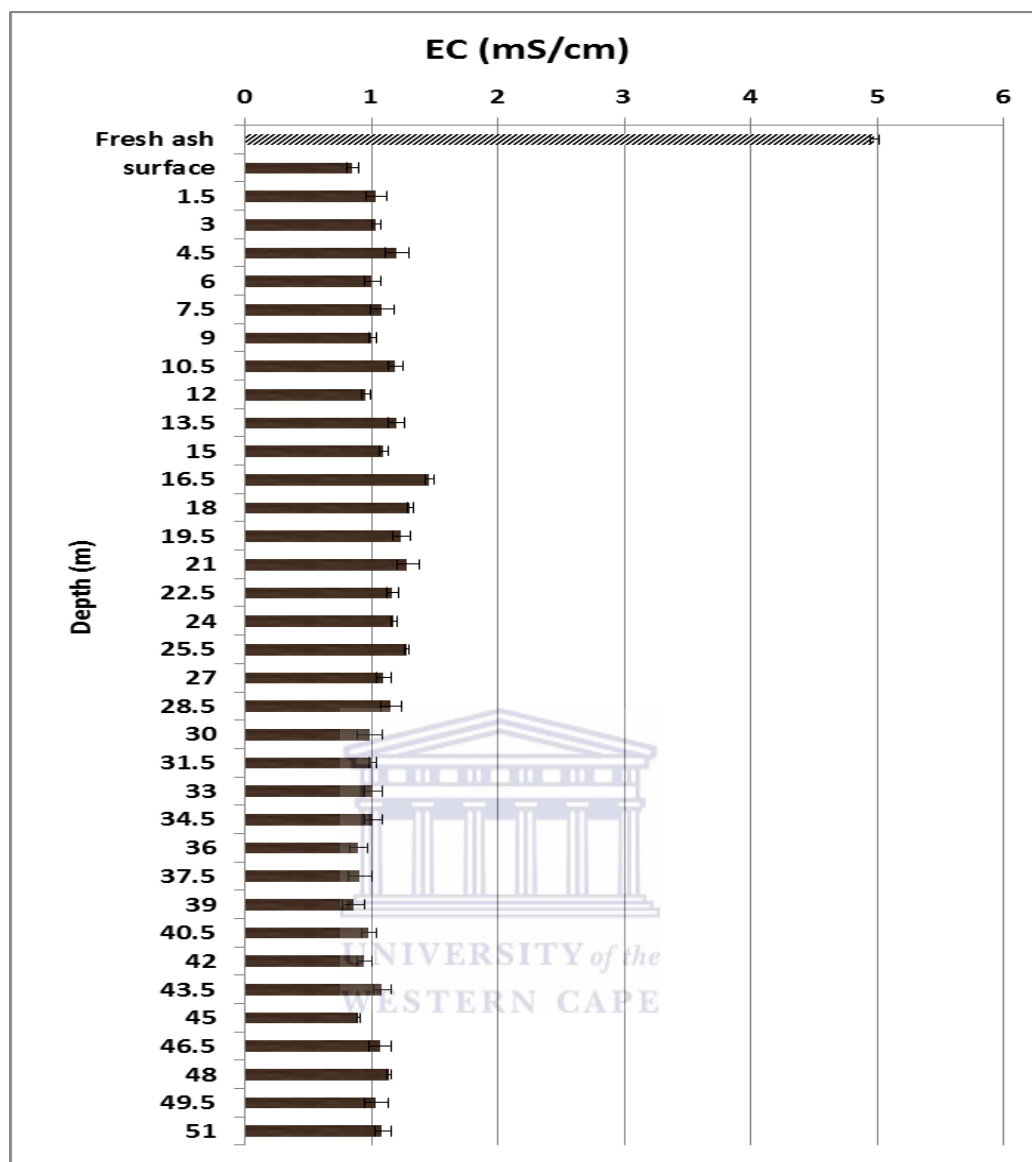
Figure 15: EC profile of Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples with respect to depth.

The EC for the fresh fly ash was 4.98 ± 0.03 mS/cm while the mean EC for the weathered fly ash core was 1.08 ± 0.14 mS/cm (Figure 15). The EC for the weathered fly ash core ranged between 0.85 mS/cm at the surface and 1.46 mS/cm at 16.5 m. The EC values are governed by the amount of ions present in the extracted pore water. Therefore, high EC values indicate the release of more ionisable species from the fly ash into solution while the opposite means lesser amount of ions are present in the aqueous extract. The decrease in EC from 4.98 mS/cm in the fresh fly ash to a mean of 1.08 mS/cm in the weathered fly ash

indicates the significant loss of ionic species in the ash dam, which may be as a result of the mobilization of dissolved ions in the aqueous phase through leaching during slurry transport of the ash, and leaching of the ash through infiltrating brine and rainwater, leading to loss of the ionic species from the disposed ash into the ground water (Bhattacharyya et al., 2009; Petrik et al., 2010). However, the wet disposal method used at Secunda power station may also contribute to the significant decrease in EC since the fly ash is mixed with brine and disposed in slurry form. After a few days or weeks of settling, the excess water that percolates through the ash dam is then drained out through a toe drain and stored in ash transport water reservoirs, probably carrying with it many of the readily dissolved ions in solution. This is expected to continue as new slurry is placed on the top of the dam and drains through the ash progressively.

4.3.3 The total dissolved solids (TDS) profile of Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples

The TDS profile of the pore water extracted from Secunda fresh fly ash and Secunda weathered fly ash as a function of depth is presented in Figure 16.
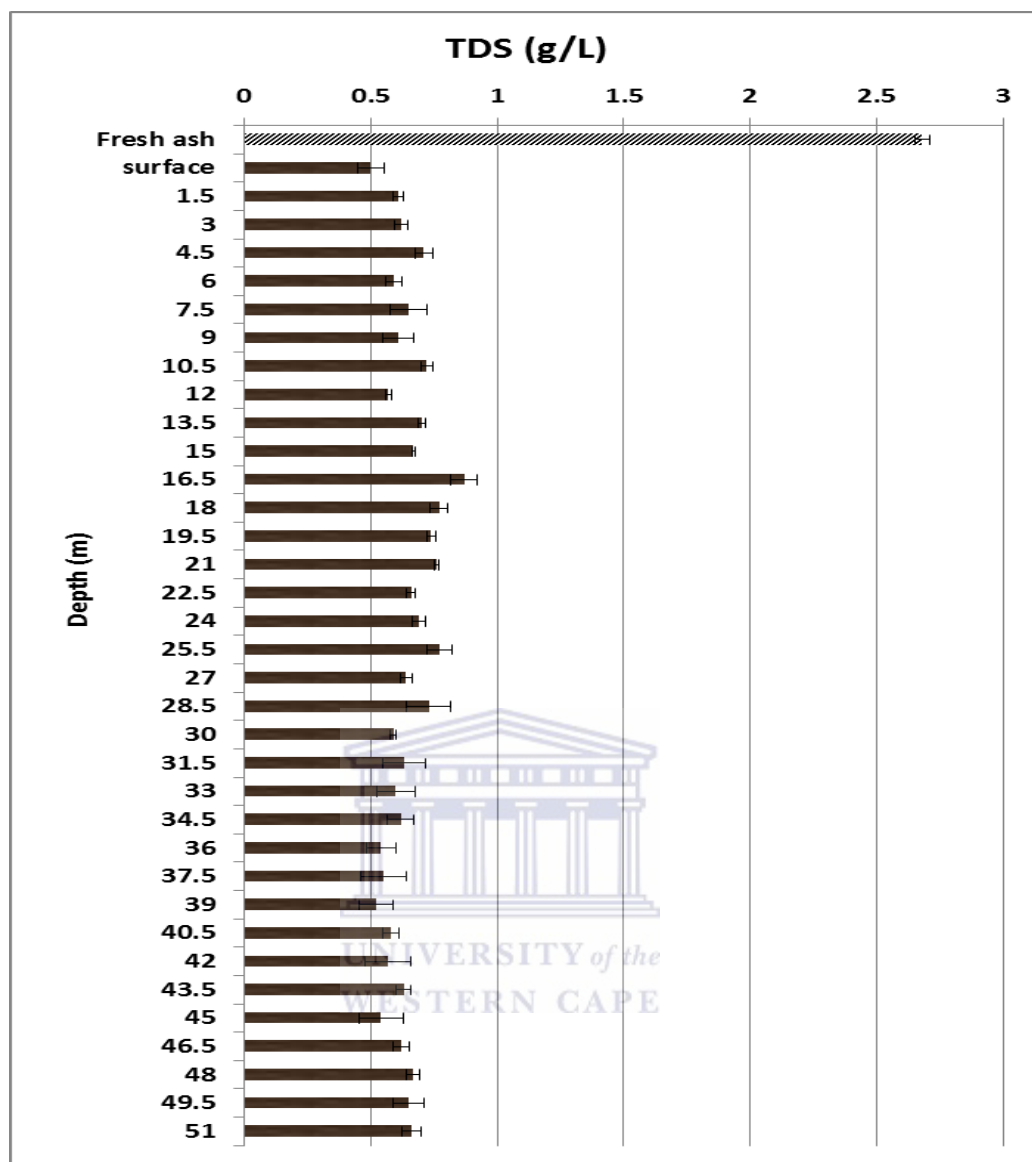
Figure 16: TDS profile of Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples with respect to depth.

The TDS profile followed the same trend as that observed for the EC since the two parameters are directly proportional to one another. The TDS for the fresh fly ash was 2.68 ± 0.03 g/L while the mean TDS for the weathered fly ash core S2 was much lower being 0.64 ± 0.08 g/L (Figure 16). The TDS for the weathered fly ash core S2 ranged between 0.5 g/L at the surface and 0.87 g/L at 16.5 m.

In conclusion, chemical interactions of the fly ash with brine, atmospheric O_2, CO_2 and percolating rain water lead to the decrease in pH of the disposed fly ash

through the loss of pH buffering constituents present in the fly ash such as CaO. The resulting lower pH affects the release of the chemical species in the fly ash. The significant decrease in EC and TDS in the weathered core compared to the fresh ash may be as a result of leaching of ionic species or the removal of excess water carrying dissolved ions.

4.3.4 The moisture content profile of Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples

Figure 17 shows the moisture content (MC) profile of Secunda fresh fly ash and the weathered Secunda fly ash from core S2 as a function of depth.

UNIVERSITY *of the*
WESTERN CAPE
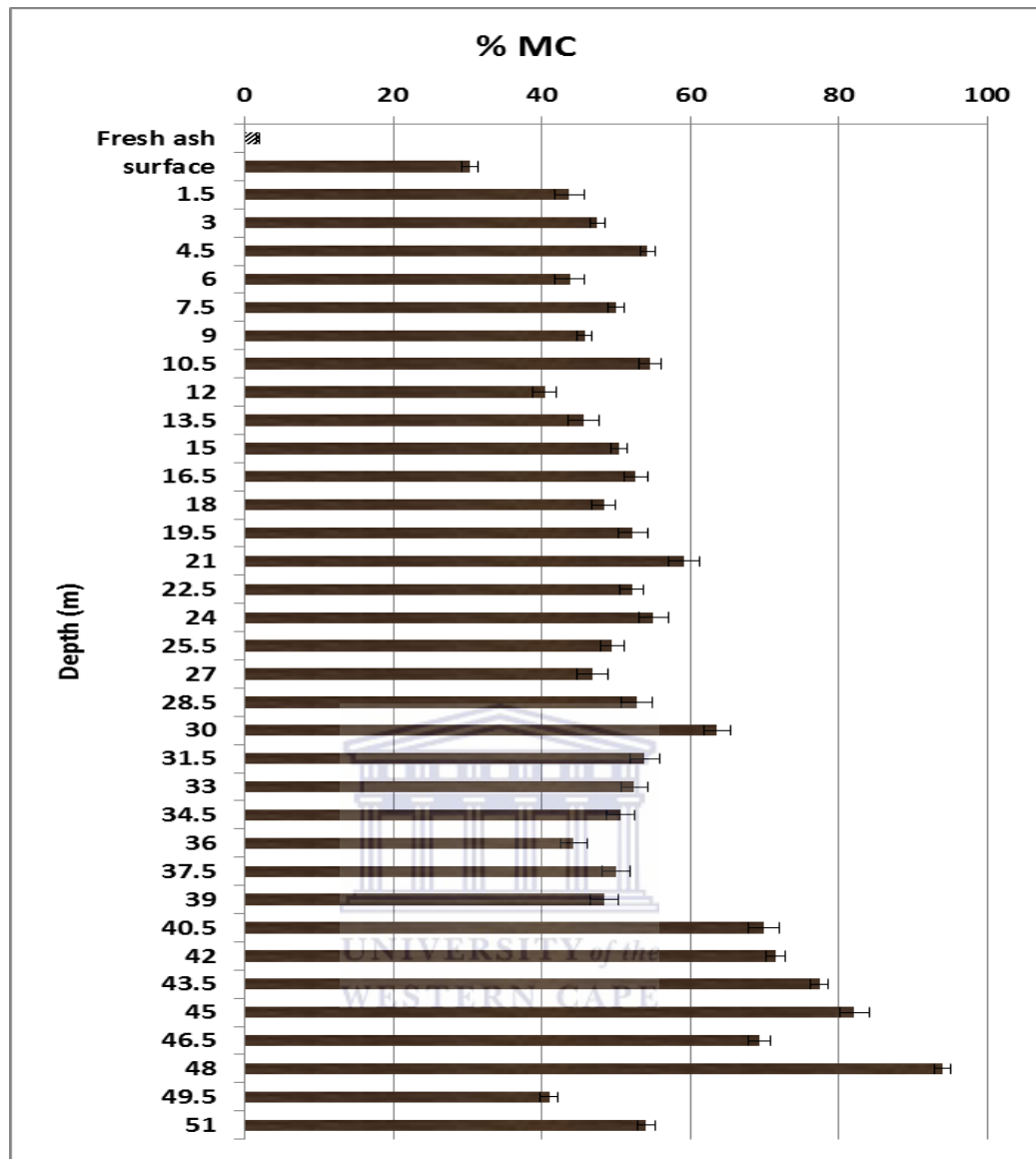
Figure 17: Moisture content profile of Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples with respect to depth.

The MC for the fresh fly ash was 1.8 ± 0.11 % while the mean MC for the weathered fly ash core S2 was 54.2 ± 12.66 % (Figure 17). The % MC data for the weathered fly ash shows a fluctuating trend with depth ranging between 30.3 % at the surface and 94 % at 48 m. The high MC observed in the weathered fly ash is due to the wet disposal method used at Secunda power station which involved mixing the fly ash with brine and transporting it to the dam in slurry form. After disposal, excess water was removed and stored in ash water dams' reservoirs. The remainder of the aqueous leachates were incorporated in the mineralization

65

processes with the ash with time to form "rock hard" ash at the surface of the dam. However, from the samples collected in this study, it was evident that the ash dam remained wet inside though the exterior surface appeared very dry at the time of drilling. The drilled core S2 was actually water logged at the bottom. This observation could be attributed to progressive seepage of rain water and ash transport water through the dam caused by natural hydraulic transport downward by gravity. Every time a new layer is formed on top of the dam with slurry and new ash, more ash transport water percolates through the dam leaving the top of the dam less wet. However, the fluctuating trend in the moisture content values at some depths could be due to different dumping conditions i.e. dumping being done on sunny and rainy days irrespective of the weather conditions or varying ash layer thickness arising from different ash placement conditions. The high water content in the ash dam may exacerbate the leaching of soluble species in the fly ash and increase the risk of the ash dam collapsing with time due to the weight of the ash layers packed on top of each other during dumping.

In conclusion, the observed high MC in the ash dam is of great concern since apart from creating favourable conditions for leaching of species, with time it may cause slumping of the dam with serious consequences as illustrated in Figure 5 in chapter two (section 2.5.3).

4.3.5 The distribution of anionic species in Secunda fresh fly ash vs. Secunda weathered fly ash core S2 samples

The identification and quantification of anions present in the extracted pore water after leaching Secunda fresh fly ash and the weathered fly ash from Secunda core S2 with ultrapure water was done using ion chromatography (IC) as described in chapter three (section 3.3.4.1). Figure 18 shows the distribution of the major anionic species (sulphates and chlorides) in the extracted pore water of the weathered fly ash from Secunda core S2 in comparison with Secunda fresh fly ash as revealed by IC analysis.
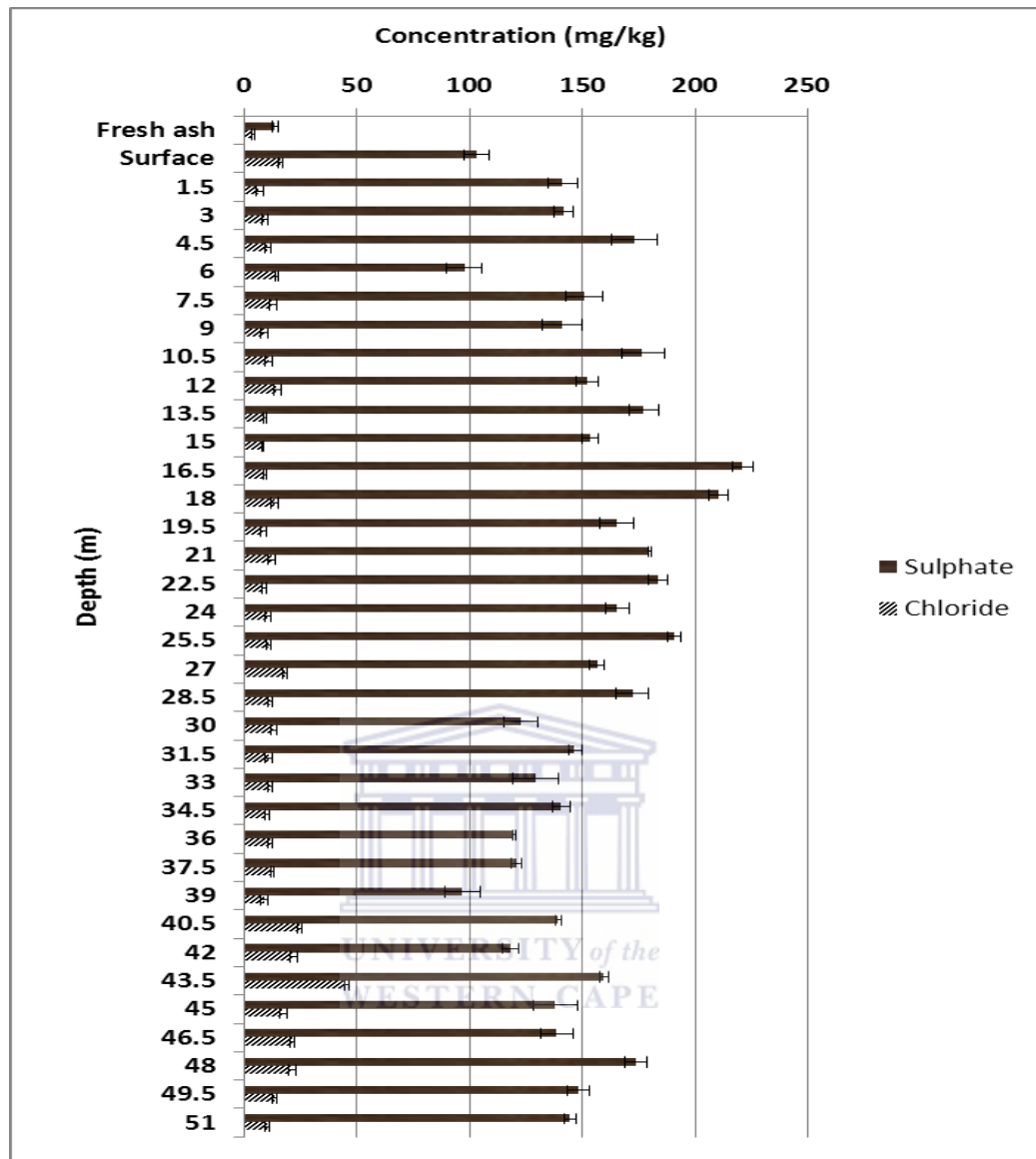
Figure 18: Distribution of sulphates and chlorides in the extracted pore water of the weathered fly ash from Secunda core S2 in comparison with Secunda fresh fly ash based on IC analysis.

4.3.5.1 Sulphates

The sulphates were significantly released from the weathered Secunda fly ash core samples, compared to Secunda fresh ash. While the concentration of sulphate released from Secunda fresh fly ash was 13.64 mg/kg, the concentration of sulphate released from the weathered Secunda fly ash core samples ranged 96.64 - 221.26 mg/kg, with a mean concentration of 151.23 mg/kg (Figure 18). Mooketsi et al., (2007) investigated the interaction of fly ash with brine and observed that

brine treated sintered ash residues had elevated leachate concentration of SO_4^{2-}, Cl^- Na^+, K^+ and Ca^{2+} compared to non (brine) treated sintered ash residues. The observed elevated leachate concentration of SO_4^{2-} was attributed to the brine treatment. Secunda brine is rich in sulphates (Nyamhingura, 2009) and upon contact of the brine with the fly ash the brine enriched the fly ash with the sulphates. The wet ash handling system practiced at Secunda, involving codisposal of fly ash with brine in slurry form, was responsible for the enrichment of sulphates in the disposed Secunda ash, hence the higher and rapid release of soluble sulphate species observed in the weathered Secunda fly ash core samples compared to Secunda fresh ash. The higher SO_4^{2-} release observed in the weathered Secunda core S2 samples compared to the fresh Secunda ash in the extracted pore water (Figure 18) agreed with XRF analysis showing S levels which will be discussed in section 4.4.1.5. The high solubility of the sulphate shows that it is not primarily associated with an insoluble phase and could rapidly leach.

4.3.5.2 Chlorides

The chlorides showed more release from the weathered Secunda fly ash core samples compared to Secunda fresh ash. The concentration of chloride released from Secunda fresh fly ash was 4.05 mg/kg while the concentration of chloride released from the weathered Secunda fly ash core samples ranged 6.85 - 45.32 mg/kg with a mean concentration of 13.66 mg/kg (Figure 18). Previous studies have shown that Secunda brine contains significant amount of chloride (Nyamhingura, 2009) and that contact of the fly ash with brine led to the enrichment of chloride in the disposed fly ash (Mooketsi et al., 2007). The trend of Cl^- release observed (Figure 18) along the core of the disposed fly ash corresponded to Na levels in the ash as reported by XRF analysis which will be discussed in section 4.4.1.2.

4.4 BULK CHEMICAL ANALYSIS BY X-RAY FLUORESCENCE (XRF)

The bulk chemical composition of Secunda fresh fly ash and the weathered Secunda fly ash core was determined by XRF as described in chapter three

(section 3.3.3). The distribution of the major and trace elements in the fresh fly ash compared to the weathered fly ash core S2 based on bulk XRF analysis is presented in Table 8 below. The raw data results of the bulk chemical composition of the fresh fly ash and the weathered fly ash core samples as a function of depth as reported by XRF analysis are presented in Appendix 2. Table 8 presents majors as oxides (weight %) and traces in ppm i.e. parts per million (mg/kg) on a dry mass basis. The ranges given show the varying concentration and large heterogeneity between samples obtained from various depths of the weathered fly ash core S2 and showed significant fluctuation as a function of depth compared to the Secunda fresh ash sample. The data presented (mean) for the weathered fly ash is averaged across all the samples taken along the whole weathered Secunda core S2 (n = 35) while the fresh fly ash analysis was triplicated (n = 3).

Table 8: The distribution of the major and trace elements in Secunda fresh fly ash compared to Secunda weathered fly ash core S2 based on bulk XRF analysis (nd = not detected)

| | Fresh fly ash (n = 3) | Weathered fly ash (n = 35) | |
Majors (wt%)		Mean	Range
SiO_2	50.86	46.24	42.97 - 48.90
Al_2O_3	25.52	24.87	23.18 - 25.77
CaO	8.95	8.51	7.34 - 9.95
LOI	4.78	8.16	6.03 - 11.68
Fe_2O_3	2.26	3.39	2.14 - 6.13
Na_2O	2.20	2.49	2.28 - 2.73
MgO	1.87	2.65	2.37 - 2.97
TiO_2	1.78	1.75	1.57 - 1.84
K_2O	0.95	1.04	0.75 - 1.18
P_2O_5	0.71	0.73	0.53 - 0.94
MnO	0.05	0.07	0.05 - 0.08
SO_3	0.03	0.09	0.07 - 0.13
Traces (mg/kg)			
Sr	4160.43	4489.80	3410.17 - 5157.50
Ba	2749.50	2803.58	1924.18 - 3338.19
Th	1921.89	2095.71	1556.71 - 2421.50
Zr	664.60	676.48	602.85 - 738.56
Ce	176.82	172.71	107.44 - 215.13
Y	155.87	164.17	139.77 - 179.00
Nb	109.03	122.67	99.50 - 149.43
As	61.39	61.39	40.57 - 81.82
Co	32.73	33.32	18.89 - 47.72
Pb	27.85	37.35	24.41 - 54.70
Ni	22.56	29.45	23.65 - 36.50
Rb	16.41	20.65	0.84 - 45.54
V	15.41	70.14	29.49 - 114.59
U	nd	36.71	7.47 - 58.00
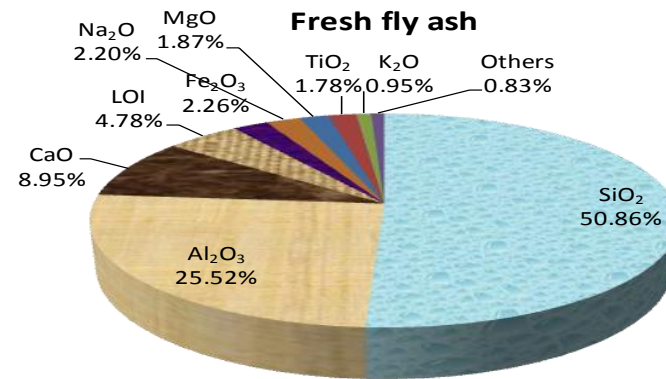
Fresh fly ash

Na_2O 2.20%, MgO 1.87%, Fe_2O_3 2.26%, TiO_2 1.78%, K_2O 0.95%, Others 0.83%, LOI 4.78%, CaO 8.95%, Al_2O_3 25.52%, SiO_2 50.86%

Others: P_2O_5, MnO, SO_3, As, Ba, Ce, Co, Nb, Ni, Pb, Rb, Sr, Th, V, Y and Zr.

Weathered fly ash

Fe_2O_3 3.39%, Na_2O 2.49%, TiO_2 1.75%, K_2O 1.04%, Others 0.90%, MgO 2.65%, LOI 8.16%, CaO 8.51%, Al_2O_3 24.87%, SiO_2 46.24%
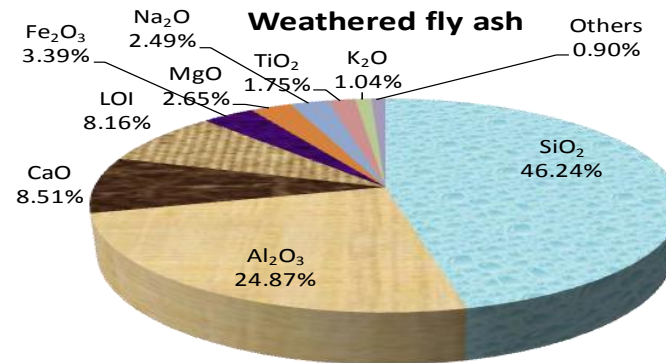
Others: P_2O_5, MnO, SO_3, As, Ba, Ce, Co, Nb, Ni, Pb, Rb, Sr, Th, V, Y, U and Zr.

The Secunda fly ash used in this study can be classified as Class F as per ASTM standards as the mean sums of SiO_2, Al_2O_3, and Fe_2O_3 for Secunda fresh fly ash and Secunda weathered fly ash are 78.64 % and 74.50 % respectively (Table 8) while the mean CaO content is 8.95 % and 8.51 % for Secunda fresh fly ash and Secunda weathered fly ash respectively (Table 8). According to ASTM C-618 (1993), Class F fly ash has combined amount of the oxides of silicon, aluminium, and iron by mass at 70 % or above and CaO<10 %. The loss on ignition (LOI) is a measure of unburnt carbon in the fly ash. The fresh fly ash reported 4.78 % LOI while the weathered fly ash had LOI ranging between 6.03 % and 11.68 % with mean LOI of 8.16 % (Table 8). The variations in LOI may be as a result of unburnt coal due to fluctuating burner conditions or chemical transformations in the fly ash caused by incorporation of water of crystallization into some phases present in the ash dam (Akinyemi et al., 2011a). However, the significant increase in LOI observed in the weathered fly ash core compared to the fresh ash could be as a result of the organics, arising from hydrocarbon processing, codisposed into the brine slurry water and thus onto the ash.

In order to further classify the Secunda fly ash used in this study, the ternary oxide plot proposed by Roy & Griffin (1982) was used. Figure 19 below presents a ternary plot of Secunda fly ash based on results obtained from the XRF analysis.
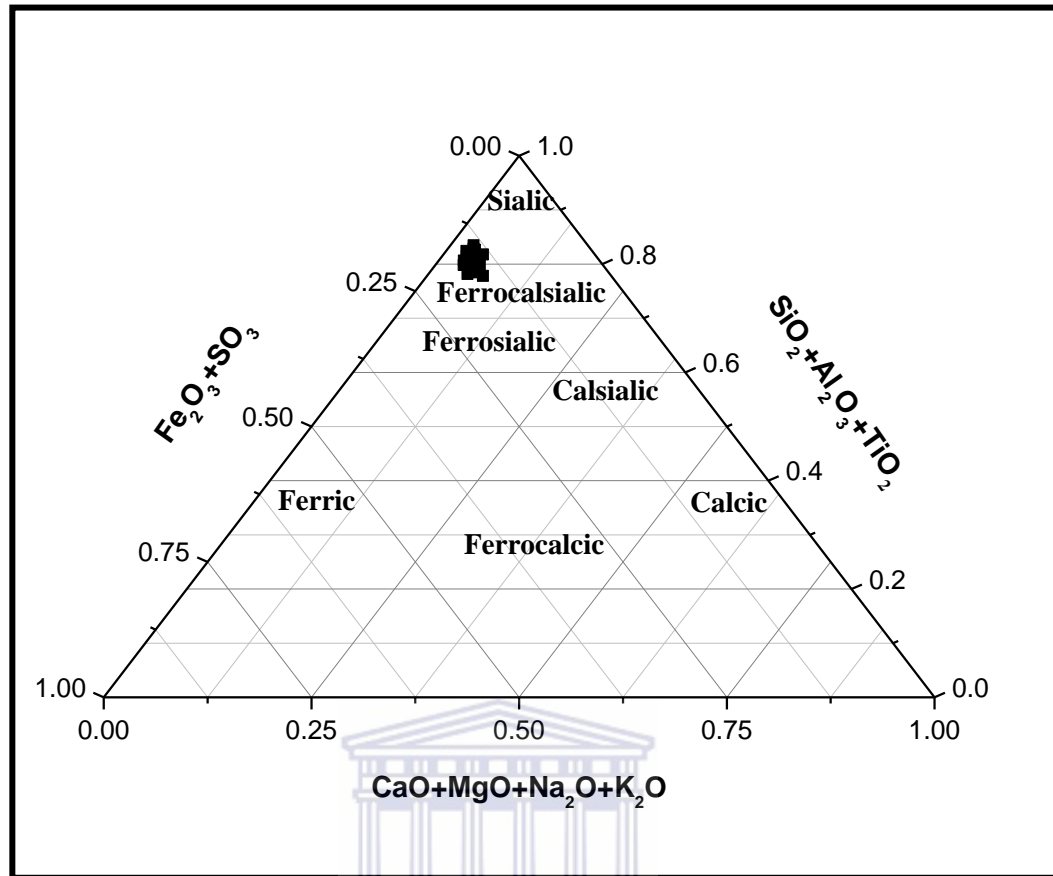
Figure 19: Ternary plot of Secunda fly ash based on XRF analysis.

The system classifies coal fly ash using three main components; sialic component (SiO_2 + Al_2O_3 + TiO_2), ferric component (Fe_2O_3 + SO_3) and calcic component (CaO + MgO + Na_2O + K_2O). Depending on the quantity of the respective components, the fly ash can then be grouped as either sialic, ferrocalsialic, ferrosialic, calsialic, ferric, calcic or ferrocalcic. The ternary plot showed that the Secunda fly ash used in this study was sialic and ferrocalsialic, highlighting the significant levels of Si, Al, Ca and Fe in the fly ash. The Secunda fly ash contained a sialic (SiO_2 + Al_2O_3 + TiO_2) component exceeding 70 %, a ferric (Fe_2O_3 + SO_3) component of between 12.5 and 25 % and a calcic (CaO + MgO + Na_2O + K_2O) component of between 37.5 and 50 % (Figure 19). Sub bituminous, low-rank bituminous and lignite coal fly ashes mostly fall on the upper middle section and right side of the ternary oxide plot (ferrocalsialic, calsialic or calcic), and are mainly dark, light grey, white or cream in colour. Bituminous coal fly ashes however mostly fall on the left side of the ternary oxide plot (ferrocalsialic

and ferrosialic) and are mainly dark, light grey, reddish or brown in colour (Roy & Griffin, 1982). South African power utilities use low grade bituminous coal (Gitari et al., 2008) therefore releasing ferrocalsialic type of fly ash.

The mobility trends of the various elements along the weathered core compared to the fresh ash based on XRF analysis are discussed below after the brief overview that follows. The major oxides identified in the fresh fly ash and the weathered fly ash were SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, Na_2O, K_2O and TiO_2 while minor oxides identified included P_2O_5, SO_3 and MnO (Table 8). The oxides of Si and Al, being the major components of fly ash, together accounted for 76.38 % of the fresh fly ash and 71.11 % of the weathered fly ash (Table 8). The trace elements identified in the fresh fly ash and the weathered fly ash were As, Ba, Ce, Co, Nb, Ni, Pb, Rb, Sr, V, Y, Zr and Th. However, U was detected in small quantities in some samples taken from the drilled core but was not detected in the fresh fly ash. Sr had the highest concentration among the trace elements while U had the lowest concentration (Table 8). Therefore, the weathered fly ash generally contained the same major and trace elements as the fresh fly ash apart from the presence of U in the drilled core, but in varying amounts.

The concentrations of Si, Al and Ca in the fresh fly ash were higher than those observed in the weathered fly ash (Table 8). The depletion of especially Si, but also Al and Ca observed in the weathered fly ash may have been as a result of weathering of the matrix of the fly ash and subsequent leaching of these elements into the environment. According to Choi et al., (2002), upon hydration and weathering, the glass aluminosilicate fraction of fly ash may undergo dissolution releasing Si and Al which are the major components of the ash matrix, while Ca, being highly soluble in fly ash particles rapidly dissolves when in contact with aqueous media such as brine or infiltrating rain water at the ash dam. The observed enrichment of Fe in certain horizons of the weathered fly ash (Table 8) could have been due to the dumping in the ash of spent Fe catalysts used in Fischer-Tropsch processes (Davis, 2003) at the Secunda industrial complex. Most of the elements reported slightly higher concentrations in the weathered fly ash

compared with the fresh fly ash (Table 8). The slight enrichment of some major and trace elements after disposal may have been due to the contact of the fly ash with Secunda brine which has been shown to contain these elements (Nyamhingura, 2009). However, the observed slight enrichment of these elements in the weathered fly ash compared with the fresh fly ash considering the amount of brine disposed on the ash over the lifetime of the dam, indicated that these species were not accumulating in the ash thus may have been released from the dam over time. For example Na_2O showed only 0.29 % mass increase from 2.20 weight % in the fresh fly ash to 2.49 weight % in the weathered fly ash (Table 8).

4.4.1 The mobility trends of the major elements in Secunda weathered fly ash core

The conversion of the major elements from % oxides into % elements as a function of depth based on XRF analysis was done as explained in chapter three (section 3.3.3). The % elemental concentration data for Secunda fresh fly ash and Secunda weathered fly ash core samples as a function of depth as determined by XRF analysis are presented in Appendix 3. The mobility trends of the major elements in Secunda weathered fly ash core as a function of depth based on bulk XRF analysis are discussed below. The data used in this section obtained from bulk XRF analysis (Table 8) will be corroborated with the total metal content data obtained from acid digestion and ICP analysis of the original ash samples discussed in the next chapter. The two sets of data give the total content of each element present in the ash. This comparison is necessary in order to show any similarities or differences arising from the two analytical techniques.

4.4.1.1 Silicon and aluminium

The elemental concentrations of Si and Al in Secunda fresh fly ash and each section of the weathered fly ash from Secunda core S2 as a function of depth, based on conversion of oxides from bulk XRF analysis of the ash core samples are presented in Figure 20 below.

Figure 20: Elemental content of Si and Al in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on conversion of oxides from bulk XRF analysis.

Si was depleted at all the depths along the weathered Secunda core S2 compared to Secunda fresh ash content while Al was depleted at most of the depths along the weathered Secunda core S2 compared to Secunda fresh ash content (Figure 20). In the fresh Secunda fly ash, Si content accounted for 23.77 weight % while Secunda weathered core had Si content ranging between 20.09 % and 22.80 %. Al content was 13.51 weight % in the fresh Secunda fly ash and ranged between 12.27 % and 13.64 % in Secunda weathered core. According to Tiruta-Barna et

al., (2004), Si and Al in coal fly ash are contained in the aluminosilicate and silicate minerals such as quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$) which may also contain other elements such as Ca, Mg, Na, K and many trace elements. The depletion of Si and Al in the weathered fly ash core may be as a result of the dissolution and subsequent leaching of the aluminosilicate ash matrix due to the high water content in the core, as observed in the moisture content data (Figure 17) and lower pH conditions in the core compared to the fresh ash as shown in Figure 14. Previous studies have shown that the dissolution of the aluminosilicate minerals in fly ash occurs at low pH conditions (Roy & Griffin, 1984; Zevenbergen et al., 1999). The dissolution of the aluminosilicate minerals would consequently release minor and trace elements into the pore water enhancing their mobility as the ash dam acidifies over time. The decrease in EC observed in the weathered Secunda fly ash core samples compared to the fresh Secunda fly ash (Figure 15) confirms the loss of ionic species in the ash dam as a result of leaching. A previous study by Olufunke (2010) on the mobility of metal species in dumped fly ash obtained from a wet ash handling system dump at Taaibos and Highveld power stations situated at Kragbron town in the Republic of South Africa showed that weathering due to infiltration of rainwater and water from the ash slurry caused the dissolution of solids and the migration of species down the ash dump. The Kragbron study further showed that there was mobility and movement of species down the ash dump with high moisture and low pH playing a significant role in the leaching of the elements.

4.4.1.2 Calcium and sodium

The elemental concentrations of Ca and Na in Secunda fresh fly ash and each section of the weathered fly ash from Secunda core S2 as a function of depth, based on conversion of oxides from bulk XRF analysis of the ash core samples are presented in Figure 21 below.

Figure 21: Elemental content of Ca and Na in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on conversion of oxides from bulk XRF analysis.

Ca was depleted at most of the depths along the weathered Secunda core S2 compared to Secunda fresh ash content while Na was very slightly enriched in the samples obtained from the weathered core compared to the fresh ash (Figure 21). Ca content was 6.40 weight % in the fresh Secunda fly ash and ranged between 5.25 % and 7.11 % in Secunda weathered core while Na content was 1.63 weight % in the fresh Secunda fly ash and ranged between 1.69 % and 2.03 % in Secunda weathered core. Ca is associated with the highly soluble phase of fly ash particles

and rapidly dissolves when in contact with aqueous media such as brine and infiltrating rain water (Choi et al., 2002). This explains the reduction in Ca observed in the weathered core (Figure 21) since the disposed fly ash at the ash dam is exposed to rain and high moisture content due to the co-disposal with brine. The reduction in Ca, which is a major contributor to the alkalinity of the fly ash, meant that the pH buffering capacity in the ash dam was reduced.

The slight enrichment of Na observed in some sections of the weathered core (Figure 21) may have come from Secunda brine which is rich in Na (Nyamhingura, 2009). However, though Na was slightly enriched along the weathered core compared to the fresh fly ash, there was no significant enrichment of Na along the core considering the volume of salt laden brine that went through the dam over the 20 year period that the dam was in operation. An estimate of the total amount of brine and the estimated content of Na salt that may have passed through the dam over the 20 year period was done (see Appendix 11). The estimates were done on the assumption that brine was the only feed stream used in ash transportation. However, it is reported that there are other feed streams at Secunda plant comprising of different forms of effluents that are contacted with brine at many different locations and sections of the processing steps before the resultant slurry is eventually pumped to the ash dams. The estimation was done considering the composition of Secunda brine as reported by Nyamhingura (2009), the 5:1 brine/ash ratio used in slurry making and the total volume of the ash present at the dam. An estimated 117.65 billion litres of brine carrying with it an estimated 277 million kg of Na salt may have passed through the dam over its entire lifetime. However, according to the XRF analysis, Na content was 1.63 weight % in the fresh ash and remained below 2 weight % at most depths along the weathered core showing no sign of significant accumulation at all (Figure 21). This observation highlights the fact that a huge quantity of Na may have been released into the environment over the years. Akinyemi (2011b) studied weathered ash obtained from drilled cores at Eskom's Tutuka station. Tutuka station practices dry ash handling where the ash is conditioned with brine in order to moisten it for dust suppression. The amount of brine introduced in the ash

dump at Tutuka was much less than the amount of brine that went through Secunda ash dam. Tutuka ash reported Na content varying between 0.6 - 1.1 weight % for 1 year old ash cores to around 0.6 - 0.8 weight % for 8 year old ash cores with even lesser Na levels reported for 20 year old ash cores. There was no evidence of Na encapsulation in the dumped Tutuka ash even though the ash dump was brine irrigated indicating that Na may have been released through leaching. It was evident that the dumped Secunda ash had higher weight % Na content than the ash at Tutuka dump due to the high volume of salt laden brine involved with the wet ash handling system at Secunda.

4.4.1.3 Iron, magnesium and potassium

The elemental concentrations of Fe, Mg and K in Secunda fresh fly ash and each section of the weathered fly ash from Secunda core S2 as a function of depth, based on conversion of oxides from bulk XRF analysis of the ash core samples are presented in Figure 22 below.
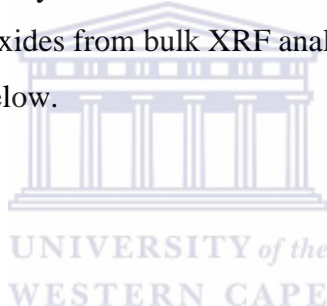
Figure 22: Elemental content of Fe, Mg and K in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on conversion of oxides from bulk XRF analysis.

Fe and Mg were considerably enriched in the weathered Secunda core S2 compared to the fresh Secunda ash while K showed an inconsistent trend, being slightly enriched at some depths and depleted at others. In the fresh fly ash, Fe content accounted for 1.58 weight % while the weathered Secunda core had Fe content ranging between 1.50 % and 4.29 %. Mg content was 1.13 weight % in the fresh Secunda fly ash and ranged between 1.43 % and 1.79 % in Secunda

weathered core while K content was 0.79 weight % in the fresh Secunda fly ash and ranged between 0.62 % and 0.98 % in Secunda weathered core.

Fe had three layers of accumulation at 1.5 m, 12 m and 28.5 m (Figure 22). Fe generally showed less variation in other sections but was enriched in most samples taken from various levels along the core. The observed enrichment of Fe in the weathered core is thought to be due to the practice of dumping of spent Fe catalysts into Secunda ash dam. Fe catalysts are used in Fischer-Tropsch processes (Davis, 2003) carried out at Secunda industrial complex. Mg enrichment and the very slight enrichment of K in the weathered core may have come from Secunda brine which is known to contain these elements (Nyamhingura, 2009). However, there was no significant accumulation of Mg and K along the core despite continuous introduction of brine into the ash dam over the 20 year period, pointing to the possible release of these elements into the environment.

4.4.1.4 Titanium and phosphorus

The elemental concentrations of Ti and P in Secunda fresh fly ash and each section of the weathered fly ash from Secunda core S2 as a function of depth, based on conversion of oxides from bulk XRF analysis of the ash core samples are presented in Figure 23 below.

Figure 23: Elemental content of Ti and P in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on conversion of oxides from bulk XRF analysis.

Ti showed an inconsistent trend, being slightly enriched at some depths and depleted at others while P generally showed very slight enrichment at the bottom of the weathered Secunda core compared to the fresh Secunda ash. Ti content was 1.07 weight % in the fresh Secunda fly ash and ranged between 0.94 % and 1.10 % in the weathered Secunda core while P content was 0.31 weight % in the fresh Secunda fly ash and ranged between 0.23 % and 0.36 % in the weathered Secunda

core. According to Dutta et al., (2009), leaching involves the dissolution and precipitation of elements. The dissolution and precipitation phenomenon may explain the periodic enrichment and depletion trends observed for Ti and P in the ash dam as a result of leaching which later led to the slight accumulation of P at the bottom of the core.

4.4.1.5 Manganese and sulphur

The elemental concentrations of Mn and S in Secunda fresh fly ash and each section of the weathered fly ash from Secunda core S2 as a function of depth, based on conversion of oxides from bulk XRF analysis of the ash core samples are presented in Figure 24 below.
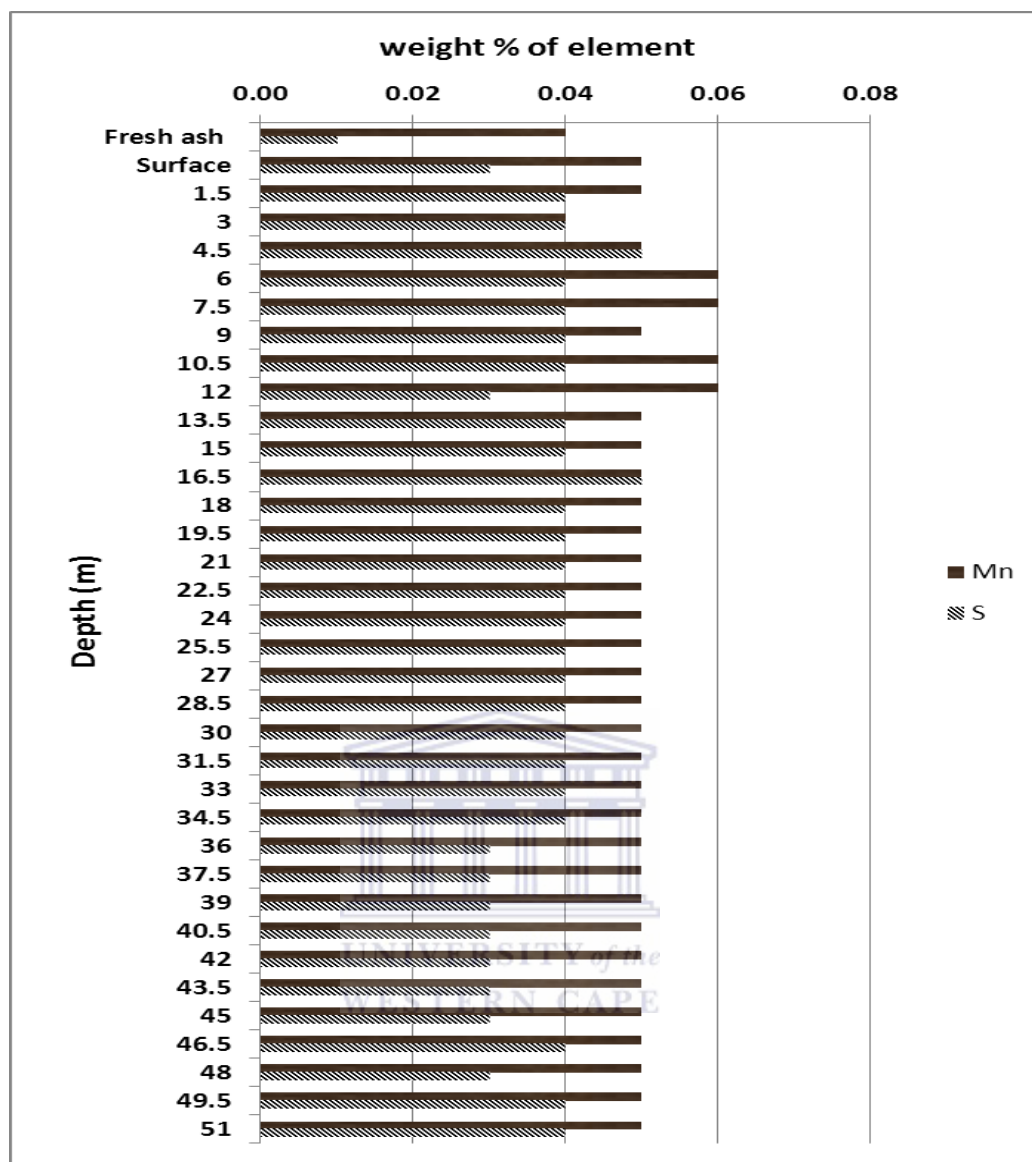
Figure 24: Elemental content of Mn and S in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on conversion of oxides from bulk XRF analysis.

Mn showed slight enrichment in the weathered Secunda core S2 compared to the fresh Secunda ash while S showed significant and consistent enrichment in the weathered Secunda core S2 compared to the fresh Secunda ash, with little variation in the enrichment levels along the core. In the fresh Secunda fly ash, Mn content accounted for 0.04 weight % while the samples taken from the weathered Secunda core S2 had Mn content ranging between 0.04 % and 0.06 %. S content was 0.01 weight % in the fresh Secunda fly ash and ranged between 0.03 % and

0.05 % in the samples taken from the weathered Secunda core S2. It is thought that, apart from Secunda brine, the spent catalysts dumped into Secunda ash dam may contain Mn as well thus explaining the slight enrichment of this element in the dumped fly ash.

Coal mine brine is rich in sulphates (Turek et al., 1995) therefore the enrichment of S in the weathered core can be attributed to the brine. Furthermore, Nyamhingura (2009) showed high levels of sulphates contained in Secunda brine. The higher S levels observed in the weathered Secunda core S2 compared to the fresh Secunda ash based on XRF analysis (Figure 24) corresponded to higher SO_4^{2-} release observed in the weathered Secunda core S2 samples compared to the fresh Secunda ash sample in the extracted pore water analysis (Figure 18). The rapid release of the sulphate anion in the pore water extraction procedure shows its high solubility.

Generally, there was very little enrichment of the major elements observed in the weathered core S2 considering the age of the dam and the amount of brine that went through, thus questioning the salt holding capacity of the Secunda ash dam.

4.4.2 The mobility trends of the trace elements in Secunda weathered fly ash core

The trace elements were determined by XRF and are reported in mg/kg as opposed to weight % due to the small concentration in which they existed in the fly ash. The mobility trends of the trace elements in Secunda weathered fly ash core S2 as a function of depth based on XRF analysis are discussed below.

4.4.2.1 Strontium and barium

The elemental concentrations of Sr and Ba for Secunda fresh fly ash and the weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis are presented in Figure 25 below.
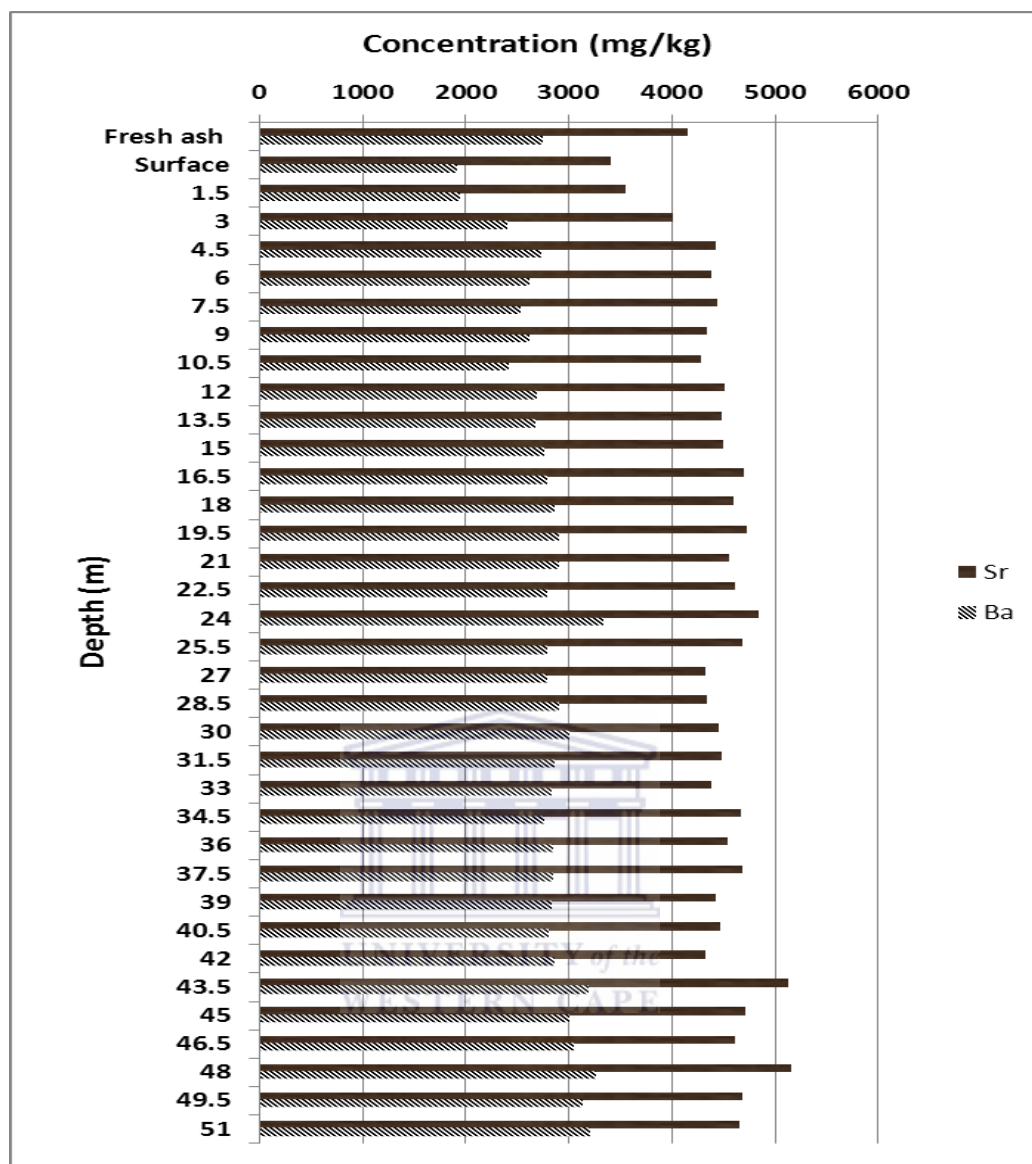
Figure 25: Elemental concentrations of Sr and Ba in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis.

Sr and Ba were very slightly enriched in samples taken from most of the depths along the weathered Secunda core S2 compared to the fresh Secunda ash. The concentration of Sr in the fresh Secunda ash was 4160.43 mg/kg while the weathered Secunda core had Sr concentration ranging between 3410.17 mg/kg and 5157.50 mg/kg, with a mean concentration of 4489.80 mg/kg, and was most enriched in the lowest part of the dam. The concentration of Ba in the fresh Secunda ash was 2749.50 mg/kg while the weathered Secunda core had Ba

concentration ranging between 1924.18 mg/kg and 3338.19 mg/kg, with a mean concentration of 2803.58 mg/kg, mostly enriched in the lowest part of the dam. The trends observed for Sr and Ba showed periodic enrichment and depletion along the core, with significant depletion at the top of the core and slight accumulation at the bottom of the core (Figure 25). The periodic enrichment and depletion of the elements along the core can be attributed to dissolution and precipitation of the elements due to leaching (Dutta et al., 2009) and inconsistencies in the leaching patterns within the ash dam. Previous studies have shown that Sr and Ba could exist in radioactive forms such as the ^{90}Sr and ^{140}Ba isotopes (Jammet, 1961) therefore significant levels of these elements in fly ash could lead to negative effects on humans and animals.

4.4.2.2 Thorium and zirconium

The elemental concentrations of Th and Zr for Secunda fresh fly ash and the weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis are presented in Figure 26 below.
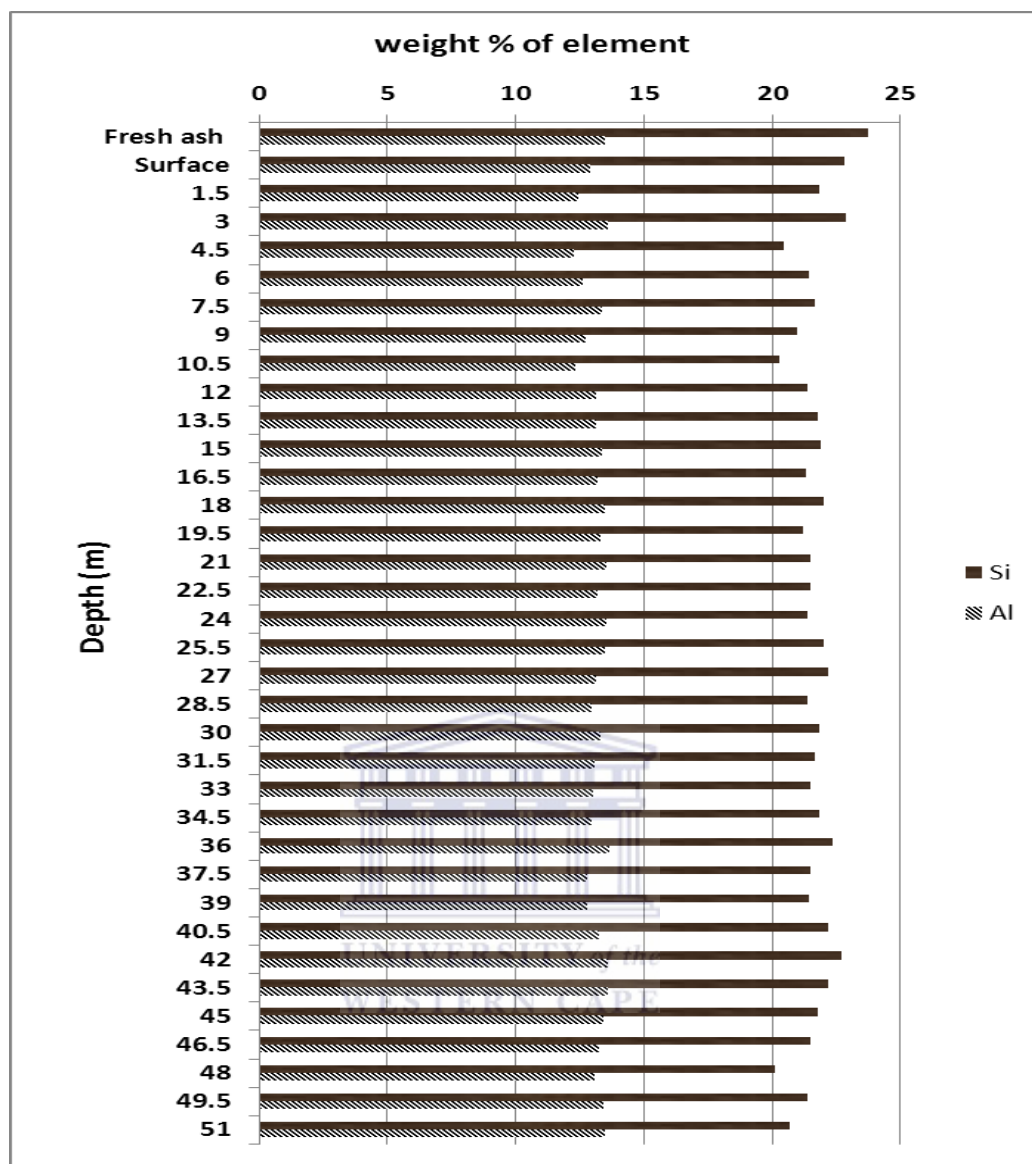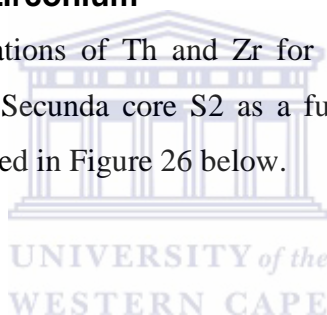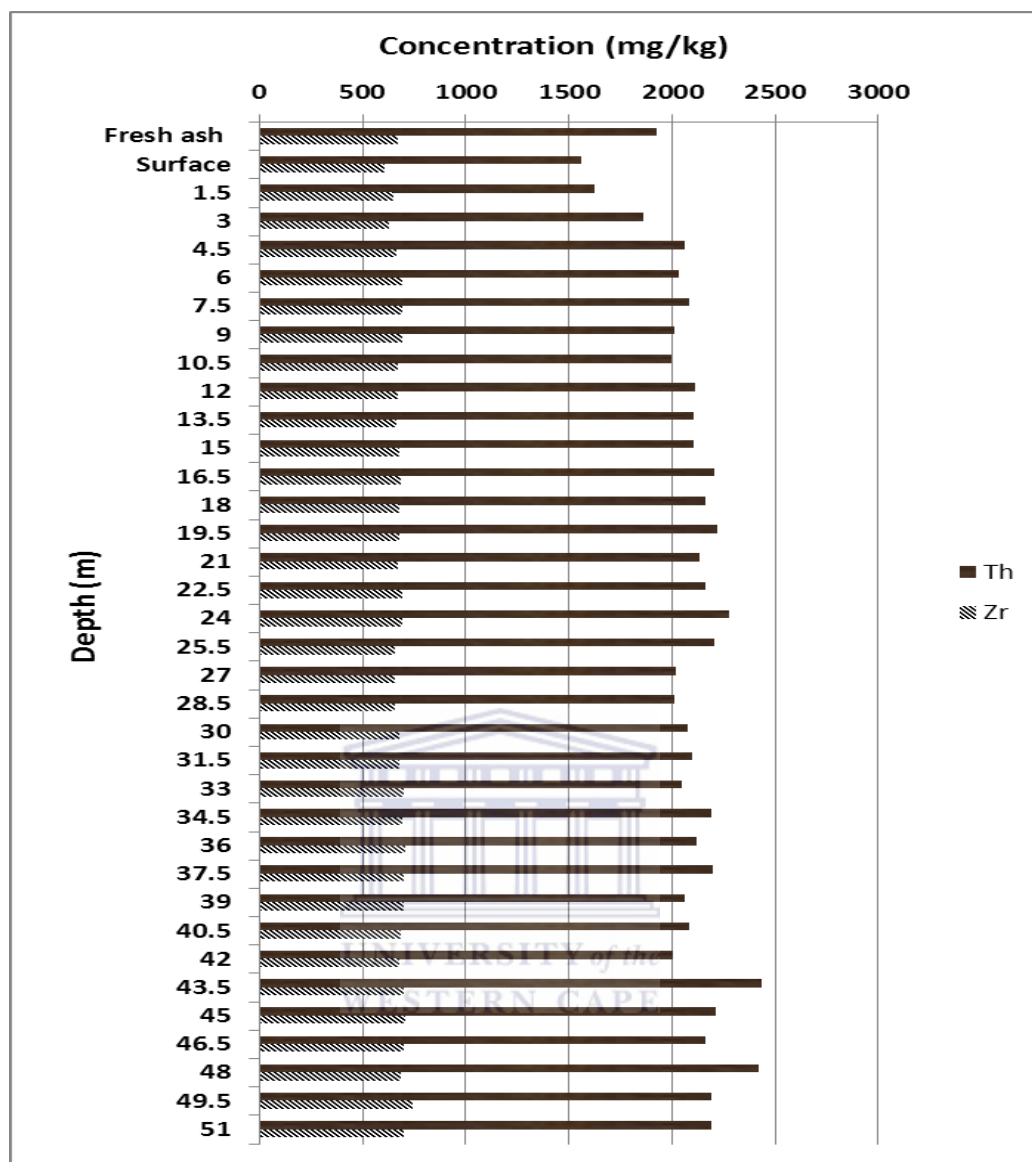
Figure 26: Elemental concentrations of Th and Zr in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis.

Th and Zr were very slightly enriched in samples taken from most of the depths along the weathered Secunda core S2 compared to the fresh Secunda ash. The concentration of Th in the fresh fly ash was 1921.89 mg/kg while the weathered core had Th concentration ranging between 1556.71 mg/kg and 2430.47 mg/kg, with a mean concentration of 2095.71 mg/kg. The concentration of Zr in the fresh fly ash was 664.60 mg/kg while the weathered core had Zr concentration ranging between 602.85 mg/kg and 738.56 mg/kg, with a mean concentration of 676.48

mg/kg. According to Jammet (1961) Th and Zr exhibit radioactive properties therefore their presence in the fly ash causes environmental concern.

4.4.2.3 Cerium and yttrium

The elemental concentrations of Ce and Y for Secunda fresh fly ash and the weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis are presented in Figure 27.
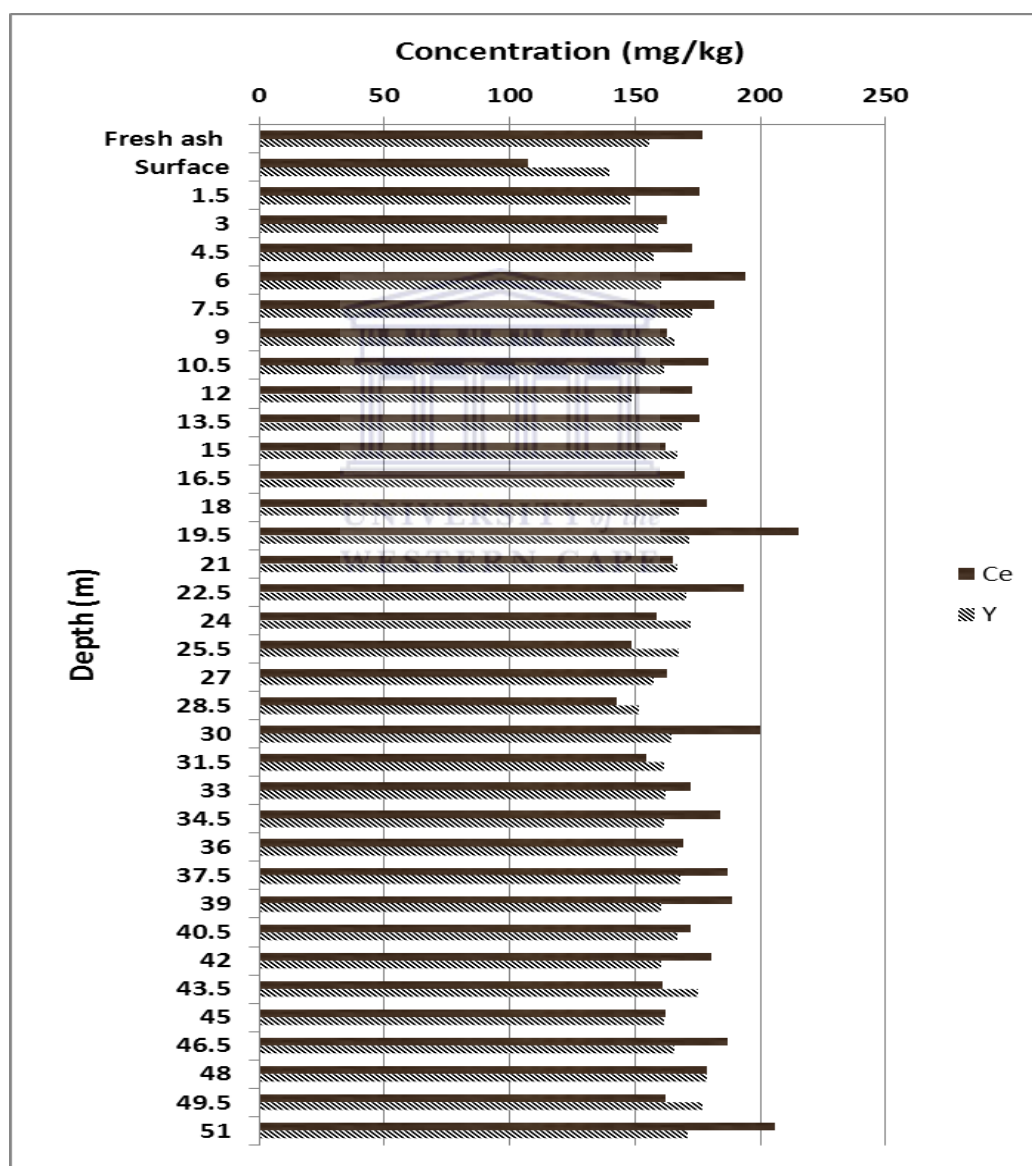
Figure 27: Elemental concentrations of Ce and Y in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis.

Ce and Y were slightly enriched in some sections of the weathered Secunda core S2 compared to the fresh Secunda ash and showed inconsistent trends, being enriched at some depths and depleted at others. The concentration of Ce in the fresh Secunda fly ash was 176.82 mg/kg while the weathered core had Ce concentration ranging between 107.44 mg/kg and 215.13 mg/kg, with a mean concentration of 172.71 mg/kg (Figure 27). The concentration of Y in the fresh Secunda fly ash was 155.87 mg/kg while the weathered core had Y concentration ranging between 139.77 mg/kg and 179.00 mg/kg, with a mean concentration of 164.17 mg/kg (Figure 27). The observed slight enrichment of these trace elements in some sections of the weathered core may be due to inconsistencies in the weathering rate of the fly ash over time. According to Akinyemi (2011b) the weathering of the major ash matrix elements Si and Al has an impact on the trace metal levels. Therefore, the slow dissolution of the Si and Al ash matrix could have left behind trace elements which had been previously trapped in the ash matrix, leading to slight accumulation of the trace elements at some depths along the core.

4.4.2.4 Niobium and arsenic

The elemental concentrations of Nb and As for Secunda fresh fly ash and the weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis are presented in Figure 28.
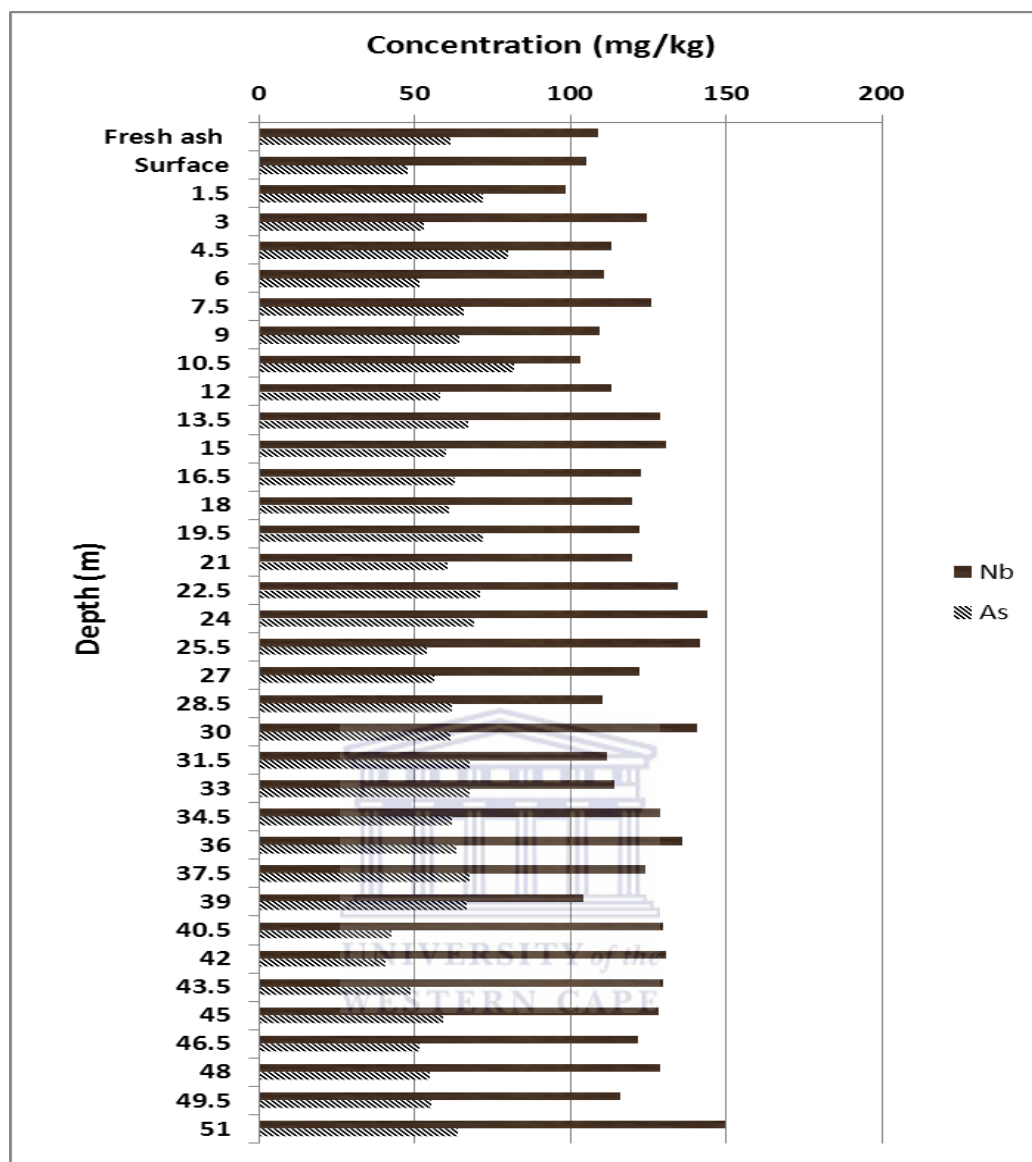
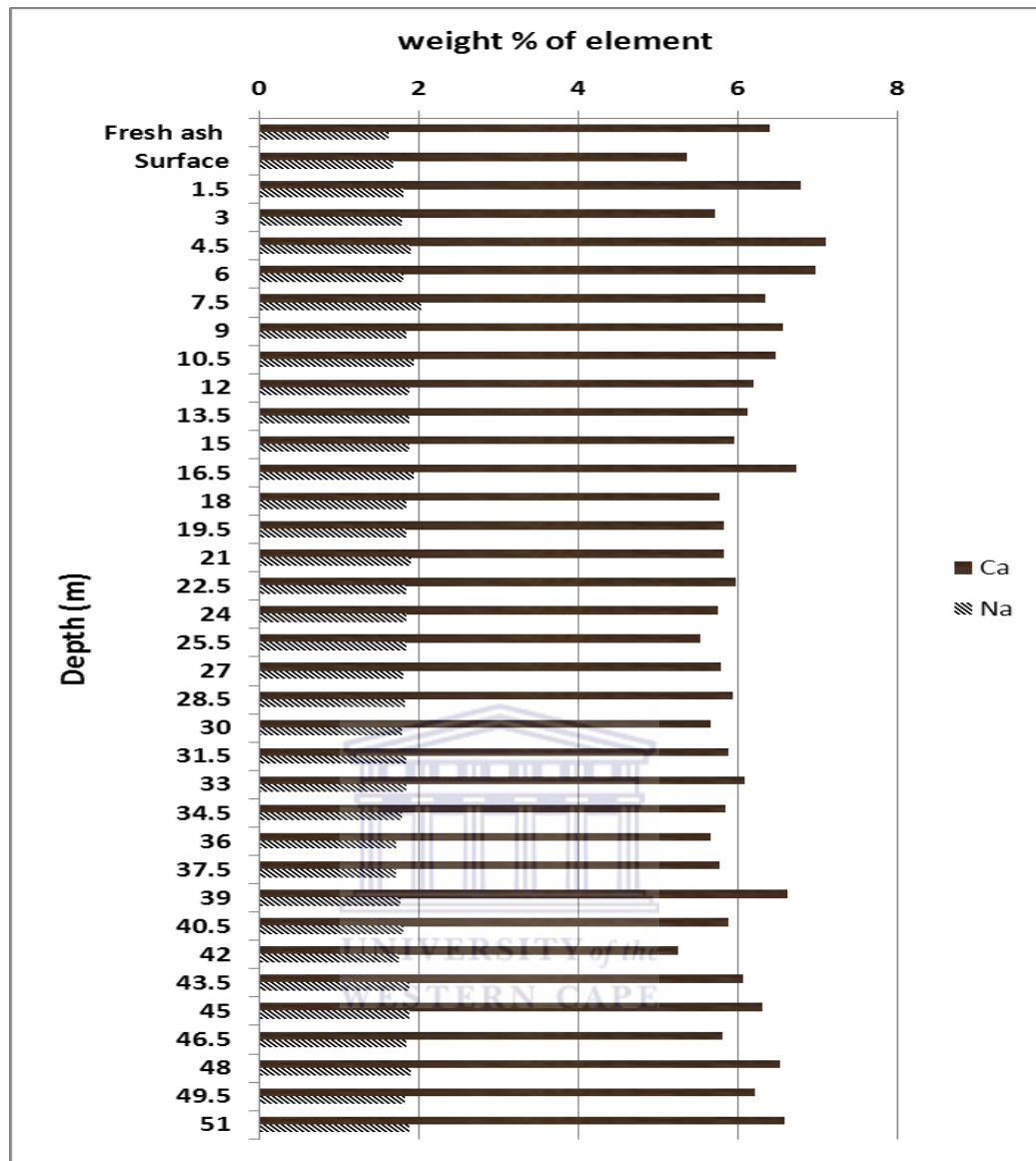Figure 28: Elemental concentrations of Nb and As in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis.

Nb and As were slightly enriched in some sections of the weathered Secunda core S2 compared to the fresh Secunda ash and showed inconsistent trends, being enriched at some depths and depleted at others. The concentration of Nb in the fresh Secunda fly ash was 109.03 mg/kg while the weathered core had Nb concentration ranging between 98.50 mg/kg and 149.43 mg/kg, with a mean concentration of 122.67 mg/kg. The concentration of As in the fresh Secunda fly ash was 61.39 mg/kg while the weathered core had As concentration ranging

between 40.57 mg/kg and 81.82 mg/kg, with a mean concentration of 61.39 mg/kg. The periodic enrichment and depletion of these trace elements observed in various sections of the weathered core may be attributed to inconsistencies in the weathering rate of the fly ash and the weathering of the major ash matrix leaving these trace elements behind (Akinyemi, 2011b).

4.4.2.5 Lead and nickel

The elemental concentrations of Pb and Ni for Secunda fresh fly ash and the weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis are presented in Figure 29 below.
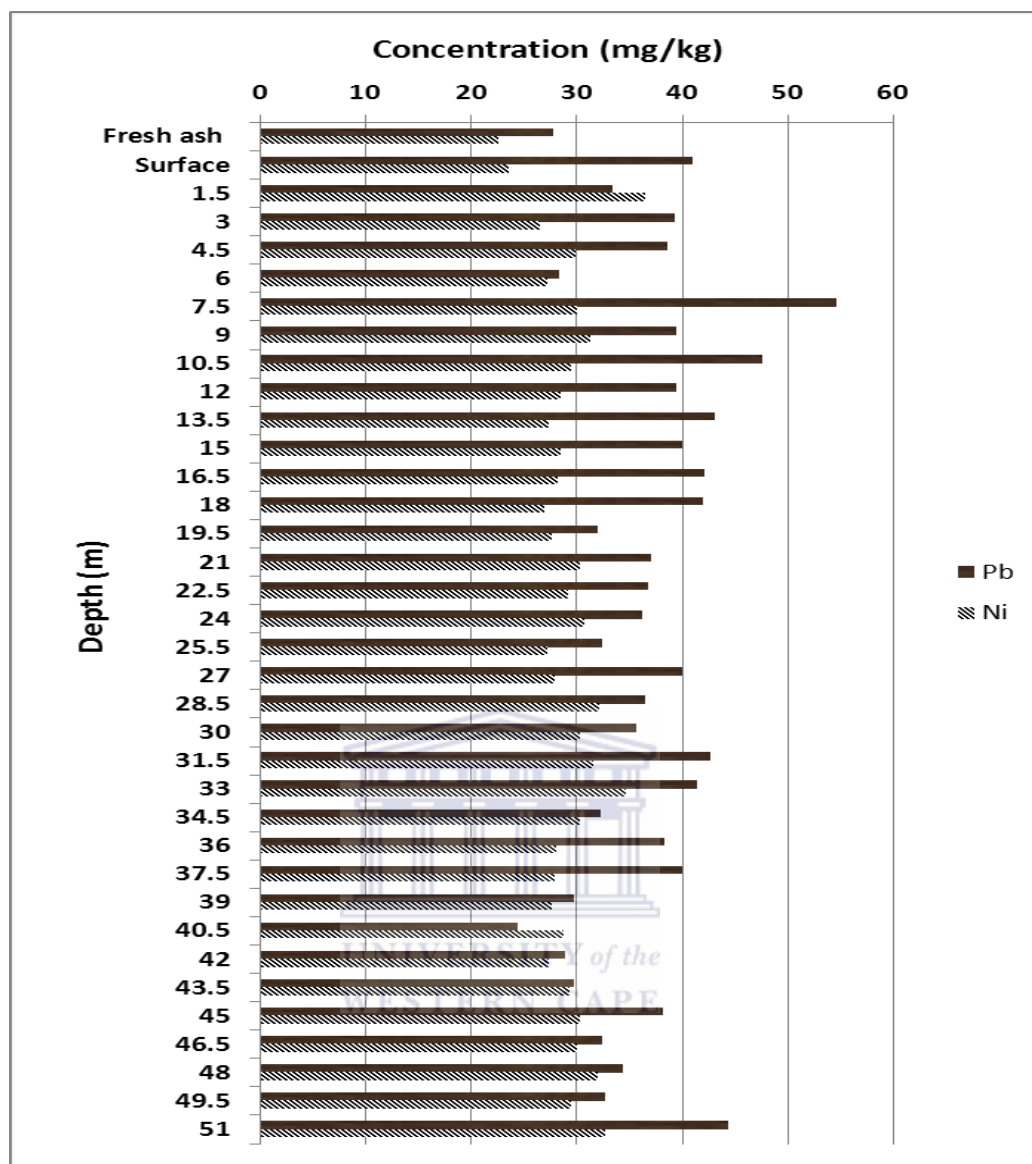
Figure 29: Elemental concentrations of Pb and Ni in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis.

Pb and Ni were generally somewhat enriched in the weathered Secunda core S2 compared to the fresh Secunda ash. The concentration of Pb in the fresh Secunda fly ash was 27.85 mg/kg while the weathered core had Pb concentration ranging between 28.46 mg/kg and 54.70 mg/kg, with a mean concentration of 37.35 mg/kg, therefore indicating slight enrichment. The concentration of Ni in the fresh Secunda fly ash was 22.56 mg/kg while the weathered Secunda core had Ni concentration ranging between 23.65 mg/kg and 36.50 mg/kg, with a mean

concentration of 29.45 mg/kg. According to Tiruta-Barna et al., (2004), the major matrix of fly ash may trap trace elements such as Pb and Ni among others. The observed slight enrichment of these trace elements in some sections of the weathered core compared to the fresh ash may be attributed to the weathering of the ash matrix over time as the pH lowered in the ash dam thus releasing these trace elements.

4.4.2.6 Cobalt and rubidium

The elemental concentrations of Co and Rb for Secunda fresh fly ash and the weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis are presented in Figure 30 below.
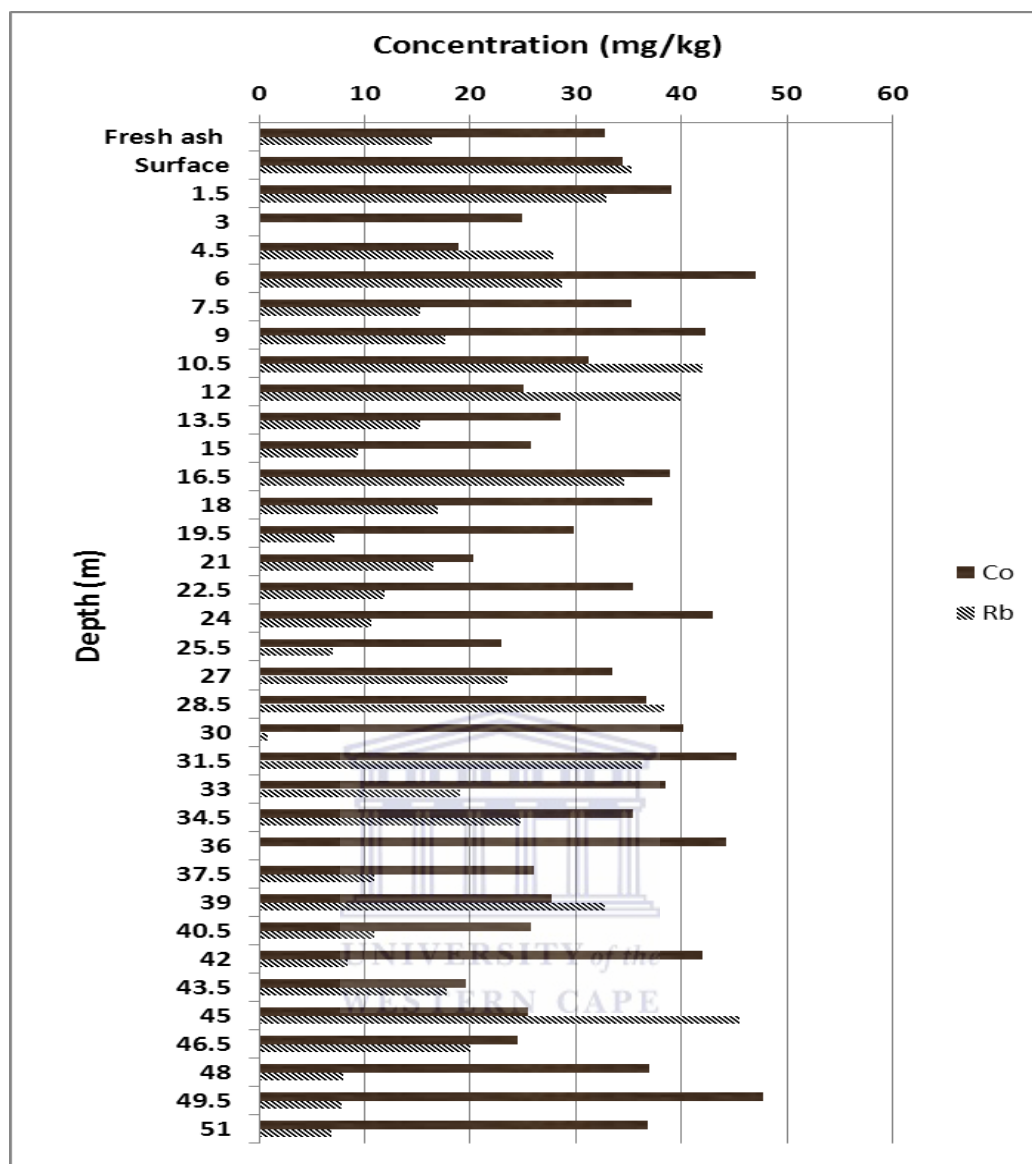
Figure 30: Elemental concentrations of Co and Rb in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis.

Co and Rb showed inconsistent trends along the core, being enriched at some depths and depleted at others. The concentration of Co in the fresh Secunda fly ash was 32.73 mg/kg while the weathered Secunda core had Co concentration ranging between 18.89 mg/kg and 47.72 mg/kg, with a mean concentration of 33.32 mg/kg. The concentration of Rb in the fresh Secunda fly ash was 16.41 mg/kg while the weathered Secunda core had Rb concentration ranging between 0.84 mg/kg and 45.54 mg/kg, with a mean concentration of 20.65 mg/kg. The

periodic enrichment and depletion trends observed for these elements shows that leaching was taking place at different rates within the ash dam as a result of the periodic dissolution and precipitation of the elements (Dutta et al., 2009).

4.4.2.7 Vanadium and uranium

The elemental concentrations of V and U for Secunda fresh fly ash and the weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis are presented in Figure 31 below.
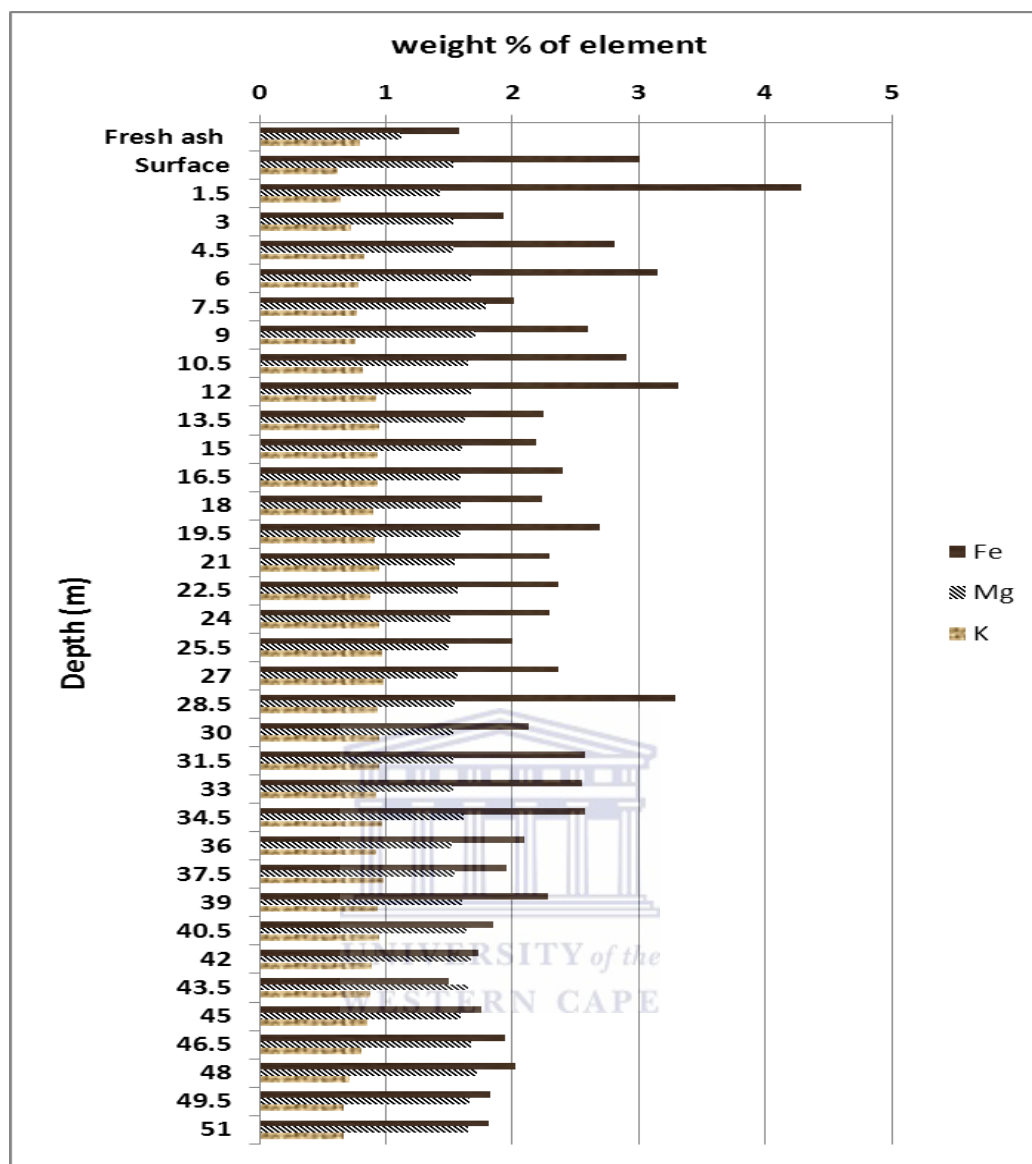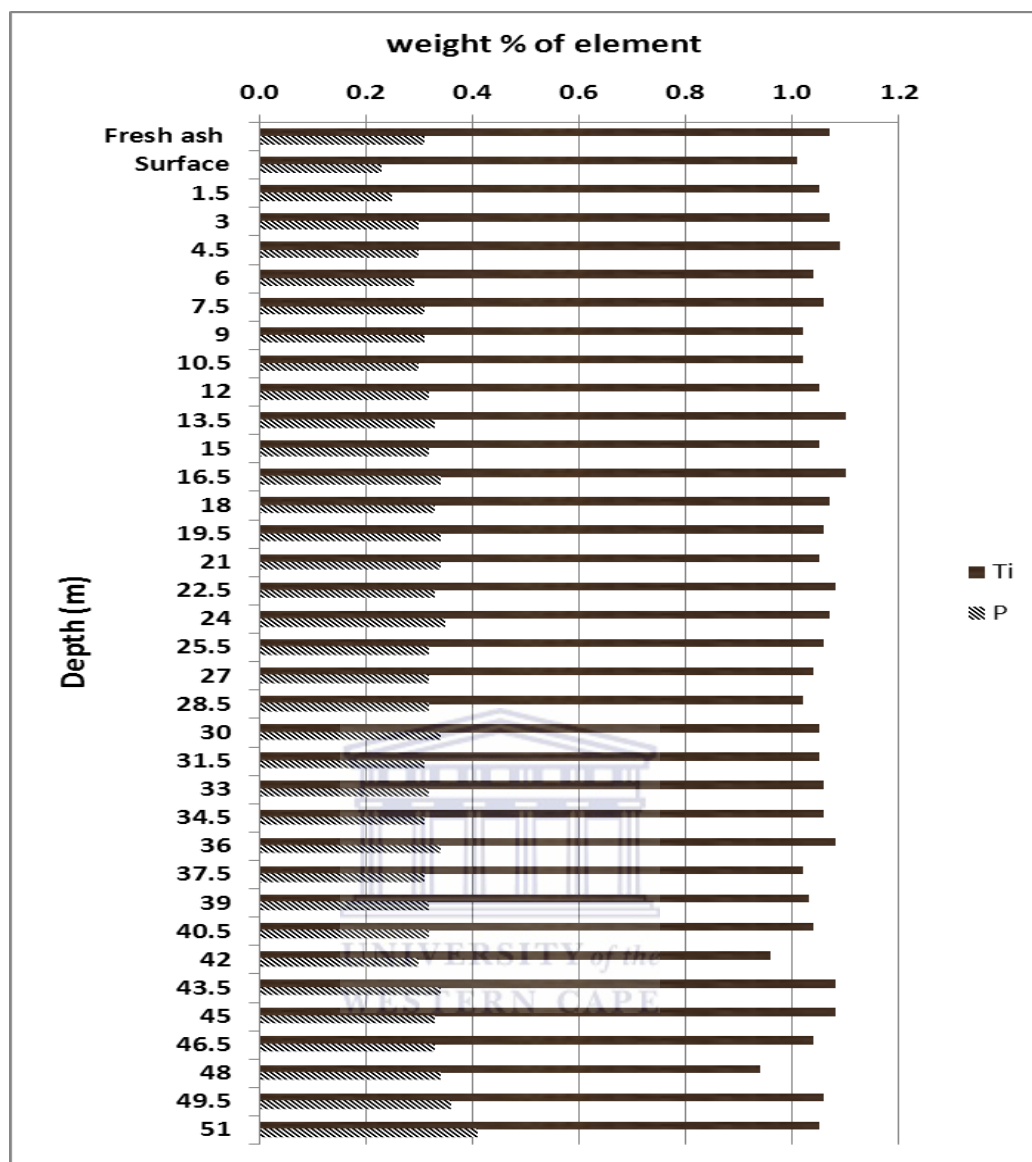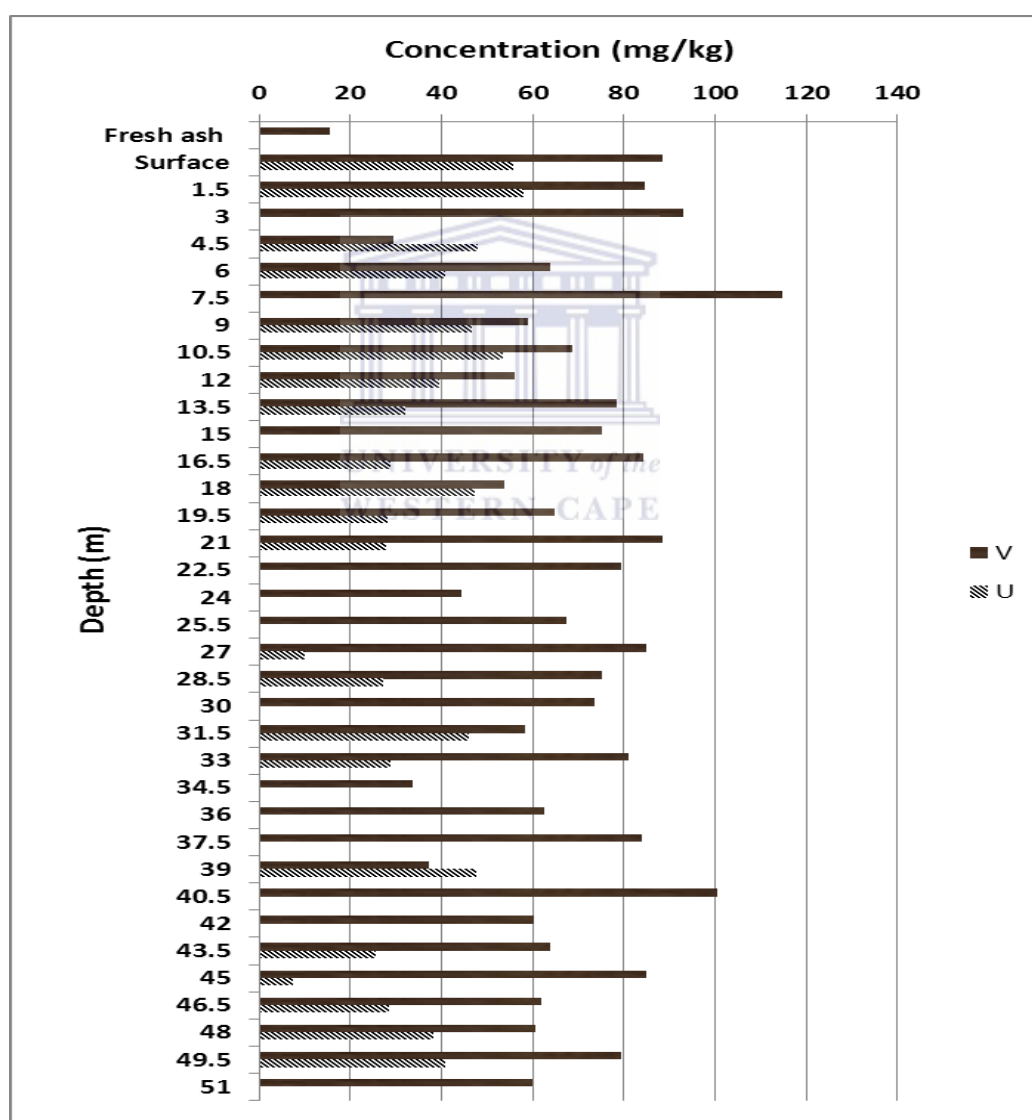

Figure 31: Elemental concentrations of V and U in Secunda fresh fly ash and weathered fly ash from Secunda core S2 as a function of depth based on bulk XRF analysis.

V was enriched in the weathered Secunda core compared to the fresh Secunda ash while U showed an inconsistent trend in the weathered Secunda core, being detected at some sections of the weathered core and going undetected at others. The concentration of V in the fresh Secunda fly ash was 15.41 mg/kg while the weathered Secunda core had V concentration ranging between 29.49 mg/kg and 114.59 mg/kg, with a mean concentration of 70.14 mg/kg. U was not detected in the fresh Secunda fly ash probably because it was present in very low quantities undetectable by XRF technique, which detects elements from ppm to percent levels (EPA, 2004) while the weathered Secunda core had U concentration ranging between 7.47 mg/kg and 58.00 mg/kg, with a mean concentration of 36.71 mg/kg. Nyamhingura (2009) showed that Secunda brine contains V thus may be responsible for the enrichment observed in the weathered core compared to the fresh Secunda ash. The inconsistency shown by U, being detected at some sections of the weathered core and going undetected at others is thought to be due to different sourcing of coal by Secunda power station over the years. Some of the coal may have been sourced from coal beds with significant amounts of U while other coal beds may have had none or less amounts of this element.

Generally, the trends observed showed periodic enrichment and depletion of the major and trace elements along the ash dam profile over time. This observation may be attributed to leaching which involves dissolution and re-precipitation of the various metal species in the fly ash (Dutta et al., 2009). The elements dissolve to become labile and then leach from an upper section of the dam and later may re-precipitate and accumulate at a lower section of the dam causing the periodic enrichment and depletion observed. According to Grisafe et al., (1988), most elements in fly ash show increasing solubility with decreasing pH except for those that form amphoteric hydroxides such as Cr and Zn. Therefore, a decrease in the ash pH over time will mobilize most of the species in the ash dam.

In conclusion, the ash dam showed inhomogeneity in terms of the leaching trends. Although various major and trace elements were somewhat enriched in the weathered Secunda core S2 compared with the fresh Secunda ash, there was no

significant accumulation of the cationic and anionic species in the disposed fly ash apart from soluble sulphate species despite continuous addition of brine into the system with each dumping session, considering the ash dam was in operation for many years. The lack of significant accumulation of the major and trace elements contained in brine that was codisposed with the ash in the ash dam points to the possibility that the fly ash may be trapping some species from the brine to reach a saturation point, above which the fly ash holds no more, therefore losing the species into the environment through leaching. The salt sink capacity of the ash is insignificant. The overall total salt capture capacity of Secunda ash dam will be discussed in chapter five.

4.5 SECTION SUMMARY

This chapter has shed light on the changes in mineralogy, chemical composition, morphology and physical characteristics of Sasol Secunda fly ash after contact with brine in a codisposal scenario as used in a wet ash handling system. It is clear that the chemistry of the fresh Secunda fly ash is different from that of the weathered Secunda fly ash which has been exposed to brine. The contact of fly ash with brine influences its chemical properties. As observed in the results, brine may have been responsible for the slight enrichment of some of the major and trace elements in the disposed fly ash, though the enrichment of these elements was not significant considering the volume of brine that was codisposed on the ash dam estimated at 117.65 billion litres over the 20 years the dam was in operation. The release of species in the ash dam seemed to be influenced by the decrease in pH which also led to the dissolution of the major ash matrix. The ash dam showed inhomogeneity in terms of the leaching trends. It can be seen that by the time the study was conducted, the disposed ash had already lost some major and trace elements as a result of weathering and leaching as depicted by the lower EC observed in the weathered core compared to the fresh ash. The salt sink capacity estimate gave a clear indication that the fly ash generated at Sasol Secunda power station cannot be used as a long term sustainable salt sink. The wet ash handling system practiced at Sasol Secunda power station led to only a slightly higher Na salt load in the disposed ash compared to the dry ash handling

system practiced at Eskom's Tutuka power station. Furthermore, the very high moisture content associated with the wet ash handling system at Sasol compared to the dry ash handling system at Tutuka station is of concern. Although both ash disposal systems were susceptible to leaching, the high moisture content observed in the wet ash handling system created an environment more conducive to the release of species in the disposed ash due to decreasing pH trends and saturated conditions of the ash. However, the wet ash handling system offers the advantage of dustless disposal while the dry ash handling system poses the danger of toxic elements in fly ash spreading due to wind-blown particulates.

In order to further investigate the leaching potential and the chemical partitioning into different mineralogical phases of the elements in the fly ash, the sequential extraction procedure was used to shed light on these aspects. The results of the sequential extraction procedure will be discussed in chapter five.

UNIVERSITY of the
WESTERN CAPE

CHAPTER FIVE

RESULTS AND DISCUSSION (II)

5. SEQUENTIAL EXTRACTION STUDIES OF FRESH AND DUMPED SASOL SECUNDA COAL FLY ASH

This chapter presents and discusses the second section of the results in this study which were obtained from the sequential extraction procedure carried out on fresh Secunda fly ash and on the weathered fly ash obtained from core S2 at Secunda ash dam. The sequential extraction procedure was used to investigate the chemical partitioning of the major elements: Si, Al, Ca, Na, Fe, Mg, K, Sr, Ba, Mn and trace elements: As, Zn, Pb, Ni, Mo, Cr and Cu in the weathered Secunda core, that had been in contact with brine as described in chapter three (section 3.3.6). The different sequential extraction steps involved have been described in chapter three (sections 3.3.6.1, 3.3.6.2, 3.3.6.3, 3.3.6.4, 3.3.6.5 and 3.3.6.6) for the water soluble fraction, exchangeable fraction, carbonate fraction, Fe & Mn fraction, residual fraction and total metal content respectively. Section 5.1 will discuss the total metal concentration for the major and the trace elements in both Secunda fresh fly ash and the weathered fly ash obtained from core S2 at Secunda ash dam. Section 5.2 will discuss the chemical partitioning of the major and trace elements in the various geochemical phases of Secunda fresh fly ash and the weathered fly ash obtained from core S2 at Secunda ash dam, while section 5.3 will discuss the statistical assessment of data quality for the major and trace elements i.e. mass balance.

5.1 TOTAL METAL CONTENT

In the total metal content analysis, the unleached Secunda fresh fly ash sample and the unleached weathered Secunda fly ash core S2 samples were digested using a combination of acids ($HClO_4$: HF: HNO_3) mixed in the ratio of 3:3:1 respectively as described in chapter three (section 3.3.6.6). Thereafter, the digested samples were analysed by ICP-OES as described in chapter three (section 3.3.6). This step was done in order to determine the total metal content of Secunda fly ash. The results obtained from the total metal content analysis

determined for unleached Secunda fresh fly ash sample and unleached weathered Secunda fly ash core samples for Si, Al, Ca, Fe, Na Mg, K, Sr, Ba, Mn, As, Zn, Pb, Ni, Mo, Cr and Cu are shown in Figure 32 below. The data presents the mean values for the weathered Secunda fly ash core samples (n = 35) while the fresh fly ash analysis was triplicated (n = 3). The ranges given show the varying concentration between samples obtained from various depths of the weathered Secunda fly ash core S2 and the significant fluctuation as a function of depth compared to the Secunda fresh ash sample. The total metal content analysis data as a function of depth are presented in Appendix 10.

	Fresh fly ash (n = 3)	Weathered fly ash (n = 35)	
Conc. (mg/kg)		Mean	Range
Si	230180.67	210628.27	190010.27 - 236408.00
Al	134015.28	131621.69	113425.72 - 166642.33
Ca	64096.73	60025.65	45379.22 - 89596.73
Fe	15874.44	23601.92	16601.14 - 40820.60
Na	16543.31	17367.29	13900.00 - 26769.92
Mg	8757.25	15948.15	14909.00 - 17154.48
K	7986.73	8468.95	7096.73 - 12241.06
Sr	3961.97	4545.72	3602.75 - 6431.26
Ba	2603.39	2818.26	2032.61 - 3639.62
Others			
Mn	429.58	514.93	365.42 - 689.28
As	60.20	61.92	9.70 - 130.10
Zn	25.77	50.44	28.64 - 88.94
Pb	26.99	36.15	9.37 - 77.84
Ni	22.03	31.54	18.98 - 44.13
Mo	17.53	18.91	3.19 - 46.33
Cr	11.27	10.17	2.39 - 20.81
Cu	9.97	4.55	2.22 - 7.90

Others: As, Cr, Cu, Mn, Mo, Ni, Pb and Zn.

Others: As, Cr, Cu, Mn, Mo, Ni, Pb and Zn.
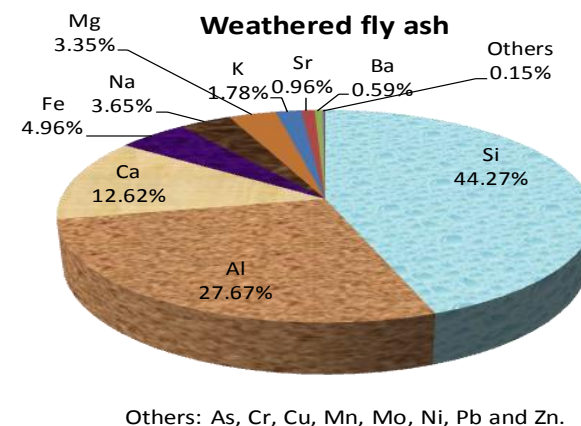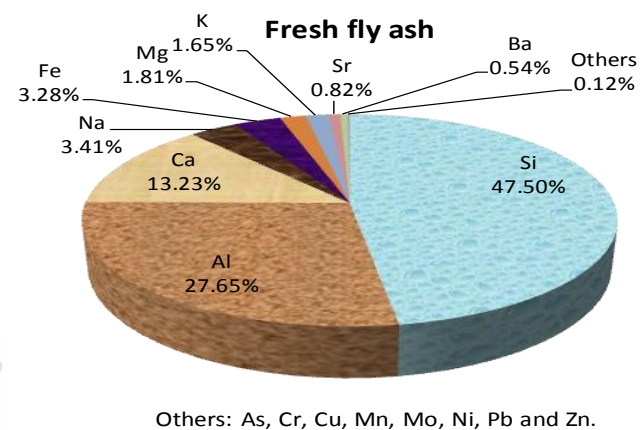
Figure 32: Total metal content of fresh Secunda fly ash and weathered Secunda fly ash core S2 samples based on acid digestion and ICP-OES analysis.

The data obtained from the total metal content analysis determined by acid digestion and ICP-OES analysis for unleached Secunda fresh fly ash and unleached weathered Secunda fly ash core (Figure 32) were closely similar to the XRF data showing the bulk chemical composition of Secunda fresh fly ash and weathered Secunda fly ash core presented in Table 8 in chapter four. The two sets of data gave the total content of each element present in the ash on a dry mass basis. Si and Al accounted for 75.15 weight % of the elements present in the fresh Secunda fly ash and 71.94 weight % of the elements present in the weathered Secunda fly ash core S2 (Figure 32). Secunda fresh fly ash contained (in weight %) Ca (13.23 %), Na (3.41 %), Fe (3.28 %), Mg (1.81 %), K (1.65 %), Sr (0.82 %) and Ba (0.54 %) while the weathered Secunda core contained (in weight %) Ca (12.62 %), Na (3.65 %), Fe (4.96 %), Mg (3.35 %), K (1.78 %), Sr (0.96 %) and Ba (0.59 %) (Figure 32). Other elements such as Mn, As, Zn, Pb, Ni, Mo, Cr and Cu, together accounted for 0.12 weight % of Secunda fresh ash and 0.15 weight % of the weathered Secunda core (Figure 32). The similarity in the data obtained from the total metal content analysis determined by acid digestion and ICP-OES analysis with that reported by bulk XRF analysis brought confidence in the reliability of the two sets of data used in this study. However, the ICP-OES analysis was done for selected trace elements due to budgetary constraints thus explaining the omission of elements such as Ti, Th, Zr, Ce, Y, Nb, Co, Rb, V and U in Figure 32 which had been reported by bulk XRF analysis (Table 8). Akinyemi (2011b) studied weathered ash obtained from a dry ash handling system at Eskom's Tutuka station and showed total Na content of 4113.23 mg/kg in 1 year old weathered fly ash, a lesser total Na content of 1025.87 mg/kg in 8 year old weathered fly ash and much lesser total Na content of 815.17 mg/kg in 20 year old weathered fly ash. Comparing these values with the average total Na content observed in the weathered Secunda core of 17,367.29 mg/kg (Figure 32), it was evident that the wet ash handling system involving codisposal of huge volumes of brine increased the overall salt load in the disposed ash at Secunda. However, according to calculations based on the difference between the Secunda fresh ash content and the weathered Secunda ash content for each element as presented in Figure 32, Secunda ash dam showed -0.01 weight % overall total salt capture

capacity indicating that the ash dam was capable of releasing elements to the environment. The detailed calculations are presented in Appendix 12. The leaching potential or lability and mineral phase associations of the elements in the fly ash as determined by the sequential extraction procedure will be discussed in the next section.

5.2 CHEMICAL PARTITIONING OF THE MAJOR AND TRACE ELEMENTS IN THE FIVE GEOCHEMICAL PHASES OF SECUNDA FRESH FLY ASH AND THE WEATHERED FLY ASH OBTAINED FROM SECUNDA CORE.

In the sequential extraction procedure, the water soluble fraction involved leaching of Secunda fresh fly ash and the weathered fly ash from Secunda core using ultrapure water as described in chapter three (section 3.3.6.1). The elements released in the water soluble fraction extraction step shed light on which metal species in the fly ash are capable of rapidly leaching out or being released due to contact of the fly ash with water. This step was conducted in order to mimic natural conditions where the ash dam gets exposed to rain water. The exchangeable fraction extraction step involved leaching of Secunda fresh fly ash and the weathered fly ash from Secunda core using 1M ammonium acetate buffer solution at pH 7 as described in chapter three (section 3.3.6.2). This step was done in order to identify the metal species that are released due to a change in the ionic strength of a medium. The carbonate fraction extraction step involved leaching of Secunda fresh fly ash and the weathered fly ash from Secunda core using 1M ammonium acetate buffer solution at pH 5 as described in chapter three (section 3.3.6.3). This step was done in order to identify the metal species that are released as pH decreases, as species associated with this fraction are pH sensitive. This step was performed to mimic the results of exposure of the ash dam to lower pH than normal rain water, which may result from acid rain ingress into the ash dam. The Fe & Mn fraction extraction step involved leaching of Secunda fresh fly ash and the weathered fly ash from Secunda core using 1 M hydroxylamine hydrochloride in 0.025 M nitric acid solution as described in chapter three (section 3.3.6.4). This step was done in order to identify the metal species that are released due to increasing oxidising or reducing conditions in the environment. In

the determination of the residual fraction, the solid residue recovered from Fe & Mn fraction for Secunda fresh fly ash and the weathered fly ash from Secunda core was digested using a combination of acids ($HClO_4$: HF: HNO_3) mixed in the ratio of 3:3:1 respectively as described in chapter three (section 3.3.6.5). This step was done in order to shed light on the quantity of metal species left behind after the four extraction steps (i.e. water soluble, exchangeable, carbonate and Fe & Mn). For the raw data results of the sequential extraction procedure for each fraction as a function of depth, the reader is referred to Appendix 5, 6, 7, 8 and 9 for the water soluble fraction, exchangeable fraction, carbonate fraction, Fe & Mn fraction and residual fraction respectively.

According to Tessier et al., (1979), different elements tend to show association or preference to specific geochemical phases or physico-chemical fractions. In this section, each of the five physico-chemical fractions i.e. water soluble fraction, exchangeable fraction, carbonate fraction, iron and manganese fraction and residual fraction has been expressed as a percentage of the total metal content (TMC) for that element in ash as obtained by acid digestion and ICP analysis (Figure 32). The total metal content data obtained by acid digestion and ICP analysis were preferred over the XRF data (Table 8) for consistency reasons, since the procedure used in the total metal content determination and that used in the determination of the residual fraction were similar. The data presented in this section is averaged across the whole weathered Secunda core S2 (n = 35). Generally, all the elements showed the highest proportion in association with the residual fraction which involved acid digestion of the residue recovered after the four extraction steps. The distribution patterns of Si, Al, Ca, Na, Fe, Mg, K, Sr, Ba, Mn, As, Zn, Pb, Ni, Mo, Cr and Cu in the geochemical phases of Secunda fresh fly ash and the weathered fly ash from Secunda core are presented below. The discussion of the results for each element follows after the presentation of the figures.

5.2.1 Silicon and aluminium

Figure 33 shows the distribution patterns of Si and Al in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2.

Figure 33: Distribution patterns of Si and Al in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2 (WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, TMC = total metal content).

The distribution of Si content into the various geochemical phases as elucidated by the sequential extraction procedure for the different fly ash samples was as follows: for Secunda fresh fly ash: residual fraction (84.98 %, 195613.57 mg/kg)> iron and manganese fraction (5.88 %, 13545.89 mg/kg)> carbonate fraction (5.40 %, 12439.00 mg/kg)> water soluble fraction (0.53 %, 1217.26 mg/kg)> exchangeable fraction (0.02 %, 47.85 mg/kg), for weathered Secunda fly ash core: residual fraction (85.81 %, 180748.48 mg/kg)> carbonate fraction (6.36 %, 13398.28 mg/kg)> iron and manganese fraction (4.64 %, 9767.39 mg/kg)> water soluble fraction (0.66 %, 1391.38 mg/kg)> exchangeable fraction (0.34 %, 721.30 mg/kg).

For Al, the distribution into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh Secunda fly ash and the weathered Secunda fly ash was as follows: for Secunda fresh fly ash: residual fraction (84.99 %, 113902.99 mg/kg)> carbonate fraction (7.36 %, 9860.47 mg/kg)> iron and manganese fraction (6.21 %, 8328.45 mg/kg)> water soluble fraction (0.37 %, 495.52 mg/kg)> exchangeable fraction (0.03 %, 46.20 mg/kg), for weathered Secunda fly ash core: residual fraction (78.34 %, 103116.07 mg/kg)> iron and manganese fraction (7.20 %, 9472.38 mg/kg)> carbonate fraction (7.05 %, 9285.38 mg/kg)> water soluble fraction (0.42 %, 555.15 mg/kg)> exchangeable fraction (0.08 %, 104.52 mg/kg).

The release of Si and Al in the respective fractions was governed by the dissolution of the aluminosilicate fraction of the fly ash which forms the ash matrix. The dissolution of aluminosilicate minerals in fly ash is pH dependent and seems to occur significantly at low pH conditions (Roy & Griffin, 1984; Zevenbergen et al., 1999). It was evident that the extraction of Si and Al from the Fe & Mn fraction and carbonate fraction, which were extracted at lower pH resulted in higher release of Si and Al following the dissolution of the aluminosilicate ash matrix, compared to the exchangeable and water soluble fractions (Figure 33). The determination of the residual fraction which involved acid digestion that dissolved the ash matrix completely, showed that the bulk of Si and Al remained in the insoluble residue after other fractions had been released.

5.2.2 Calcium and sodium

Figure 34 shows the distribution patterns of Ca and Na in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2.

Figure 34: Distribution patterns of Ca and Na in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2 (WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, TMC = total metal content).

The distribution of Ca content into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh Secunda fly ash and the weathered Secunda fly ash was as follows: for Secunda fresh fly ash: residual fraction (84.97 %, 54462.22 mg/kg)> carbonate fraction (6.13 %, 3927.94 mg/kg)> iron and manganese fraction (3.36 %, 2152.95 mg/kg)> exchangeable fraction (2.18 %, 1399.64 mg/kg)> water soluble fraction (1.24 %, 792.11 mg/kg), for weathered Secunda fly ash core: residual fraction (86.86 %, 52136.87 mg/kg)> carbonate fraction (2.36 %, 1418.15 mg/kg)> iron and manganese fraction (1.76 %, 1053.71 mg/kg)> exchangeable fraction (0.85 %, 512.91 mg/kg)> water soluble fraction (0.68 %, 409.94 mg/kg). There was more Ca release in the carbonate fraction than the water soluble and exchangeable fractions (Figure 34). This observation can be attributed to the dissolution of calcite mineral ($CaCO_3$) which is mainly associated with the carbonate fraction in the fly ash (Johnson et al., 1995; Iwashita et al., 2005). The XRD analysis (Figure 12) had shown the presence of this mineral in the weathered fly ash.

The distribution of Na content into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh Secunda fly ash and the weathered Secunda fly ash was as follows: for Secunda fresh fly ash: residual fraction (84.76 %, 14021.82 mg/kg)> water soluble fraction (9.78 %, 1618.30 mg/kg)> iron and manganese fraction (2.44 %, 404.45 mg/kg)> carbonate fraction (1.25 %, 207.30 mg/kg)> exchangeable fraction (0.09 %, 14.43 mg/kg), for weathered Secunda fly ash core: residual fraction (87.84 %, 15254.86 mg/kg)> water soluble fraction (10.35 %, 1797.92 mg/kg)> exchangeable fraction (0.81 %, 140.85 mg/kg)> carbonate fraction (0.43 %, 74.68 mg/kg)> iron and manganese fraction (0.27 %, 47.57 mg/kg). A significant proportion of the total Na in the ash was released in the water soluble fraction (Figure 34). A proportion of the total Na exists as soluble salts on the surface of fly ash particles and its leaching behaviour is not pH dependent (Warren & Dudas, 1984; Tiruta-Barna et al., 2004). Na salts pose a major environmental challenge due to their high solubility in the ash dam. Olufunke (2010) carried out sequential extraction studies on weathered fly ash obtained from Taaibos and Highveld power stations which practiced wet ash handling system and found that Na was associated with the water soluble fraction

phase showing its presence in readily soluble forms. Nevertheless, most of the Na was associated with the mineral phases remaining in the residue after extraction (Figure 34). This indicates that Na is mainly present in fly ash not as a salt but as a component of insoluble mineral phases. This would imply that most of the Na in the residue of the fly ash was part of the original mineral phases in the fly ash and highly unlikely to have originated from the brine salts. It is noteworthy that as shown in Figure 21 (section 4.4.1.2) by XRF analysis there was no significant enrichment of Na along the weathered Secunda core compared to the fresh Secunda ash considering the volume of brine that went through the ash dam over the 20 year period, estimated at 117.65 billion litres of brine carrying with it an estimated 277 million kg of Na salt.

5.2.3 Iron, magnesium and potassium

Figure 35 shows the distribution patterns of Fe, Mg and K in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2.
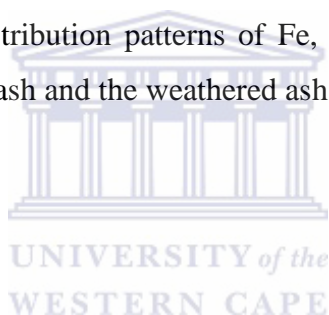
Figure 35: Distribution patterns of Fe, Mg and K in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2 (WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, TMC = total metal content).

112

The observed enrichment of Fe, Mg and K in the weathered Secunda core compared to the fresh Secunda ash as shown by the TMC values (Figure 35) agreed with the XRF data which showed the enrichment of Fe, Mg and K in the weathered Secunda core compared to the fresh Secunda ash (Figure 22).

The distribution of Fe content into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh Secunda fly ash and the weathered Secunda fly ash was as follows: for Secunda fresh fly ash: residual fraction (84.75 %, 13453.27 mg/kg)> iron and manganese fraction (12.58 %, 1996.23 mg/kg)> carbonate fraction (1.20 %, 189.70 mg/kg)> exchangeable fraction (0.34 %, 53.79 mg/kg)> water soluble fraction (0.04 %, 5.61 mg/kg), for weathered Secunda fly ash core: residual fraction (84.95 %, 20049.98 mg/kg)> iron and manganese fraction (4.98 %, 1174.74 mg/kg)> carbonate fraction (1.07 %, 253.59 mg/kg)> exchangeable fraction (0.83 %, 195.82 mg/kg)> water soluble fraction (0.06 %, 13.10 mg/kg). The significant proportion of the total Fe released in the iron and manganese fraction (Figure 35) may be due to the dissolution of $Fe(OH)_3$ in the fly ash (Garavaglia & Caramuscio, 1994), which is pH dependant.

For Mg, the distribution into the various geochemical phases as elucidated by the sequential extraction procedure for the different fly ash samples was as follows: for Secunda fresh fly ash: residual fraction (84.77 %, 7423.67 mg/kg)> iron and manganese fraction (7.46 %, 653.33 mg/kg)> exchangeable fraction (2.87 %, 251.11 mg/kg)> carbonate fraction (2.31 %, 202.16 mg/kg)> water soluble fraction (0.23 %, 20.34 mg/kg), for weathered Secunda fly ash core: residual fraction (84.60 %, 13491.89 mg/kg)> iron and manganese fraction (4.51 %, 719.23 mg/kg)> exchangeable fraction (1.89 %, 301.77 mg/kg)> carbonate fraction (1.36 %, 216.71 mg/kg)> water soluble fraction (1.22 %, 193.92 mg/kg). Mg reported significant release in the iron and manganese fraction though it was also present in the carbonate, exchangeable and water soluble fractions (Figure 35). The presence of Mg in association with the carbonate fraction may be due to the dissolution of dolomite $[CaMg(CO_3)_2]$ in the fly ash (Garavaglia & Caramuscio, 1994). Though dolomite was not detected in the XRD results as it

may have been in an amorphous state, the XRF results showed significant quantities of Ca and Mg in the fly ash which are associated with this mineral.

For K, the distribution into the various geochemical phases as elucidated by the sequential extraction procedure for the different fly ash samples was as follows: for Secunda fresh fly ash: residual fraction (84.99 %, 6788.12 mg/kg)> exchangeable fraction (6.43 %, 513.61 mg/kg)> water soluble fraction (4.45 %, 355.22 mg/kg)> carbonate fraction (1.85 %, 147.47 mg/kg)> iron and manganese fraction (1.23 %, 98.03 mg/kg), for weathered Secunda fly ash core: residual fraction (86.66 %, 7339.39 mg/kg)> water soluble fraction (2.31 %, 195.29 mg/kg)> exchangeable fraction (1.65 %, 140.01 mg/kg)> iron and manganese fraction (0.61 %, 51.28 mg/kg)> carbonate fraction (0.60 %, 50.86 mg/kg). A considerable proportion of the total amount of K in the fly ash was present in the water soluble and exchangeable fractions (Figure 35). K exists as soluble salts on fly ash particles and may be released upon contact of the fly ash with water (Warren & Dudas, 1984; Tiruta-Barna et al., 2004).

5.2.4 Strontium and barium

Figure 36 shows the distribution patterns of Sr and Ba in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2.
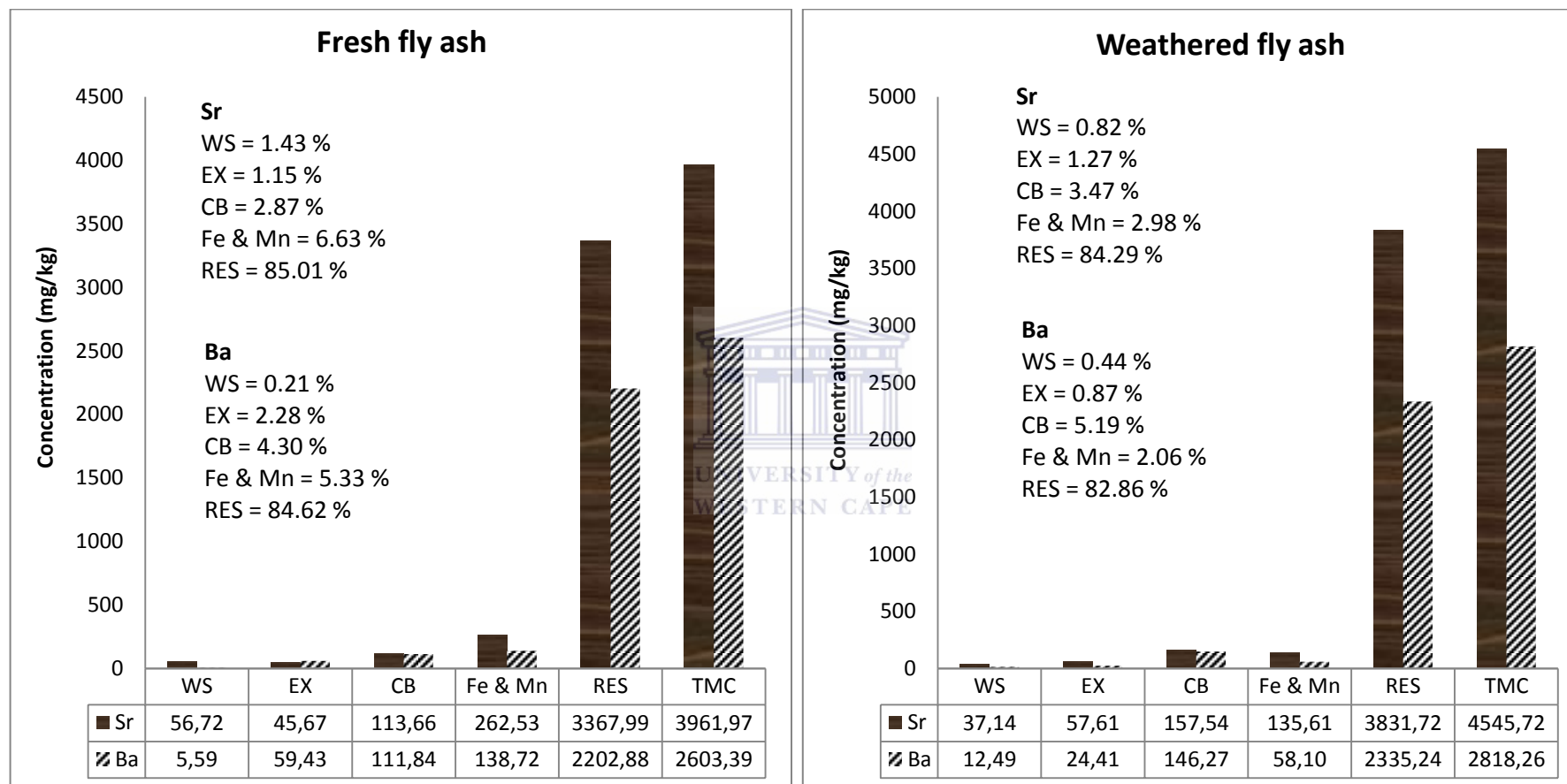
Figure 36: Distribution patterns of Sr and Ba in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2 (WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, TMC = total metal content).

The distribution of Sr content into the various geochemical phases as elucidated by the sequential extraction procedure for the different fly ash samples was as follows: for Secunda fresh fly ash: residual fraction (85.01 %, 3367.99 mg/kg)> iron and manganese fraction (6.63 %, 262.53 mg/kg)> carbonate fraction (2.87 %, 113.66 mg/kg)> water soluble fraction (1.43 %, 56.72 mg/kg)> exchangeable fraction (1.15 %, 45.67 mg/kg), for weathered Secunda fly ash core: residual fraction (84.29 %, 3831.72 mg/kg)> carbonate fraction (3.47 %, 157.54 mg/kg)> iron and manganese fraction (2.98 %, 135.61 mg/kg)> exchangeable fraction (1.27 %, 57.61 mg/kg)> water soluble fraction (0.82 %, 37.14 mg/kg).

For Ba, the distribution into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh Secunda fly ash and the weathered Secunda fly ash was as follows: for Secunda fresh fly ash: residual fraction (84.62 %, 2202.88 mg/kg)> iron and manganese fraction (5.33 %, 138.72 mg/kg)> carbonate fraction (4.30 %, 111.84 mg/kg)> exchangeable fraction (2.28 %, 59.43 mg/kg)> water soluble fraction (0.21 %, 5.59 mg/kg), for weathered Secunda fly ash core: residual fraction (82.86 %, 2335.24 mg/kg)> carbonate fraction (5.19 %, 146.27 mg/kg)> iron and manganese fraction (2.06 %, 58.10 mg/kg)> exchangeable fraction (0.87 %, 24.41 mg/kg)> water soluble fraction (0.44 %, 12.49 mg/kg). Considerable proportions of the total Sr and Ba in the fly ash were significantly released in the Fe & Mn and carbonate fractions at lower pH (Figure 36). According to Choi et al., (2002), coal fly ash particles either adsorb elements on their surfaces or trap them in the glass aluminosilicate fraction. Consequently, the dissolution of the aluminosilicate fraction may be responsible for the release of minor and trace elements previously trapped in it. The proportions of Sr and Ba released in the Fe & Mn and carbonate fractions may have been previously trapped in the aluminosilicate ash matrix which then led to their release at lower pH due to significant dissolution of the ash matrix.

5.2.5 Manganese and arsenic

Figure 37 shows the distribution patterns of Mn and As in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2.
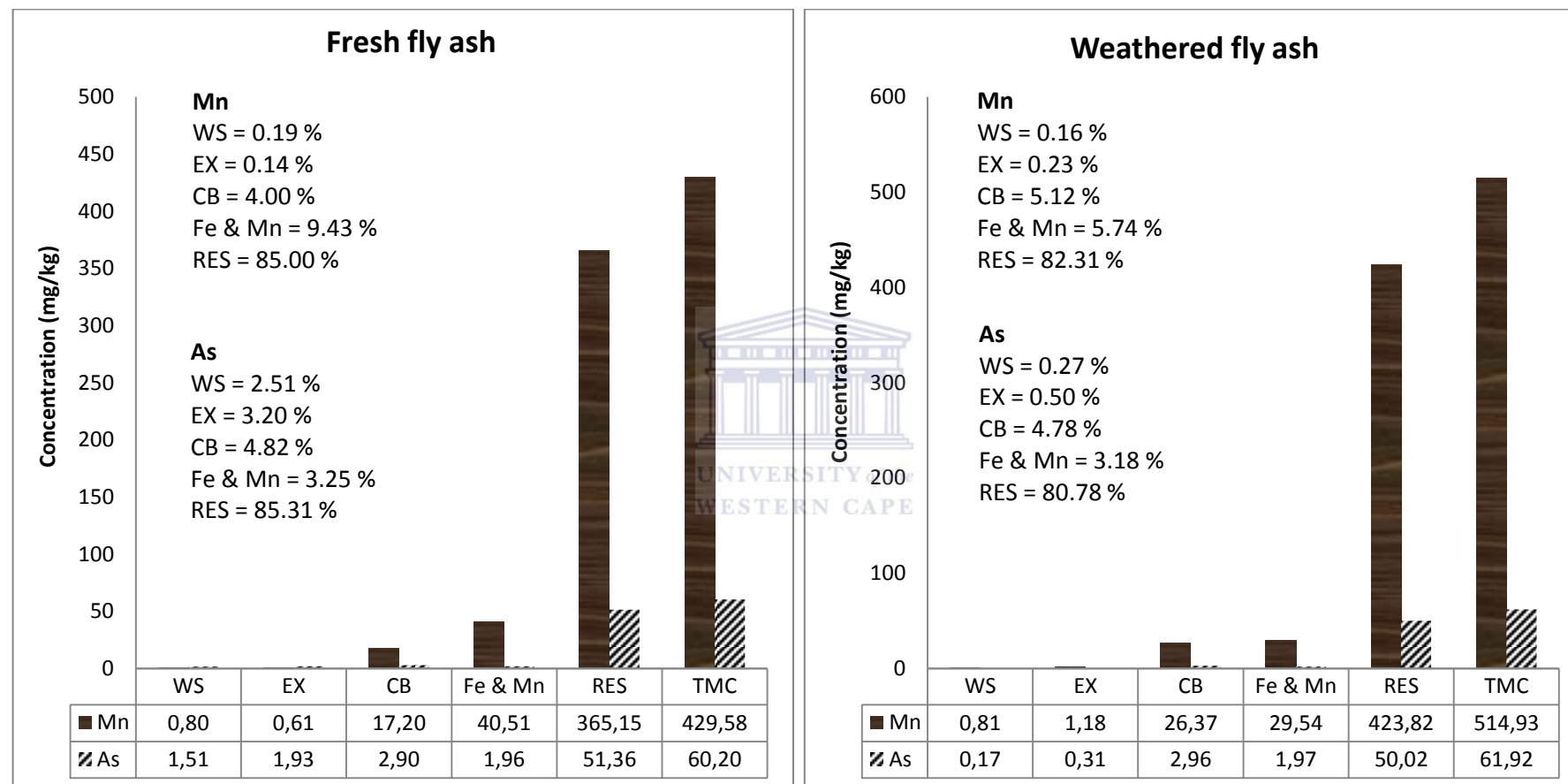
Figure 37: Distribution patterns of Mn and As in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2 (WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, TMC = total metal content).

The observed enrichment of Mn and As in the weathered Secunda core compared to the fresh Secunda ash as shown by the TMC values (Figure 37) corresponded with the XRF data which showed the enrichment of Mn (Figure 24) and As (Figure 28) in the weathered Secunda core compared to the fresh Secunda ash.

The distribution of Mn content into the various geochemical phases as elucidated by the sequential extraction procedure for the different fly ash samples was as follows: for Secunda fresh fly ash: residual fraction (85.00 %, 365.15 mg/kg)> iron and manganese fraction (9.43 %, 40.51 mg/kg)> carbonate fraction (4.00 %, 17.20 mg/kg)> water soluble fraction (0.19 %, 0.80 mg/kg)> exchangeable fraction (0.14 %, 0.61 mg/kg), for weathered Secunda fly ash core: residual fraction (82.31 %, 423.82 mg/kg)> iron and manganese fraction (5.74 %, 29.54 mg/kg)> carbonate fraction (5.12 %, 26.37 mg/kg)> exchangeable fraction (0.23 %, 1.18 mg/kg)> water soluble fraction (0.16 %, 0.81 mg/kg).

The distribution of As content into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh Secunda fly ash and the weathered Secunda fly ash was as follows: for Secunda fresh fly ash: residual fraction (85.31 %, 51.36 mg/kg)> carbonate fraction (4.82 %, 2.90 mg/kg)> iron and manganese fraction (3.25 %, 1.96 mg/kg)> exchangeable fraction (3.20 %, 1.93 mg/kg)> water soluble fraction (2.51 %, 1.51 mg/kg), for weathered Secunda fly ash core: residual fraction (80.78 %, 50.02 mg/kg)> carbonate fraction (4.78 %, 2.96 mg/kg)> iron and manganese fraction (3.18 %, 1.97 mg/kg)> exchangeable fraction (0.50 %, 0.31 mg/kg)> water soluble fraction (0.27 %, 0.17 mg/kg). A significant proportion of the total Mn in the fly ash was released in the Fe & Mn fraction. According to (Yuan, 2009), iron and manganese oxides act as scavengers for trace elements therefore the release of Mn and As observed in the Fe & Mn fraction (Figure 37) may have been due to the dissolution of these oxides. The dissolution of iron and manganese oxides may also affect the release of other toxic elements.

5.2.6 Zinc and lead

Figure 38 shows the distribution patterns of Zn and Pb in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2.
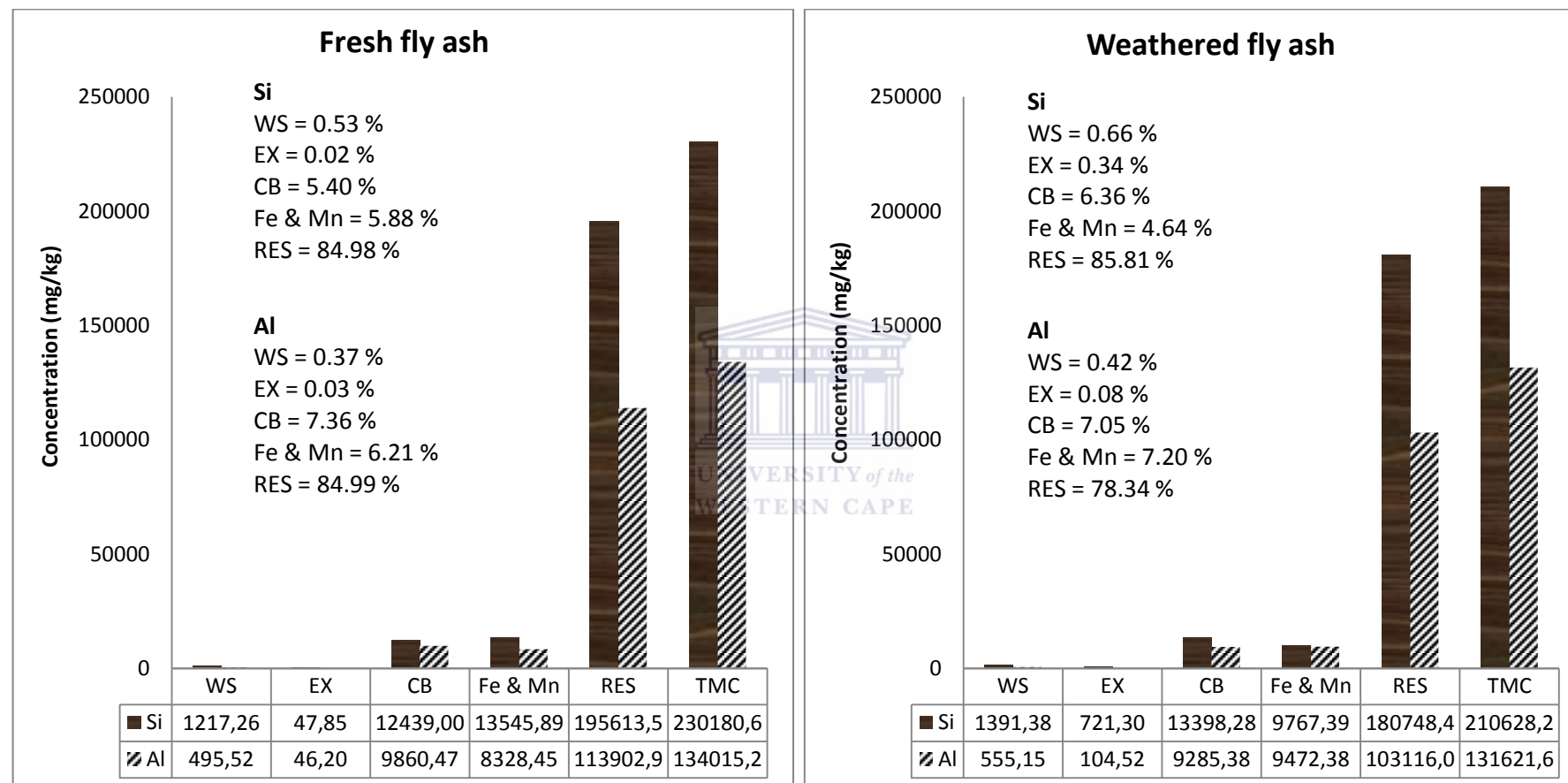
118
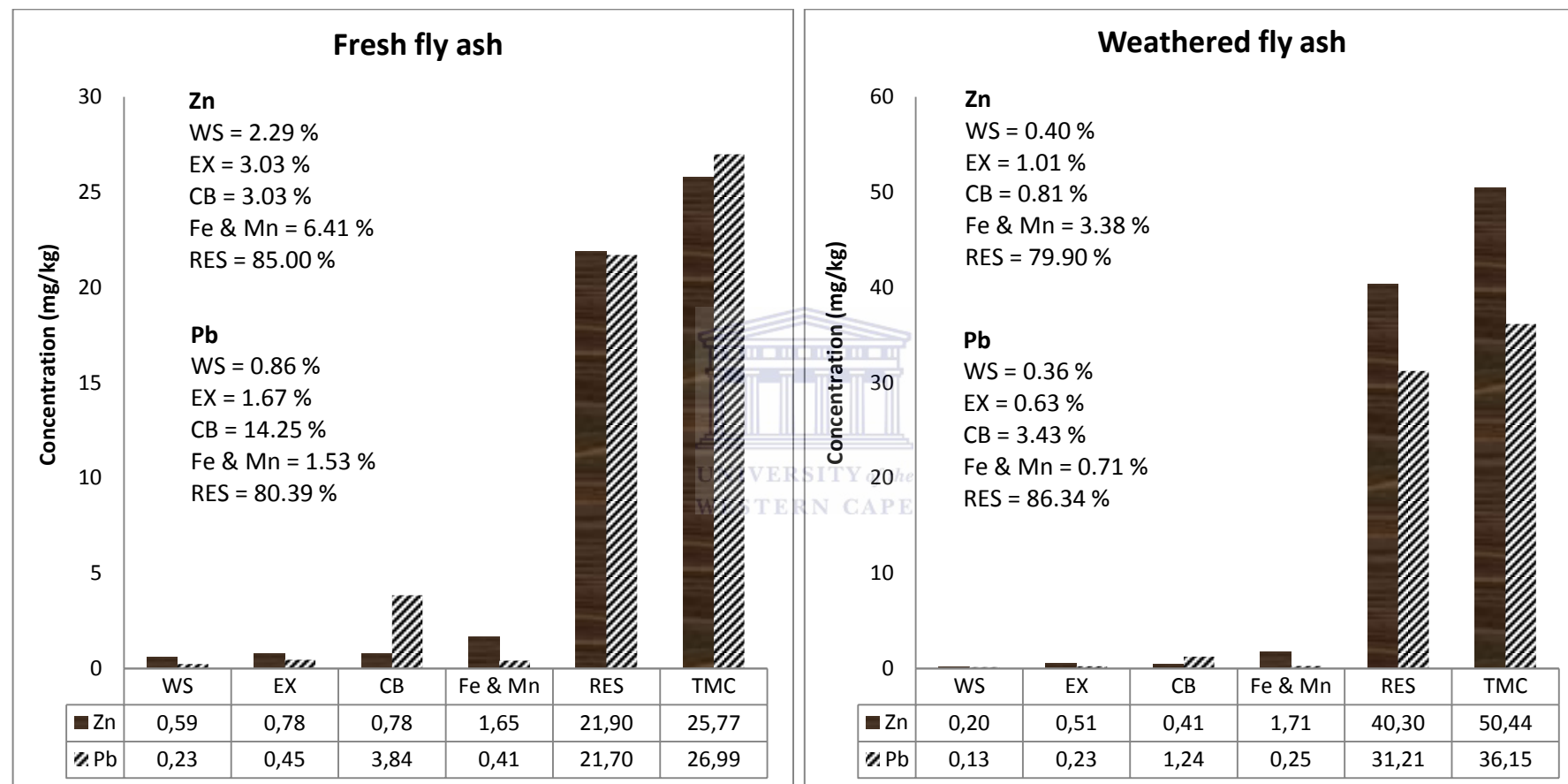
Figure 38: Distribution patterns of Zn and Pb in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2 (WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, TMC = total metal content).

119

The distribution of Zn content into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh fly ash and the weathered fly ash was as follows: for Secunda fresh fly ash: residual fraction (85.00 %, 21.90 mg/kg)> iron and manganese fraction (6.41 %, 1.65 mg/kg)> carbonate fraction (3.03 %, 0.78 mg/kg)> exchangeable fraction (3.03 %, 0.78 mg/kg)> water soluble fraction (2.29 %, 0.59 mg/kg), for weathered Secunda fly ash core: residual fraction (79.90 %, 40.30 mg/kg)> iron and manganese fraction (3.38 %, 1.71 mg/kg)> exchangeable fraction (1.01 %, 0.51 mg/kg)> carbonate fraction (0.81 %, 0.41 mg/kg)> water soluble fraction (0.40 %, 0.20 mg/kg).

For Pb, the distribution into the various geochemical phases as elucidated by the sequential extraction procedure for the different fly ash samples was as follows: for Secunda fresh fly ash: residual fraction (80.39 %, 21.70 mg/kg)> carbonate fraction (14.25 %, 3.84 mg/kg)> exchangeable fraction (1.67 %, 0.45 mg/kg)> iron and manganese fraction (1.53 %, 0.41 mg/kg)> water soluble fraction (0.86 %, 0.23 mg/kg), for weathered Secunda fly ash core: residual fraction (86.34 %, 31.21 mg/kg)> carbonate fraction (3.43 %, 1.24 mg/kg)> iron and manganese fraction (0.71 %, 0.25 mg/kg)> exchangeable fraction (0.63 %, 0.23 mg/kg)> water soluble fraction (0.36 %, 0.13 mg/kg). Considerable proportions of the total Zn and Pb in the fly ash were released in the Fe & Mn and carbonate fractions (Figure 38). According to Ward & French (2005), the glassy matrix within the fly ash is capable of adsorbing trace elements such as Zn and Pb. The release of these elements in the Fe & Mn and carbonate fractions may have been due to the progressive dissolution of the glassy aluminosilicate matrix which occurred at the lower pH associated with these fractions.

5.2.7 Nickel and molybdenum

Figure 39 shows the distribution patterns of Ni and Mo in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2.
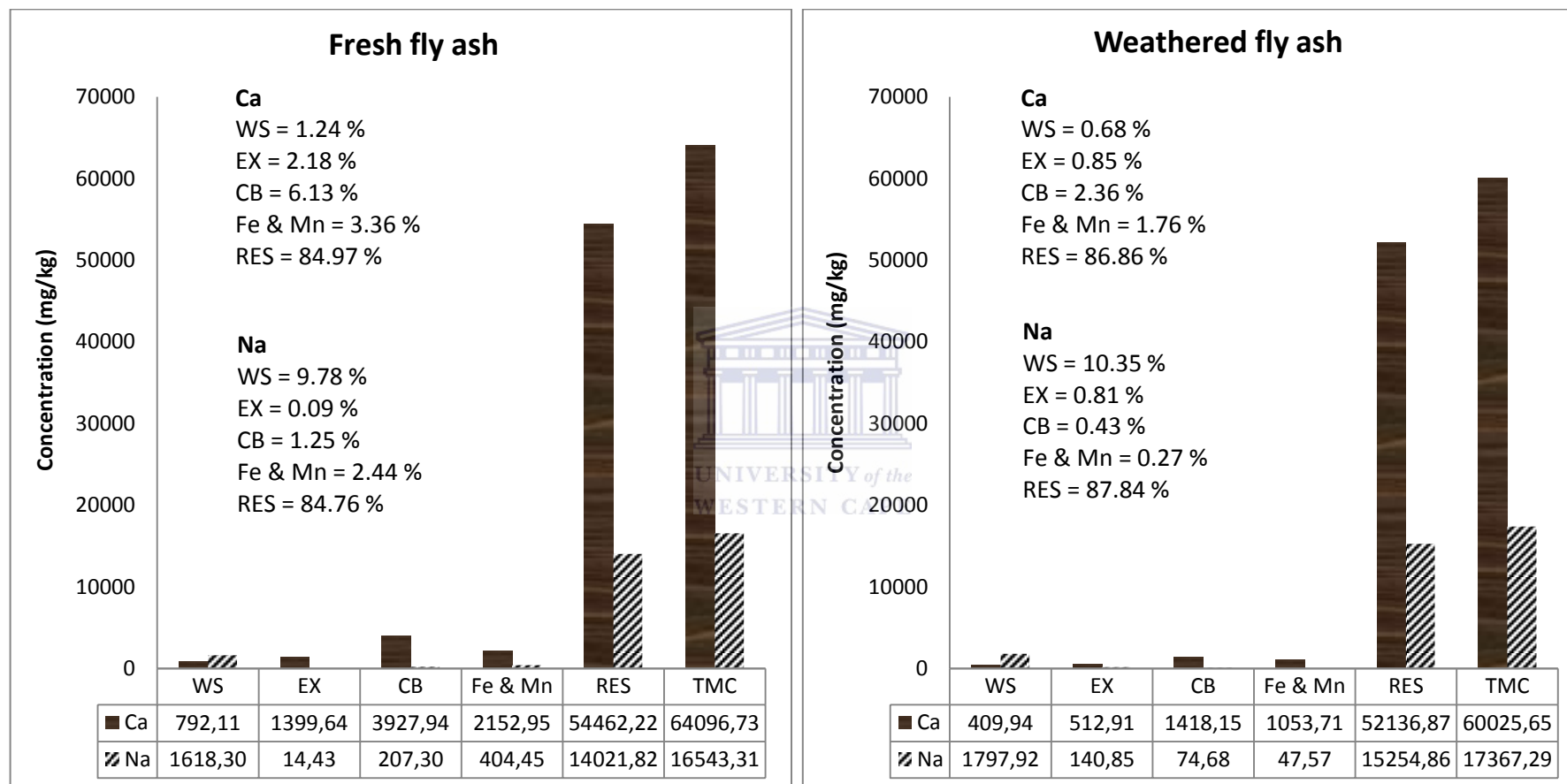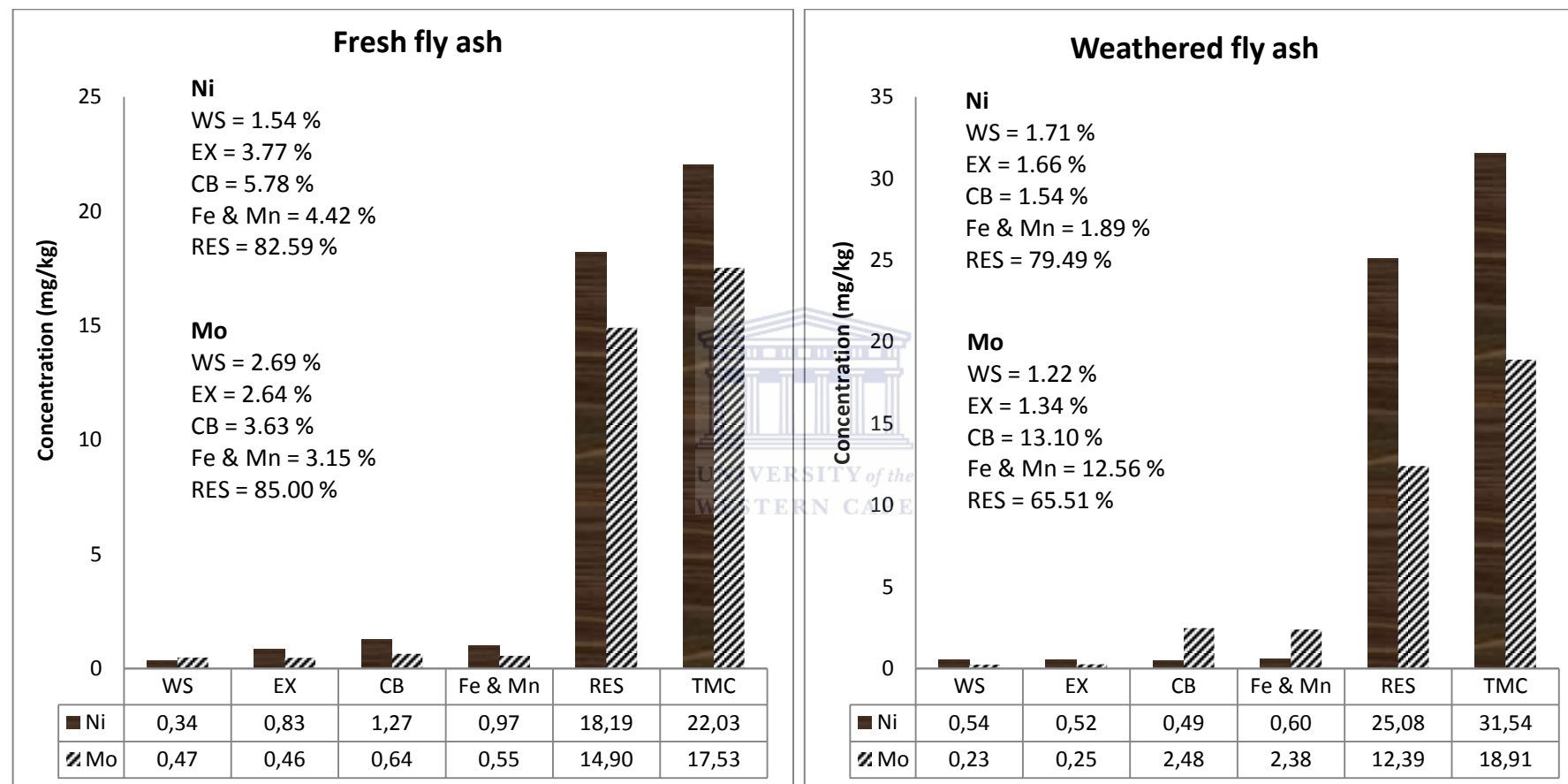
Figure 39: Distribution patterns of Ni and Mo in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2 (WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, TMC = total metal content).

The distribution of Ni content into the various geochemical phases as elucidated by the sequential extraction procedure for the different fly ash samples was as follows: for Secunda fresh fly ash: residual fraction (82.59 %, 18.19 mg/kg)> carbonate fraction (5.78 %, 1.27 mg/kg)> iron and manganese fraction (4.42 %, 0.97 mg/kg)> exchangeable fraction (3.77 %, 0.83 mg/kg)> water soluble fraction (1.54 %, 0.34 mg/kg), for weathered Secunda fly ash core: residual fraction (79.49 %, 25.08 mg/kg)> iron and manganese fraction (1.89 %, 0.60 mg/kg)> water soluble fraction (1.71 %, 0.54 mg/kg)> exchangeable fraction (1.66 %, 0.52 mg/kg)> carbonate fraction (1.54 %, 0.49 mg/kg).

For Mo, the distribution into the various geochemical phases as elucidated by the sequential extraction procedure for the different fly ash samples was as follows: for Secunda fresh fly ash: residual fraction (85.00 %, 14.90 mg/kg)> carbonate fraction (3.63 %, 0.64 mg/kg)> iron and manganese fraction (3.15 %, 0.55 mg/kg)> water soluble fraction (2.69 %, 0.47 mg/kg)> exchangeable fraction (2.64 %, 0.46 mg/kg), for weathered Secunda fly ash core: residual fraction (65.51 %, 12.39 mg/kg)> carbonate fraction (13.10 %, 2.48 mg/kg)> iron and manganese fraction (12.56 %, 2.38 mg/kg)> exchangeable fraction (1.34 %, 0.25 mg/kg)> water soluble fraction (1.22 %, 0.23 mg/kg). According to Marsh (1991), the release of trace elements such as Ni, Mo, Cr, Cu, Co and Zn is associated with the release of Al during weathering of the ash. The considerable proportions of the total Ni and Mo present in the fly ash released in the Fe & Mn and carbonate fractions (Figure 39) corresponded to considerable release of Al as was observed in the Fe & Mn and carbonate fractions (Figure 33) at low pH due to the dissolution of the aluminosilicate ash matrix.

5.2.8 Chromium and copper

Figure 40 shows the distribution patterns of Cr and Cu in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2.
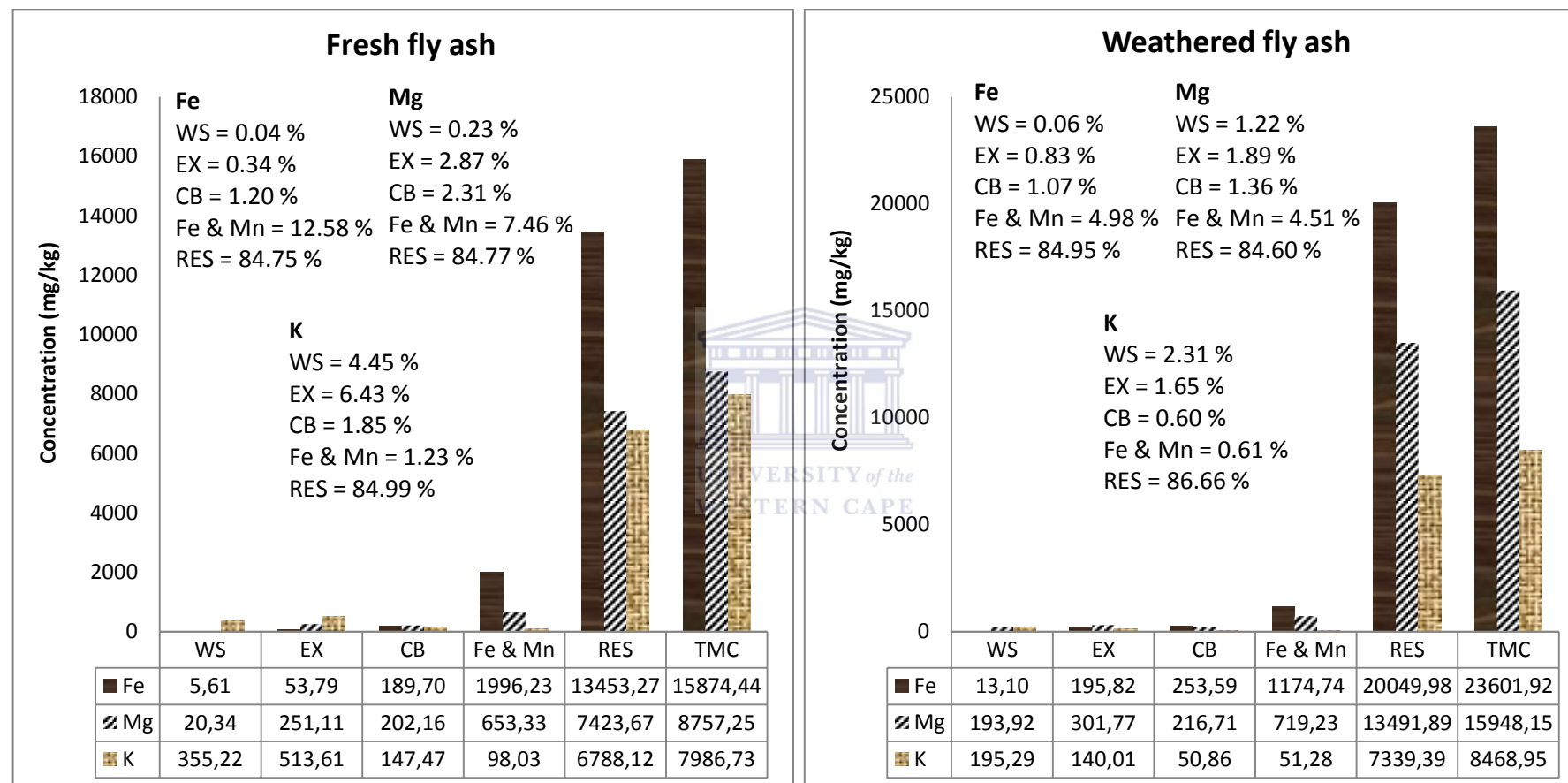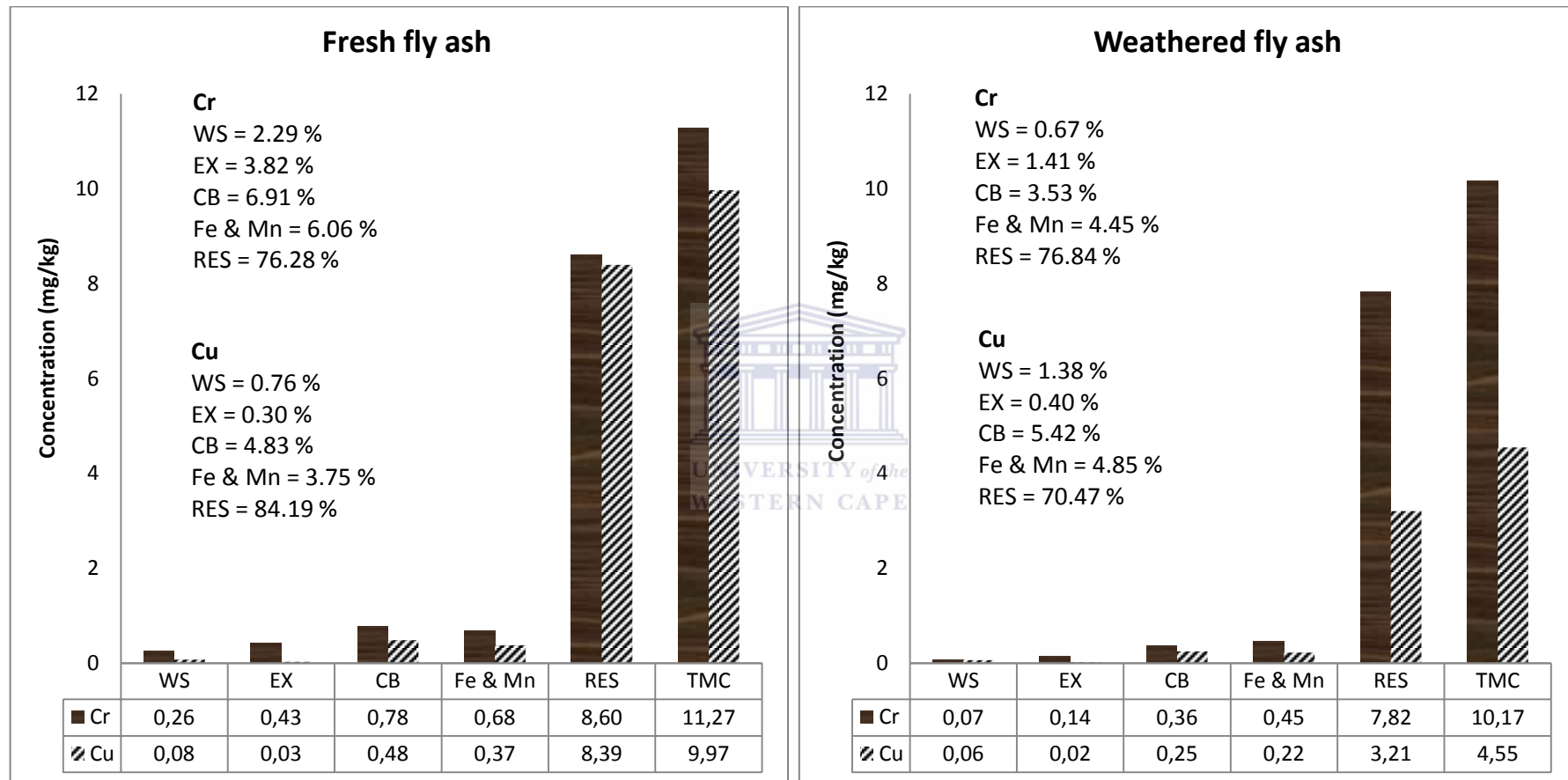
Figure 40: Distribution patterns of Cr and Cu in the geochemical phases of Secunda fresh ash and the weathered ash from Secunda core S2 (WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, TMC = total metal content).

The distribution of Cr content into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh fly ash and the weathered fly ash was as follows: for Secunda fresh fly ash: residual fraction (76.28 %, 8.60 mg/kg)> carbonate fraction (6.91 %, 0.78 mg/kg)> iron and manganese fraction (6.06 %, 0.68 mg/kg)> exchangeable fraction (3.82 %, 0.43 mg/kg)> water soluble fraction (2.29 %, 0.26 mg/kg), for weathered Secunda fly ash core: residual fraction (76.84 %, 7.82 mg/kg)> iron and manganese fraction (4.45 %, 0.45 mg/kg)> carbonate fraction (3.53 %, 0.36 mg/kg)> exchangeable fraction (1.41 %, 0.14 mg/kg)> water soluble fraction (0.67 %, 0.07 mg/kg).

The distribution of Cu content into the various geochemical phases as elucidated by the sequential extraction procedure for the fresh fly ash and the weathered fly ash was as follows: for Secunda fresh fly ash: residual fraction (84.19 %, 8.39 mg/kg)> carbonate fraction (4.83 %, 0.48 mg/kg)> iron and manganese fraction (3.75 %, 0.37 mg/kg)> water soluble fraction (0.76 %, 0.08 mg/kg)> exchangeable fraction (0.30 %, 0.03 mg/kg), for weathered Secunda fly ash core: residual fraction (70.47 %, 3.21 mg/kg)> carbonate fraction (5.42 %, 0.25 mg/kg)> iron and manganese fraction (4.85 %, 0.22 mg/kg)> water soluble fraction (1.38 %, 0.06 mg/kg)> exchangeable fraction (0.40 %, 0.02 mg/kg). The considerable release of Cr and Cu in the Fe & Mn and carbonate fractions at low pH may have been influenced by the release of Al (Marsh, 1991) as a result of the dissolution of the aluminosilicate ash matrix at the low pH associated with the Fe & Mn and carbonate fractions.

In conclusion, the sequential extraction of different elements showed that each element existed in association with various geochemical phases, and the proportion of each element associated with labile phases indicated a significant risk of leaching over time. The elements showed the highest concentration in the residual fraction. This step involved total digestion of the residue that was recovered after the four extraction steps. Si, Al, Sr and Ba showed more release from the Fe & Mn and carbonate fractions while Ca was released more from the carbonate fraction. A significant proportion of Na was present in the water soluble fraction while significant proportions of K and Mg were present in the water

soluble fraction and exchangeable fraction. Significant release of Fe and Mn was observed in the extracted Fe & Mn fraction, while significant proportions of all the trace elements As, Pb, Cr, Mo, Cu, Ni and Zn were released from the Fe & Mn fraction.

5.3 STATISTICAL ASSESSMENT OF DATA QUALITY FOR TOTAL METAL CONCENTRATION FOR THE MAJOR AND TRACE ELEMENTS (MASS BALANCE)

As an assessment of the accuracy of the sequential extraction procedure, the concentrations obtained from individual fractions for each element were summed up and compared with the total concentration (as obtained by acid digestion and ICP analysis) of that particular element (Tessier et al., 1979). This step has been described in chapter three (section 3.3.6.7). The variability between the sum of individual fractions and the total element concentration was calculated and is reported in the discussion below. This variability arises from element loss during filtering in the laboratory and is more likely to occur when working within small concentration ranges. The total metal content (TMC) data obtained by acid digestion and ICP analysis (Figure 32) were preferred over the XRF data (Table 8) for this section for consistency reasons, since the procedure used in the total metal content determination and that used in the determination of the residual fraction were similar.

5.3.1 Major elements

Table 9 shows the mean values of each major element leached out from the four extraction steps and the residual and total metal contents for Secunda fresh fly ash vs. weathered Secunda fly ash core samples. Table 9 also shows the accuracy level of the procedure used, as shown in the calculated variance values. The variance between the sum of the individual fractions and the TMC is as a result of element loss in the laboratory during filtering as earlier mentioned. The slight element loss as a result of filtering means that the weight of the dry solid sample leached in the exchangeable fraction was slightly less than the weight of the original sample leached in the water soluble fraction, while the weight of the dry solid sample leached in the carbonate fraction was slightly less than the weight of

the sample leached in the exchangeable fraction. The weight of the dry solid sample leached in the Fe & Mn fraction was slightly less than the weight of the sample leached in the carbonate fraction. This explanation accounts for the variance observed between the sum of the individual fractions and the TMC.

Table 9: Mass balance for the major elements in Secunda fresh fly ash vs. weathered fly ash from Secunda core S2

mg/kg	WS		EX		CB		Fe&Mn		RES		SUM		TMC		SUM= TMC VARIANCE (%)	
Majors	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered
Si	1217.26	1391.38	47.85	721.30	12439.00	13398.28	13545.89	9767.39	195613.57	180748.48	222863.57	206026.83	230180.67	210628.27	3.18	2.18
Al	495.52	555.15	46.20	104.52	9860.47	9285.38	8328.45	9472.38	113902.99	103116.07	132633.63	122533.51	134015.28	131621.69	1.03	6.90
Ca	792.11	409.94	1399.64	512.91	3927.94	1418.15	2152.95	1053.71	54462.22	52136.87	62734.86	55531.58	64096.73	60025.65	2.12	7.49
Na	1618.30	1797.92	14.43	140.85	207.30	74.68	404.45	47.57	14021.82	15254.86	16266.30	17315.88	16543.31	17367.29	1.67	0.30
Fe	5.61	13.10	53.79	195.82	189.70	253.59	1996.23	1174.74	13453.27	20049.98	15698.60	21687.24	15874.44	23601.92	1.11	8.11
Mg	20.34	193.92	251.11	301.77	202.16	216.71	653.33	719.23	7423.67	13491.89	8550.60	14923.53	8757.25	15948.15	2.36	6.42
K	355.22	195.29	513.61	140.01	147.47	50.86	98.03	51.28	6788.12	7339.39	7902.45	7776.83	7986.73	8468.95	1.06	8.17
Sr	56.72	37.14	45.67	57.61	113.66	157.54	262.53	135.61	3367.99	3831.72	3846.58	4219.61	3961.97	4545.72	2.91	7.17
Ba	5.59	12.49	59.43	24.41	111.84	146.27	138.72	58.10	2202.88	2335.24	2518.47	2576.52	2603.39	2818.26	3.26	8.58
Mn	0.80	0.81	0.61	1.18	17.20	26.37	40.51	29.54	365.15	423.82	424.26	481.72	429.58	514.93	1.24	6.45

WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, SUM = WS + EX + CB + Fe & Mn + RES, TMC = total metal content.

All the major elements had a variability of less than 10 % which affirmed the accuracy of the method used (Table 9). The close similarity between the sum of the individual fractions and the TMC data showed that the extraction experiments were performed correctly and that the data obtained were reliable.

The water soluble, exchangeable and carbonate fractions were singled out as the most vulnerable to leaching at the ash dam; together they were referred to as the labile phases. Table 10 shows the mean values of the quantity and the percentage of each major element leached out in the labile phases with respect to the sum of the individual fractions. The sum of the individual fractions as obtained by ICP analysis (i.e. the sum of water soluble, exchangeable, carbonate, Fe & Mn and residual fractions) was used in this calculation as opposed to the TMC in order to get a more accurate picture by eliminating the small variance error arising from element loss in the laboratory during filtering as earlier mentioned.

Table 10: Element leachability chart for the major elements in Secunda fresh fly ash vs. weathered fly ash from Secunda core S2

mg/kg	SUM		Labile phases		% Leached	
Majors	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered
Si	222863.57	206026.83	13704.12	15510.96	6.15	7.53
Al	132633.63	122533.51	10402.19	9945.05	7.84	8.12
Ca	62734.86	55531.58	6119.69	2341.00	9.75	4.22
Na	16266.30	17315.88	1840.03	2013.45	11.31	11.63
Fe	15698.60	21687.24	249.10	462.51	1.59	2.13
Mg	8550.60	14923.53	473.60	712.40	5.54	4.77
K	7902.45	7776.83	1016.30	386.16	12.86	4.97
Sr	3846.58	4219.61	216.05	252.28	5.62	5.98
Ba	2518.47	2576.52	176.86	183.18	7.02	7.11
Mn	424.26	481.72	18.61	28.36	4.39	5.89

SUM = WS + EX + CB + Fe & Mn + RES, Labile phases = WS + EX + CB

(WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction)

From Table 10 it can be seen that Na had the highest concentration leached out in the labile phases with 11.63 % from weathered Secunda fly ash core while Secunda fresh fly ash leached out 11.31 % of Na (Table 10). This highlights the ease at which Na can leach from the ash dam considering the effect of infiltrating rain water over time at the ash dam, thus Na shows no real accumulation in the disposed fly ash. However, all the major elements investigated showed the potential to leach. For the other major elements, the % leached out in the labile phases (Table 10) was as follows: for Secunda fresh fly ash: Si (6.15 %), Al (7.84 %), Ca (9.75 %), Fe (1.59 %), Mg (5.54 %), Sr (5.62 %), Ba (7.02 %), Mn (4.39 %); for weathered Secunda fly ash core: Si (7.53 %), Al (8.12 %), Ca (4.22 %), Fe (2.13 %), Mg (4.77 %), Sr (5.98 %), Ba (7.11 %), Mn (5.89 %). It is noteworthy that significant proportions of Si and Al, which are major components of the ash, were labile. This would imply the possible release of fairly large amounts of Si and Al from the ash dam over time considering that over 4 million tons of ash are dumped annually at Secunda according to Mahlaba et al., (2011a).

5.3.2 Trace elements

Table 11 shows the mean values of each trace element leached out from the four extraction steps and the residual and total metal contents for Secunda fresh fly ash vs. weathered Secunda fly ash core. The accuracy of the method used in terms of the calculated variance values is also shown.

Table 11: Mass balance for the trace elements in Secunda fresh fly ash vs. weathered fly ash from Secunda core S2

mg/kg	WS		EX		CB		Fe&Mn		RES		SUM		TMC		SUM= TMC VARIANCE (%)	
Traces	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered
As	1.51	0.17	1.93	0.31	2.90	2.96	1.96	1.97	51.36	50.02	59.65	55.42	60.20	61.92	0.91	10.48
Zn	0.59	0.20	0.78	0.51	0.78	0.41	1.65	1.71	21.90	40.30	25.71	43.12	25.77	50.44	0.24	14.50
Pb	0.23	0.13	0.45	0.23	3.84	1.24	0.41	0.25	21.70	31.21	26.63	33.07	26.99	36.15	1.30	8.54
Ni	0.34	0.54	0.83	0.52	1.27	0.49	0.97	0.60	18.19	25.08	21.61	27.22	22.03	31.54	1.90	13.71
Mo	0.47	0.23	0.46	0.25	0.64	2.48	0.55	2.38	14.90	12.39	17.02	17.72	17.53	18.91	2.89	6.26
Cr	0.26	0.07	0.43	0.14	0.78	0.36	0.68	0.45	8.60	7.82	10.75	8.84	11.27	10.17	4.65	13.11
Cu	0.08	0.06	0.03	0.02	0.48	0.25	0.37	0.22	8.39	3.21	9.35	3.75	9.97	4.55	6.17	17.49

WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction, SUM = WS + EX + CB + Fe & Mn + RES, TMC = total metal content.

Pb and Mo had variability of less than 10 % (Table 11). However, As, Zn, Ni, Cr and Cu reported variability of 10.48 %, 14.50 %, 13.71 %, 13.11 % and 17.49 % respectively for the weathered Secunda fly ash core (Table 11). The slightly higher variability observed for the trace elements compared to the major elements was expected due to the small concentration ranges involved with trace elements analysis. Table 12 shows the mean values of the quantity and the percentage of each trace element leached out in the labile phases with respect to the sum of the individual fractions.

Table 12: Element leachability chart for the trace elements in Secunda fresh fly ash vs. weathered fly ash from Secunda core S2

mg/kg	SUM		Labile phases		% Leached	
Traces	Fresh	Weathered	Fresh	Weathered	Fresh	Weathered
As	59.65	55.42	6.34	3.44	10.63	6.20
Zn	25.71	43.12	2.15	1.12	8.37	2.59
Pb	26.63	33.07	4.53	1.60	17.00	4.83
Ni	21.61	27.22	2.44	1.55	11.31	5.68
Mo	17.02	17.72	1.57	2.96	9.22	16.71
Cr	10.75	8.84	1.47	0.57	13.65	6.45
Cu	9.35	3.75	0.59	0.33	6.27	8.72

SUM = WS + EX + CB + Fe & Mn + RES, Labile phases = WS + EX + CB

(WS = water soluble fraction, EX = exchangeable fraction, CB = carbonate fraction, Fe & Mn = iron and manganese fraction, RES = residual fraction)

The % leached out in the labile phases for the trace elements (Table 12) was as follows: for Secunda fresh fly ash: As (10.63 %), Zn (8.37 %), Pb (17.00 %), Ni (11.31 %), Mo (9.22 %), Cr (13.65 %), Cu (6.27 %); for weathered Secunda fly ash core: As (6.20 %), Zn (2.59 %), Pb (4.83 %), Ni (5.68 %), Mo (16.71 %), Cr (6.45 %), Cu (8.72 %). Other trace elements present in the fly ash and detected by XRF such as Ti, Th, Zr, Ce, Y, Nb, Co, Rb, V and U (Table 8) were not included

in this section of the results because they were not analysed by the ICP-OES due to budgetary constraints.

5.4 SECTION SUMMARY

This chapter has shown the leaching potential, the chemical partitioning and mineralogical phase association of each element in the fly ash dumped at Sasol Secunda power station. It is evident that the pH of the fly ash influences the leaching patterns of the metal species. The different elements showed proportional association or fractionation between specific geochemical phases or physico-chemical fractions. Si, Al, Sr and Ba were mainly associated with the Fe & Mn and carbonate fractions compared to the exchangeable and water soluble fractions. Ca was mainly associated with the carbonate fraction than the other extraction steps. A significant proportion of Na was associated with the water soluble fraction while K and Mg were mainly associated with the water soluble and exchangeable fractions. Fe and Mn were mainly associated with the Fe & Mn fraction, while all the trace elements As, Pb, Cr, Mo, Cu, Ni and Zn were significantly leached from the Fe & Mn fraction showing their pH dependant nature. Na was the most labile among the major elements in the ash dam while Mo was the most labile element in the ash dam among the trace elements. The sequential extraction data presented in this chapter agreed with the XRF analysis findings presented in chapter four confirming that leaching is highly likely from the ash dam. For example, the total content of Na as determined by acid digestion and ICP analysis presented in this chapter showed 3.41 % (16,543.31 mg/kg) Na content in the fresh Secunda ash while the average Na content in the weathered Secunda core was 3.65 % (17,367.29 mg/kg), showing no sign of significant accumulation considering the large volumes of highly saline brine codisposed with the ash, much higher levels would have been expected. This observation was supported by XRF data presented in chapter four which demonstrated that Na content was 1.63 mass % in the fresh ash and remained below 2 mass % at most depths along the weathered core with no significant accumulation observed. The overall total salt capture capacity of Secunda ash dam was -0.01 weight % which meant that the ash dam was capable of releasing elements to the environment. The

wet ash handling system practiced at Sasol Secunda station led to slightly higher concentrations of the total amount of Na contained in the disposed ash compared to the dry ash handling system practiced at Eskom's Tutuka station, but the accumulated Na was readily leached from the labile phases. The high volumes of brine passing through the ash dam at Secunda would thus present a higher environmental impact than the Tutuka dry ash disposing method which involves small amounts of brine entering the ash dumps, considering that brine introduces some toxic elements into the fly ash during codisposal of the two wastes.

CHAPTER SIX

6. CONCLUSIONS AND RECOMMENDATIONS

This chapter summarizes the major findings obtained from this study and also gives recommendations for further work.

6.1 GENERAL CONCLUSIONS

The aim of this study was to investigate and understand the chemical, physical, morphological and mineralogical characteristics of Secunda fly ash co-disposed with brine in a wet disposal method, in order to evaluate the weathering patterns and mobility of metal species so at to establish if the ash dam could act as a salt sink.

This study showed that the fly ash generated at Sasol Secunda power station could not be used as a long term sustainable salt sink.

According to the chemical composition, the Secunda fly ash was classified as class F based on the sum of the oxides of silicon, aluminium and iron by mass and the CaO content, and further classified as sialic and ferrocalsialic type highlighting the significant levels of Si, Al, Ca and Fe in the fly ash.

The mineralogy of Secunda fly ash showed that quartz, mullite and calcite were the dominant mineral phases in samples taken from Secunda weathered fly ash core while Secunda fresh fly ash contained quartz, mullite and lime.

The morphological properties of Secunda fly ash showed that weathering and leaching had occurred in the ash dam as revealed by the morphological changes of the ash which showed spherical particles with smooth outer surfaces for Secunda fresh ash, while the weathered Secunda ash core samples consisted of agglomerated, irregular particles appearing to be encrusted, etched and corroded.

134

The physico-chemical properties of Secunda fly ash showed that the pH in the ash dam lowered over time and this coupled with high moisture content led to the release of species from the ash dam through leaching.

The lower pH in the ash dam created an environment conducive to the release of species through leaching. Secunda fresh ash had a pH of 12.38 while the weathered Secunda ash core had an average pH of 10.04.

The disposed ash at Secunda ash dam lost ionic species as a result of leaching confirmed by a decrease in EC in the disposed ash compared to the fresh ash, despite the EC measurement for the fresh ash and the weathered ash being conducted under the same conditions. While Secunda fresh ash had EC value of 4.98 mS/cm, the weathered Secunda ash core had an average EC value of 1.08 mS/cm.

Secunda ash dam was very damp with high moisture content averaging 54.2 % that created favourable conditions for the leaching of species in the ash dam as well as possible slumping of the dam due to the high water content.

This study showed that pH plays an important role in the mobility patterns of the various species in the ash dam. The decrease in pH in the ash dam led to the progressive dissolution of the major aluminosilicate ash matrix which influenced the release of minor and trace elements into the pore water enhancing their mobility as the ash dam acidified over time.

The high moisture content and periodic dissolution and precipitation of transient mineral phases in the disposed fly ash may have influenced the mobility patterns of elements. It also appears that contact of the disposed fly ash with pore water entrapped in the pore spaces of the ash particles may have led to rapid flushing and subsequent leaching of some elements in the ash dam.

This study revealed that the major and trace elements contained in both Secunda fresh fly ash and the disposed Secunda weathered fly ash could leach upon exposure to different environmental conditions. The elements showed different association with five geochemical phases i.e. water soluble fraction, exchangeable

fraction, carbonate fraction, Fe & Mn fraction and residual fraction. The labile phases consisted of the water soluble fraction, exchangeable fraction and carbonate fraction. Na was the most labile among the major elements in the ash dam while Mo was the most labile among the trace elements.

According to the mobility patterns of the different elements along the ash dam, brine codisposal may have been responsible for the slight enrichment of some species e.g. Mg, K, SO_4^{2-} and Na in the disposed Secunda weathered fly ash. However, there was no significant accumulation of the various species in the disposed fly ash despite continuous addition of an estimated 117.65 billion litres of brine over the 20 year period that the dam existed. Furthermore, Secunda ash dam showed an overall total salt capture capacity of only -0.01 weight % indicating that the ash dam was incapable of holding salts and would release elements to the environment over the lifetime of the dam.

The wet ash handling system of codisposing fly ash with brine as a slurry led to a slightly higher salt load in the disposed ash compared to the dry ash handling system. Although both wet and dry ash disposal systems were susceptible to leaching, the high moisture content associated with the wet ash handling system created an environment more conducive to the release of species in the disposed ash compared to the dry ash handling system. The high volumes of brine that passed through the ash dam in the wet ash handling system presented a greater environmental concern than the dry ash handling system which involved small amounts of brine entering the ash dumps, considering that brine introduced some toxic elements into the fly ash during codisposal of the two wastes. However, the wet ash handling system offered the advantage of dustless disposal while the dry ash handling system posed the danger of possible inhalation of toxic elements from the disposed fly ash as a result of wind-blown particulates.

6.2 RECOMMENDATIONS

It is necessary to thoroughly investigate the link between mineral phases and the various geochemical phases analysed so as to establish possible sinks for some of the species. Furthermore, geochemical modelling of the extracted pore water can

also be done in order to give an idea of the mineral phases likely to control some of the geochemical phases which in turn influence the mobility patterns of some of the species.

It is of absolute importance for South African power utilities to adopt better disposal methods that will minimize leaching of toxic elements from fly ash after the disposal process. The construction of some form of lining on the ground level before the dumping begins may minimize the leaching of major and toxic elements, without the risk of diffusing toxic gases into the atmosphere due to accumulation. Investing more into research so as to come up with more utilization options for coal fly ash and brine is also crucial. This will convert the huge amount of waste into abundance of resource.

UNIVERSITY *of the*
WESTERN CAPE

REFERENCES

Al-Faifi, H., Al-Omran, A.M., Nadeem, M., El-Eter, A., Khater, H.A., El-Maghraby, S.E. (2010), "Soil deterioration as influenced by land disposal of reject brine from Salbukh water desalination plant at Riyadh, Saudi Arabia", *Desalination;* 250 (2), 479 - 484.

Ahmaruzzaman, M. (2010), "A review on the utilization of fly ash", *Progress in Energy and Combustion Science*; 36, 327 - 363.

Ahmed, M., Shayya, W.H., Hoey, D., Mahendran, D., Morris, A., Al-Handaly, J. (2000), "Use of evaporation ponds for brine disposal in desalination plants", *Desalination;* 130, 155 - 168.

Ahmed, M., Shayya, W.H., Hoey, D., Al-Handaly, J. (2001), "Brine disposal from reverse osmosis desalination plants in Oman and the United Arab Emirates", *Desalination*; 133, 135 - 147.

Ahmed, M., Al-Belushi, A., Al-Haddabi, M., Goosen, M.F.A., Thumarukudy, M.R., Hoey, D., Arakel, A. (2003), "Feasibility of salt production from inland RO desalination plant reject brine", *Desalination;* 158, 109 - 117.

Akinyemi, S.A., Akinlua, A., Gitari, W.M., Petrik, L.F. (2011a), "Mineralogy and mobility patterns of chemical species in weathered coal fly ash", *Energy Sources, Part A;* 33, 768 - 784.

Akinyemi, S.A. (2011b), "Geochemical and mineralogical evaluation of toxic contaminants mobility in weathered coal fly ash: as a case study, Tutuka dump site, South Africa", Ph.D. thesis submitted in the Department of Geology, University of the Western Cape.

Al-Agha, M.R., Mortaja, R.S. (2005), "Desalination in the Gaza Strip: drinking water supply and environmental impact", *Desalination;* 173, 157 - 171.

Alvarez-Ayuso, E., Querol, X., Tomas, A. (2006), " Environmental impact of a coal combustion-desulphurization plant: Abatement capacity of desulphurization process and environmental characterization of combustion by-products", *Chemosphere;* 65, 2009 - 2017.

Anshits, N.N., Mikhailova, O.A., Salanov, A.N., Anshits, A.G. (2010), "Chemical composition and structure of the shell of fly ash non-perforated cenospheres produced from the combustion of the Kuznetsk coal (Russia)", *Fuel;* 89, 1849 - 1862.

Arnal, J.M., Sancho, M., Iborra, I., Gozálvez, J.M., Santafé, A., Lora, J. (2005), "Concentration of brines from RO desalination plants by natural evaporation", *Desalination;* 182, 435 - 439.

Asif, M., Muneer, T. (2007), "Energy supply, its demand and security issues for developed and emerging economies", *Renewable and Sustainable Energy Reviews*; 11, 1388 - 1413.

ASTM C-618, American Society for Testing and Materials (1993), "Standard speciation for fly ash and raw or calcined natural pozzolan for uses as a mineral admixture in Portland cement concrete", American Society for Testing and Materials, Philadelphia, Pennsylvania.

Babajide, O., Petrik, L., Musyoka, N., Amigun, B., Ameer, F. (2010), "Use of coal fly ash as a catalyst in the production of biodiesel", *Petroleum & Coal;* 52 (4), 261 - 272.

Bandopadhyay, A.K. (2010), "A study on the abundance of quartz in thermal coals of India and its relation to abrasion index: Development of predictive model for abrasion", *International Journal of Coal Geology;* 84, 63 - 69.

Bayat, O. (1998), "Characterisation of Turkish fly ashes", *Fuel;* 77 (9/10), 1059 - 1066.

Benitez, F.J., Acero, J.L., Leal, A.I. (2003), "Purification of storage brines from the preservation of table olives", *Journal of Hazardous Materials;* B96, 155 - 169.

Bhattacharyya, S., Donahoe, R.J., Patel, D. (2009), "Experimental study of chemical treatment of coal fly ash to reduce the mobility of priority trace elements", *Fuel;* 88, 1173 - 1184.

Bogner, A., Jouneau, P.H., Thollet, G., Basset, D., Gauthier, C. (2007), "A history of scanning electron microscopy developments: Towards ''wet-STEM'' imaging", *Micron;* 38, 390 - 401.

Borm, P.J.A. (1997), "Toxicity and occupational health hazards of coal fly ash-A review of data and comparison to coal mine dust", *British Occupational Hygiene;* 41 (6), 659 - 676.

BP (2006), British Petroleum Statistical Review of World Energy, June 2006. Available at www.bp.com (Accessed on 24th February, 2011).

BP (2010), British Petroleum Statistical Review of World Energy, June 2010. Available at www.bp.com (Accessed on 24th February, 2011).

Bufflap, S.E., Allen, H.E. (1994), "Sediment pore water collection methods for trace metal analysis: A review", *Water Reserves;* 29 (1), 165 - 177.

Campbell, A.E. (1999), "Chemical, physical and mineralogical properties associated with the hardening of some South African fly ashes", M.Sc. thesis submitted in the Department of Geological Sciences, University of Cape Town.

Carlson, C.L., Adriano, D.C. (1993), "Environmental impacts of coal combustion residues", *Journal of Environmental Quality;* 22, 227 - 247.

Cheng, Z., Zheng, Y., Mortlock, R., Geen, A. (2004), "Rapid multi-element analysis of groundwater by high-resolution inductively coupled plasma mass spectrometry", *Anal Bioanal Chem;* 379, 512 - 518.

Choi, S.K., Lee, S., Song, Y.K., Moon, H.S. (2002), "Leaching characteristics of selected Korean fly ashes and its implications for the groundwater composition near the ash disposal mound", *Fuel;* 81, 1083 - 1090.

Czichos, H., Saito, T., Smith, L. (2006), "Springer Handbook of Materials Measurement Methods", Berlin, Germany.

Davis, B.H. (2003), "Fischer-Tropsch synthesis: relationship between iron catalyst composition and process variables", *Catalysis Today;* (84), 83 - 98.

DME (2006), Department of Minerals and Engineering, "Operating and Developing Coal Mines in the Republic of South Africa", Department of Minerals and Energy, Republic of South Africa.

Dutta, B.K., Khanra, S., Mallick, D. (2009), "Leaching of elements from coal fly ash: Assessment of its potential for use in filling abandoned coal mines", *Fuel;* 88, 1314 - 1323.

Dyk, J.C., Keyser, M.J., Coertzen, M. (2006), "Syngas production from South African coal sources using Sasol-Lurgi gasifiers", *International Journal of Coal Geology*; 65, 243 - 253.

Ecke, H., Menad, N., Lagerkvist, A. (2003), "Carbonation of MSWI fly ash and the impact on the metal mobility", *Journal of Environmental Engineering;* 129 (5), 435 - 440.

El-Manharawy, S., Hafez, A. (2001), "Water type and guidelines for RO system design", *Desalination;* 139, 97 - 113.

EPA (2001), U.S. Environmental Protection Agency, "Collection of interstitial water" in "Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses", Technical manual, Washington D.C, Office of Science and Technology, 208.

EPA (2004), U.S. Environmental Protection Agency, "Contaminated sediments science priorities", Science policy council, Washington D.C.

EPA (2009), U. S. Environmental Protection Agency Superfund Division, "Frequently Asked Questions Regarding the Disposal of Coal Ash at the Perry County Arrowhead Landfill Uniontown, Alabama".

Fatoba, O. (2010), "Chemical interactions and mobility of species in fly ash-brine co-disposal systems", Ph.D. thesis submitted in the Department of Chemistry, University of the Western Cape.

Fatoba, O. (2007), "Chemical compositions and leaching behaviour of some South African fly ashes", M.Sc. thesis submitted in the Department of Chemistry, University of the Western Cape.

Filgueiras, A.V., Lavilla, I., Bendicho, C. (2002), "Chemical sequential extraction for metal partitioning in environmental solid samples", *Journal of Environmental Monitoring;* 4, 823 - 857.

Fritz, J.S. (1977), "Applications of chromatography in the analysis of inorganic materials", *Pure and Applied Chemistry;* 49, 1547 - 1554.

Frynas, J.G., Paulo, M. (2007), "A New Scramble for African Oil? Historical, Political, and Business Perspectives", *Oxford Journals;* 106 (423), 229 - 251.

Garavaglia, R., Caramuscio, P. (1994), "Coal Fly-Ash Leaching Behaviour and Solubility Controlling Solids". In Goumans, J.M., Sloot, H.A., Aalbers, G. Editors, "Environmental Aspects of Construction with Waste Materials", Elsevier Science, Amsterdam.

Gasification World Database (2007), US Department of Energy, Office of Fossil Energy and National Energy Technology Laboratory.

Gitari, W.M., Petrik, L.F., Etchebers, O., Key, D.L., Okujeni, C. (2008), "Utilization of fly ash for treatment of coal mines wastewater: Solubility controls on major inorganic contaminants", *Fuel;* 87, 2450 - 2462.

Goldemberg, J. (2006), "The promise of clean energy", *Energy Policy*; 34, 2185 - 2190.

Goldstein, J., Newbury, D., Joy, D., Lyman, C., Echlin, P., Lifshin, E., Sawyer, L., Michael, J. (2003), "Scanning electron microscopy and X-ray microanalysis", Third edition, Kluwer academic/plenum publishers, New York.

Grisafe, D.A., Angino, E.E., Smith, S.M. (1988), "Leaching characteristics of a high-calcium fly ash as a function of pH: a potential source of selenium toxicity", *Applied Geochemistry;* 3, 601 - 608.

Holloway, P., Vaidyanathan, P.N. (2009), "Characterization of Metals and Alloys", Materials characterization, Momentum Press Publishers.

Hui, K.S., Chao, C.Y.H., Kot, S.C. (2005), "Removal of mixed heavy metal ions in wastewater by zeolite 4A and residual products from recycled coal fly ash", *Journal of Hazardous Materials;* B127, 89 - 101.

Iwashita, A., Sakaguchi, Y., Nakajima, T., Takanashi, H., Ohki, A., Kambara, S. (2005), "Leaching characteristics of boron and selenium for various coal fly ashes", *Fuel;* 84, 479 - 485.

Jala, S., Goyal, D. (2006), "Fly ash as a soil ameliorant for improving crop production-A review", *Bioresource Technology;* 97, 1136 - 1147.

Jammet, H.P. (1961), "Radioactive pollution of the atmosphere", *Journal of Monograph series, World Health Organization;* 0512 - 3038, 381 - 432.

Jegadesaan, G., Al-Abed, S.R., Pinto P. (2008), "Influence of trace metal distribution on its leachability from coal fly ash", *Fuel;* 87, 1887 - 1893.

Johannsen, P., Karlapudi, R., Reinhold, G. (2006), "High pressure reverse osmosis for wastewater minimization and zero liquid discharge applications", *Desalination;* 199, 84 - 85.

Johnson, C.A., Brandenberger, S., Baccini, P. (1995), "Acid neutralization capacity of municipal waste incinerator bottom ash", *Environmental Science Technology;* 29, 142 - 147.

Jones, D.R. (1995), "The leaching of major and trace elements from coal ash" in "Environmental aspects of trace elements in coal", Kluwer Academic Publishers, Netherlands, 221 - 262.

Karbasi, M., Jahanparast, B., Shamsipur, M., Hassan, J. (2009), "Simultaneous trace multielement determination by ICP-OES after solid phase extraction with modified octadecyl silica gel", *Journal of Hazardous Materials;* 170, 151 - 155.

Kolbe, J.L., Lee, L.S., Jafvert, C.T., Murarka, I.P. (2011), "Use of Alkaline Coal Ash for Reclamation of a Former Strip Mine", World of Coal Ash (WOCA) Conference, May 9 - 12, Denver, Colorado, USA.

Kowarik, G., Brunmayr, M., Aumayr, F. (2009), "Electron emission from tungsten induced by slow, fusion-relevant ions", *Nuclear Instruments and Methods in Physics Research;* B 267, 2634 - 2637.

Leblanc, J., Akbarzadeh, A., Andrews, J., Lu, H., Golding, P. (2010), "Heat extraction methods from salinity-gradient solar ponds and introduction of a novel system of heat extraction for improved efficiency", *Solar Energy;* doi:10.1016/j.solener.2010.06.005.

Lenntech (2011), Water Treatment Solutions, Available at www.lenntech.com (Accessed on 28th July, 2011).

Levandowski, J., Kalkreuth, W. (2009), "Chemical and petrographical characterization of feed coal, fly ash and bottom ash from the Figueira Power Plant, Paraná, Brazil", *International Journal of Coal Geology;* 77, 269 - 281.

Lewis, A., Nathoo, J., Reddy, T., Randall, D., Zibi, L., Jivanji, R. (2010), "Novel technology for recovery of water and solid salts from hyper saline brines: Eutectic Freeze Crystallization", Water Research Commission (WRC) report.

Liu, G., Vassilev, S.V., Gao, L., Zheng, L., Peng, Z. (2005), "Mineral and chemical composition and some trace element contents in coals and coal ashes from Huaibei coal field, China", *Energy Conversion and Management;* 46, 2001 - 2009.

Lunderberg, J.M., Bartlett, R.J., Behm, A.M., Contreras, C., DeYoung, P.A., Hoogeveen, N.L., Huisman, A.J., Peaslee, G.F., Postma, J.K. (2008), "PIXE as a complement to trace metal analysis of sediments by ICP-OES", *Nuclear Instruments and Methods in Physics Research;* B266, 4782 - 4787.

Madzivire, G., Petrik, L.F., Gitari, W.M., Ojumu, T.V., Balfour, G. (2010), "Application of coal fly ash to circumneutral mine waters for the removal of sulphates as gypsum and ettringite", *Minerals Engineering;* 23, 252 - 257.

Marsh, J.S. (1991), "REE fractionation and Ce anomalies in weathered Karoo dolerite", *Chemical Geology;* 90, 189 - 194.

Martin, J.M., Nirel, P., Thomas, A.J. (1987), "Sequential Extraction Techniques: Promises and Problems", *Marine Chemistry;* 22, 313 - 341.

Mahlaba, J.S., Kearsley, E.P., Kruger, R.A. (2011a), "Physical, chemical and mineralogical characterisation of hydraulically disposed fine coal ash from Sasol Synfuels", *Fuel;* 90, 2491 - 2500.

Mahlaba, J.S., Kearsley, E.P., Kruger, R.A. (2011b), "Effect of fly ash characteristics on the behaviour of pastes prepared under varied brine conditions", *Minerals Engineering;* 24, 923 - 929.

May, J.C., Grim, E., Wheeler, R.M., West, J. (1982), "Determination of residual moisture in freeze-dried viral vaccines: Karl Fischer, gravimetric and thermogravimetric methodologies", *Journal of Biological Standardization;* 10 (3), 249 - 259.

McKaveney, J.P., Fassinger, W.P., Stivers, D.A. (1972), "Removal of heavy metals from water and brine using silicon alloys", *Environmental science and technology;* 6 (13), 1109 - 1113.

Minchener, A.J. (2005), "Coal gasification for advanced power generation", *Fuel;* 84, 2222 - 2235.

Mishra, D.P., Das, S.K. (2010), "A study of physico-chemical and mineralogical properties of Talcher coal fly ash for stowing in underground coal mines", *Materials characterization;* 61, 1252 - 1259.

Moitsheki, L.J., Matjie, R.H., Baran, A., Mooketsi, O.I., Schobert, H.H. (2010), "Chemical and mineralogical characterization of a South African bituminous coal and its ash, and effect on pH of ash transport water", *Minerals Engineering*; 23, 258 - 261.

Montes-Hernandez, G., Pérez-López, R., Renard, F., Nieto, J.M., Charlet, L. (2009), "Mineral sequestration of CO_2 by aqueous carbonation of coal combustion fly ash", *Journal of Hazardous Materials;* 161, 1347 - 1354.

Mooketsi, I.O., Ginster, M., Matjie, H.R., Riedel, J.K. (2007), "Leachate characteristics of ash residues from a laboratory scale brine encapsulation simulation process", World of Coal Ash (WOCA), Kentucky, USA.

Navarro, C.R., Agudo, E.R., Luque, A., Navarro, A.B.R., Huertas, M.O. (2009), "Thermal decomposition of calcite: Mechanisms of formation and textural evolution of CaO nanocrystals", *American Mineralogist;* 94, 578 - 593.

New Mexico State University (2006), Department of Chemistry and Biochemistry, available at http://www.chemistry.nmsu.edu/Instrumentation/IC.html (Accessed on 7th July, 2011).

Ngu, L., Wu, H., Zhang, D. (2007), "Characterization of Ash Cenospheres in Fly Ash from Australian Power Stations", *Energy Fuels;* 21 (6), 3437 - 3445.

Ninomiya, Y., Sato, A. (1997), "Ash melting behavior under coal gasification conditions", *Energy Conversion Management;* 38 (10 - 13), 1405 - 1412.

Nyambura, M.G., Mugera, G.W., Petrik, L.F., Ndungu P.G. (2011), "Carbonation of brine impacted fractionated coal fly ash: Implications for CO_2 Sequestration", *Journal of Environmental Management;* 92, 655 - 664.

Nyamhingura, A. (2009), "Characterization and Chemical Speciation Modelling of Saline Effluents at Sasol Synthetic Fuels Complex-Secunda and Tutuka Power Station", M.Sc. thesis submitted in the Department of Chemistry, University of the Western Cape.

Olesik, J.W., Kinzer, J.A., Harkleroad, B. (1994), "Inductively coupled plasma optical emission spectrometry using nebulizers with widely different sample consumption rates", *Analytical Chemistry;* 66, 2022 - 2030.

Olufunke, I.O. (2010), "Mineralogy and chemical mobility in a weathered ash dump site, South Africa", M.Sc. thesis submitted in the Department of Earth Sciences, University of the Western Cape.

Pandian, N.S. (2004), "Fly ash characterization with reference to geotechnical applications", *Indian Institute of Science;* 84, 189 - 216.

Peppas, T.K., Karfopoulos, K.L., Karangelos, D.J., Rouni, P.K., Anagnostakis, M.J., Simopoulos, S.E. (2010), "Radiological and instrumental neutron activation analysis determined characteristics of size-fractionated fly ash", *Journal of Hazardous Materials;* 181, 255 - 262.

Petrik, L.F., White, R.A., Klink, M.J., Somerset, V.S., Burgers, C.L., Fey, M.V. (2003), "Utilization of South African Fly Ash to Treat Acid Coal Mine Drainage, and Production of High Quality Zeolites from the Residual Solids", International Ash Utilization Symposium, October 20 - 22, Lexington, Kentucky, USA.

Petrik, L., Lewis, A.E., Hendry, B.A. (2007), "Brine treatment and disposal", Coaltech Report, South Africa.

Petrik, L., Gitari, W., Etchebers, O., Nel, J., Kumar, V.V.R., Fatoba, O., Nyamihingura, A., Akinyemi, S.A., Antonie, M.J. (2008), "Towards the development of sustainable salt sinks: Fundamental studies on the co-disposal of brines within inland ash dams", Sasol/Eskom phase one final report.

Petrik, L., Akinyeye, R.O., Gitari, W.M., Nel, J., Fatoba, O., Akinyemi, S.A., Eze, P., Nyale, S. (2010), "Towards the Development of Sustainable Salt Sinks: Fundamental Studies on the Co-Disposal of Brines within Inland Ash Dams", Sasol/Eskom phase two 6th Quarter interim report.

Piehler, G., El-baroudi, H., Brellenthin, J., Barry G.L. (1982), "Environmental Evaluation of Coal Combustion By-product Utilizations", *Resources and Conservation;* 9, 323 - 331.

Pluta, I., Zuber, A. (1995), "Origin of brines in the upper Silesian Coal Basin (Poland) inferred from stable isotope and chemical data", *Applied Geochemistry;* 10, 447 - 460.

Qdais, A. (1999), "Environmental impacts of desalination plants on the Arabian Gulf", IDA San Diego Proceedings, Volume III.

Querol, X., Moreno, N., Umańa, J.C., Alastuey, A., Hernández, E., López-Soler, A., Plana, F. (2002), "Synthesis of zeolites from coal fly ash: An overview", *International Journal of Coal Geology;* 50, 413 - 423.

Rao, C.P., Gluskoter, H.J. (1973), "Occurrence and distribution of minerals in Illinois coals", Illinois State Geological Survey, Circular 476.

Roy, R.W., Griffin, R.A. (1982), "A Proposed Classification System for Coal Fly Ash in Multidisciplinary Research", *Journal of Environmental Quality;* 11, 563 - 568.

Roy, W. R., Griffin, R.A. (1984), "Illinois basin coal fly ashes. 2. Equilibria relationships and quantitative modelling of ash-water reactions", *Environ. Sci. Technol;* 18 (10), 739 - 742.

Safer environment (2009), "Coal Ash Disposal becoming burning issue - Needs to be resolved in eco-friendly manner". Available at http://saferenvironment.wordpress.com (Accessed on 7th June, 2011).

Sarkar, A., Rano, R., Udaybhanu, G., Basu, A.K. (2006), "A comprehensive characterisation of fly ash from a thermal power plant in Eastern India", *Fuel Processing Technology;* 87, 259 - 277.

Sethi, S., Walker, S., Drewes, J., Xu, P. (2006), "Existing and emerging concentrate minimization & disposal practices for membrane systems", *Florida Water Resoures Journal;* 38 - 48.

Shafiee, S., Topal, E. (2009), "When will fossil fuel reserves be diminished?", *Energy Policy Journal*; 37, 181 - 189.

Shannon, R.D., White, J.R. (1991), "The selectivity of a sequential extraction procedure for the determination of iron oxyhydroxides and iron sulfides in lake sediments", *Biogeochemistry;* 14, 193 - 208.

Shaw, M.J., Haddad, P.R. (2004), "The determination of trace metal pollutants in environmental matrices using ion chromatography", *Environment International;* 30, 403 - 431.

Singh, G., Paul, B.C. (2001), "Assessment of ground water quality impacts due to use of coal combustion by products to control subsidence from underground mines", *Environmental International;* 26, 567 - 571.

Skodras, G., Grammelis, P., Kakaras, E., Karangelos, D., Anagnostakis, M., Hinis, E. (2007), "Quality characteristics of Greek fly ashes and potential uses", *Fuel Processing Technology;* 88, 77 - 85.

Snyman, C.P. (1989), "The role of coal petrography in understanding the properties of South African coal", *International Journal of Coal Geology;* 14, 83 - 101.

Somerset, V., Petrik, L., Iwuoha, E. (2005), "Alkaline Hydrothermal Conversion of Fly Ash Filtrates Into Zeolites 2: Utilization in Wastewater Treatment", *Journal of Environmental Science and Health;* 40, 1627 - 1636.

Styszko-Grochowiak, K., Gloas, J., Jankowskib, H., Koziński, S. (2004), "Characterization of the coal fly ash for the purpose of improvement of industrial on-line measurement of unburned carbon content", *Fuel;* 83, 1847 - 1853.

Svensson, M. (2005), "Desalination and the environment: Options and considerations for brine disposal in inland and coastal locations". A study for Yara International and Aqualyng.

Tahir, A.R., Neethirajan, S., Jayas, D.S., Shahin, M.A., Symons, S.J., White, N.D.G. (2007), "Evaluation of the effect of moisture content on cereal grains by digital image analysis", *Food Research International;* 40, 1140 - 1145.

Tessier, A., Campbell, P.G.C., Bisson, M. (1979), "Sequential Extraction Procedure for the Speciation of Particulate Trace Metals", *Analytical Chemistry;* 51, 844 - 850.

Thompson, D., Argent, B.B. (1999), "Coal ash composition as a function of feedstock composition", *Fuel;* 78, 539 - 548.

Tiruta-Barna, L., Inyim, A., Barna, R. (2004), "Long-term prediction of the leaching behaviour of pollutants from solidified wastes", *Advance in Environmental Research;* 8, 697 - 711.

Tiwari, G.N., Singh, H.N., Tripathi, R. (2003), "Present status of solar distillation", *Solar Energy;* 75 (5), 367 - 373.

Thomas, R. (2001), "A beginner's guide to ICP-MS", Spectroscopy Tutorial, available at www.spectroscopyonline.com (Accessed on 20th July, 2011).

Turek, M., Mrowiec-Bialoń, J., Gnot, W. (1995), "Utilization of coal mine brines in the chlorine production process", *Desalination;* 101, 57 - 67.

Turek, M. (2004), "Electrodialytic desalination and concentration of coal-mine brine", *Desalination;* 162, 355 - 359.

Turek, M., Bandura, B., Dydo, P. (2008a), "Power production from coal-mine brine utilizing reversed electrodialysis", *Desalination;* 221, 462 - 466.

Turek, M., Dydo, P., Klimek, R. (2008b), "Salt production from coal-mine brine in NF - evaporation - crystallization system", *Desalination;* 221, 238 - 243.

UND EERC (2011), Energy and Environmental Research Centre, University of North Dakota. The International Centre for Applied Energy Technology, available at http://www.undeerc.org/ (Accessed on 9th February, 2011).

USGS (1997), United States Geological Survey, "X-ray powder diffraction", A Hand out available at http://www.bccmeteorites.com/XRD.PDF (Accessed on 18th July, 2011).

USGS (2009), United States Geological Survey, "Assessment of Undiscovered Oil and Gas Resources of the Williston Basin Province of North Dakota, Montana and South Dakota", US Geological Survey, AAPG Convention, Denver, Colorado, June 7 - 10, 2009.

USGS (2011), Toxic substances hydrology program. Available at http://toxics.usgs.gov/definitions/pore_water.html (Accessed on 23th June, 2011).

Vassilev, S., Vassileva, C. (2007), "A new approach for the classification of coal fly ashes based on their origin, composition, properties and behavior", *Fuel;* 86, 1490 - 1512.

Vijay, R. (2007), "Discovery and mechanistic investigation of nitrogen oxides traps and ammonia decomposition catalysts using high-throughput experimentation", A thesis submitted in the Department of Chemical Engineering, University of Delaware.

Wagner, N.J., Hlatshwayo, B. (2005), "The occurrence of potentially hazardous trace elements in five Highveld coals, South Africa", *International Journal of Coal Geology;* 63 (3 - 4), 228 - 246.

Wagner, N.J., Matjie, R.H., Slaghuis, J.H., Heerden, J.H.P. (2008), "Characterization of unburned carbon present in coarse gasification ash", *Fuel;* 87, 683 - 691.

Walton, J.C., Lu, H., Swift, A.H.P. (2001), "Desalination coupled with salinity-gradient solar ponds", *Desalination;* 136, 13 - 23.

Wang, S.B., Wu, H.W. (2006), "Environmental-benign utilisation of fly ash as low-cost adsorbents", *Journal of Hazardous Materials;* B136, 482 - 501.

Ward, C.R., French, D. (2005), "Relation between Coal and Fly Ash Mineralogy, Based on Quantitative X-Ray Diffraction methods", World of Coal Ash (WOCA), April 11 - 15, Lexington, Kentucky, USA.

Ward, C.R., French, D., Jankowski, J., Dubikova, M., Li, Z., Riley, K.W. (2009), "Element mobility from fresh and long-stored acidic fly ashes associated with an Australian power station", *International Journal of Coal Geology;* 80, 224 - 236.

Warren, C., Dudas, M. (1984), "Weathering processes in relation to leachate properties of alkaline fly ash", *Journal of Environmental Quality;* 19, 188 - 201.

Water Encyclopedia. (2011), Science and Issues. Available at http://www.waterencyclopedia.com/Bi-Ca/Brines-Natural.html (Accessed on 27th July, 2011)

Weltje, G.J., Tjallingii, R. (2008), "Calibration of XRF core scanners for quantitative geochemical logging of sediment cores: Theory and application", *Earth and Planetary Science Letters;* 274, 423 - 438.

WEO (2007), World Energy Outlook, International Energy Agency Executive Summary, China and India Insights, Available at www.iea.org/books (Accessed on 6th April, 2011)

Williams, R.H. (2001), "Toward zero emissions for transportation using fossil fuels", VIII Biennal Conference on Transportation, Energy and Environmental Policy, Center for Energy and Environmental Studies, Princeton University, Monterey, CA, USA.

www.sasol.com (Accessed on 26th March, 2010).

www.tutorvista.com/content/chemistry/chemistry-i/coal-petroleum/coal.php
(Accessed on 19th February, 2010).

www.tutorvista.com/content/chemistry/chemistry-i/coal-petroleum/fossil-fuels.php (Accessed on 19th February, 2010).

Yuan, C. G. (2009), "Leaching characteristics of metals in fly ash from coal-fired power plant by sequential extraction procedure", *Microchimica Acta;* 165 (1 - 2), 91 - 96.

Zevenbergen, C., Bradley, J.P., Reeuwijk, L.P., Shyam, A.K. (1999), "Clay formation during weathering of alkaline coal fly ash", International Ash Utilization Symposium, Centre for Applied Energy Research, University of Kentucky.

UNIVERSITY *of the*

WESTERN CAPE

APPENDICES

Appendix 1: Pore water analysis and moisture content (MC) data of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples as a function of depth

Sample	pH	EC	TDS	% MC
Fresh ash	12.38	4.98	2.68	1.80
surface	9.43	0.85	0.50	30.30
1.5m	10.89	1.04	0.61	43.70
3m	10.00	1.04	0.62	47.50
4.5m	9.96	1.20	0.71	54.30
6m	11.36	1.01	0.59	43.80
7.5m	9.94	1.09	0.65	50.00
9m	9.53	1.01	0.61	45.80
10.5m	9.99	1.19	0.72	54.60
12m	10.23	0.96	0.57	40.40
13.5m	9.37	1.20	0.70	45.60
15m	10.04	1.10	0.67	50.40
16.5m	9.99	1.46	0.87	52.70
18m	10.01	1.31	0.77	48.40
19.5m	10.23	1.24	0.74	52.30
21m	10.06	1.29	0.76	59.10
22.5m	9.29	1.17	0.66	52.20
24m	9.69	1.18	0.69	55.10
25.5m	9.84	1.28	0.77	49.50
27m	9.41	1.10	0.64	46.80
28.5m	10.82	1.16	0.73	52.80
30m	10.12	0.99	0.59	63.60
31.5m	9.49	1.01	0.63	53.90
33m	10.17	1.02	0.60	52.50
34.5m	10.05	1.02	0.62	50.60
36m	9.72	0.90	0.54	44.30
37.5m	9.99	0.91	0.55	50.00
39m	10.99	0.86	0.52	48.40
40.5m	9.59	0.98	0.58	69.90
42m	11.11	0.95	0.57	71.50
43.5m	10.10	1.09	0.63	77.40
45m	9.55	0.90	0.54	82.10
46.5m	10.14	1.07	0.62	69.30
48m	10.11	1.14	0.67	94.00
49.5m	10.12	1.04	0.65	41.00
51m	10.10	1.09	0.66	54.10

mg/kg	Sulphate	Chloride
Fresh ash	13.64	4.05
surface	103.16	16.09
1.5m	141.20	6.85
3m	141.59	9.17
4.5m	172.99	10.52
6m	97.79	14.35
7.5m	150.81	12.66
9m	141.01	9.02
10.5m	176.82	10.96
12m	152.35	14.57
13.5m	177.25	8.92
15m	153.53	8.14
16.5m	221.26	9.05
18m	210.38	13.56
19.5m	165.21	8.71
21m	179.89	12.37
22.5m	183.72	8.78
24m	165.54	10.34
25.5m	191.03	10.93
27m	156.65	18.10
28.5m	172.30	11.58
30m	122.74	12.92
31.5m	146.70	10.86
33m	129.48	11.57
34.5m	140.68	10.08
36m	119.92	11.48
37.5m	121.07	12.28
39m	96.64	8.97
40.5m	139.47	24.74
42m	118.00	21.88
43.5m	159.76	45.32
45m	138.25	17.31
46.5m	138.83	21.33
48m	173.96	21.17
49.5m	148.38	13.54
51m	144.58	10.16

UNIVERSITY of the
WESTERN CAPE

Appendix 2: Bulk chemical composition of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples showing the major and trace elements based on XRF analysis (nd = not detected)

Majors (wt%)	SiO₂	Al₂O₃	CaO	LOI	Fe₂O₃	Na₂O	MgO	TiO₂	K₂O	P₂O₅	MnO	SO₃	Traces (mg/kg)	Sr	Ba	Th	Zr	Ce	Y	Nb	As	Co	Pb	Ni	Rb	V	U
Fresh ash	50.86	25.52	8.95	4.78	2.26	2.20	1.87	1.78	0.95	0.71	0.05	0.03		4160.43	2749.50	1921.89	664.60	176.82	155.87	109.03	61.39	32.73	27.85	22.56	16.41	15.41	nd
surface	48.78	24.44	7.50	7.04	4.30	2.28	2.55	1.69	0.75	0.53	0.06	0.07		3410.17	1924.18	1556.71	602.85	107.44	139.77	104.86	48.07	34.47	41.11	23.65	35.32	88.32	55.64
1.5m	46.76	23.50	9.48	6.03	6.13	2.45	2.37	1.75	0.77	0.57	0.07	0.10		3555.50	1952.00	1620.00	641.50	175.50	148.00	98.50	72.00	39.00	33.50	36.50	33.00	84.50	58.00
3m	48.90	25.76	7.99	6.12	2.76	2.42	2.55	1.79	0.87	0.68	0.05	0.09		4016.42	2408.59	1856.97	622.65	162.46	159.52	124.40	53.04	24.94	39.36	26.58	nd	93.04	nd
4.5m	43.77	23.18	9.95	10.21	4.02	2.58	2.53	1.82	1.00	0.68	0.07	0.12		4419.43	2743.18	2058.20	661.35	172.57	157.84	113.15	80.33	18.89	38.59	29.93	27.95	29.49	47.91
6m	45.83	23.89	9.75	7.23	4.51	2.46	2.79	1.73	0.94	0.67	0.08	0.09		4378.24	2623.87	2030.34	685.67	193.72	160.51	110.88	51.77	47.01	28.46	27.25	28.67	63.79	40.98
7.5m	46.31	25.22	8.88	7.40	2.88	2.73	2.97	1.77	0.93	0.72	0.08	0.09		4440.98	2531.09	2077.77	689.38	181.73	172.96	125.93	65.78	35.25	54.70	30.12	15.25	114.59	nd
9m	44.86	24.06	9.19	9.31	3.72	2.50	2.83	1.71	0.91	0.70	0.07	0.10		4339.13	2629.75	2008.52	689.34	162.58	166.13	109.37	64.52	42.30	39.44	31.37	17.65	58.95	46.69
10.5m	43.42	23.34	9.06	11.07	4.15	2.61	2.73	1.71	0.99	0.68	0.08	0.11		4282.74	2430.08	1992.04	667.51	179.44	161.91	103.09	81.82	31.25	47.65	29.47	42.08	68.70	53.59
12m	45.79	24.82	8.68	6.93	4.73	2.54	2.79	1.75	1.11	0.73	0.08	0.08		4512.00	2696.50	2107.50	669.00	172.50	148.50	113.00	58.50	25.00	39.50	28.50	40.00	56.00	39.50
13.5m	46.58	24.80	8.56	7.66	3.21	2.55	2.71	1.83	1.13	0.76	0.06	0.11		4482.54	2684.92	2103.61	661.99	175.85	168.84	128.71	67.35	28.53	43.13	27.41	15.23	78.34	32.07
15m	46.87	25.25	8.32	7.45	3.13	2.53	2.66	1.76	1.12	0.73	0.06	0.10		4504.82	2760.85	2102.21	675.83	162.38	167.23	130.73	60.40	25.70	40.12	28.48	9.36	75.13	nd
16.5m	45.59	24.91	9.42	7.39	3.43	2.62	2.64	1.84	1.12	0.79	0.07	0.13		4694.86	2796.66	2206.56	683.91	169.74	165.89	122.60	62.89	38.91	42.20	28.26	34.67	84.32	28.82
18m	47.04	25.47	8.07	7.27	3.20	2.49	2.64	1.79	1.08	0.75	0.07	0.10		4596.41	2874.27	2157.56	674.35	178.58	167.80	119.67	61.05	37.18	41.99	26.93	16.90	53.84	47.18
19.5m	45.37	25.17	8.16	8.46	3.85	2.51	2.63	1.77	1.10	0.79	0.07	0.10		4731.50	2916.27	2217.39	670.43	215.13	171.94	122.29	71.88	29.86	32.09	27.71	7.21	64.72	28.32
21m	46.02	25.59	8.15	7.98	3.28	2.56	2.57	1.76	1.14	0.77	0.06	0.10		4548.59	2907.07	2131.35	664.58	165.05	166.84	119.61	60.79	20.24	37.04	30.38	16.59	88.51	27.98
22.5m	45.97	24.90	8.35	8.48	3.38	2.51	2.60	1.81	1.05	0.75	0.06	0.10		4617.40	2793.70	2163.61	690.38	193.22	170.61	134.54	71.00	35.44	36.90	29.24	11.94	79.29	nd
24m	45.73	25.62	8.05	8.44	3.27	2.50	2.51	1.78	1.13	0.80	0.06	0.10		4837.23	3338.19	2274.95	686.91	158.58	172.60	143.84	69.32	43.05	36.34	30.81	10.69	44.40	nd
25.5m	47.07	25.47	7.73	8.05	2.86	2.50	2.48	1.77	1.17	0.73	0.06	0.10		4685.97	2802.68	2205.54	650.17	148.78	167.55	141.63	54.15	22.99	32.41	27.22	7.01	67.50	nd
27m	47.40	24.86	8.09	7.44	3.38	2.44	2.61	1.73	1.18	0.73	0.06	0.09		4333.00	2796.50	2016.00	654.50	162.50	157.50	122.02	56.50	33.50	40.00	28.00	23.50	85.00	10.19
28.5m	45.73	24.51	8.30	7.96	4.71	2.47	2.57	1.71	1.12	0.74	0.07	0.09		4346.05	2915.98	2012.26	654.54	142.49	151.66	110.37	62.30	36.64	36.61	32.22	38.36	74.99	27.36
30m	46.71	25.14	7.92	8.36	3.05	2.43	2.56	1.75	1.15	0.78	0.06	0.09		4453.94	3016.56	2077.42	670.94	200.12	164.37	140.66	61.83	40.21	35.65	30.28	0.84	73.50	nd
31.5m	46.40	24.72	8.24	8.12	3.68	2.51	2.55	1.75	1.14	0.71	0.07	0.09		4485.25	2863.63	2093.67	671.00	154.59	161.85	111.66	67.55	45.29	42.72	31.57	36.30	58.25	46.00
33m	45.97	24.63	8.51	8.40	3.65	2.49	2.56	1.77	1.11	0.74	0.07	0.09		4389.50	2842.50	2042.00	692.00	172.00	162.00	114.00	68.00	38.50	41.50	34.65	19.00	81.00	29.00
34.5m	46.73	24.52	8.18	7.98	3.69	2.42	2.68	1.77	1.17	0.70	0.06	0.09		4672.87	2764.71	2185.26	690.96	183.74	161.85	128.96	62.08	35.36	32.31	30.34	24.74	33.61	nd
36m	47.83	25.77	7.90	6.83	2.99	2.33	2.52	1.80	1.11	0.77	0.06	0.08		4546.09	2850.46	2117.07	703.05	169.06	166.80	136.06	63.36	44.19	38.36	28.03	nd	62.55	nd
37.5m	45.99	24.18	8.07	10.32	2.79	2.32	2.57	1.71	1.18	0.72	0.06	0.08		4690.00	2847.00	2195.00	698.00	187.00	168.00	124.00	68.00	26.00	40.00	28.00	11.00	84.00	nd
39m	45.81	24.20	9.27	8.65	3.26	2.40	2.66	1.72	1.12	0.74	0.07	0.08		4430.01	2840.65	2061.16	697.54	188.68	160.62	104.20	66.65	27.75	29.77	27.64	32.78	37.25	47.58
40.5m	47.46	25.10	8.24	7.63	2.64	2.44	2.72	1.74	1.15	0.74	0.06	0.08		4469.03	2812.66	2080.93	680.08	171.91	166.77	129.97	42.85	25.74	24.41	28.81	10.98	100.30	nd
42m	48.63	25.71	7.34	7.24	2.47	2.37	2.78	1.60	1.07	0.68	0.06	0.07		4322.63	2867.43	2002.64	670.27	180.53	160.26	130.76	40.57	42.03	29.03	27.33	8.36	60.19	nd
43.5m	47.46	25.70	8.48	7.17	2.14	2.53	2.73	1.80	1.05	0.78	0.06	0.08		5122.88	3196.78	2430.47	691.63	161.21	175.23	129.95	48.71	19.56	29.77	29.41	17.81	63.83	25.76
45m	46.57	25.38	8.81	7.78	2.52	2.55	2.63	1.81	1.02	0.76	0.07	0.08		4707.39	3017.12	2211.54	699.05	162.40	161.58	128.25	59.38	25.41	38.23	30.35	45.54	85.02	7.47
46.5m	45.94	25.03	8.13	9.25	2.77	2.51	2.78	1.73	0.98	0.76	0.06	0.09		4617.50	3055.50	2157.50	695.00	187.00	165.83	121.50	51.50	24.50	32.50	30.00	20.00	62.00	28.39
48m	42.97	24.72	9.13	11.68	2.89	2.56	2.85	1.57	0.85	0.78	0.06	0.08		5157.50	3271.50	2421.50	683.50	178.50	179.00	129.00	55.00	37.00	34.50	32.00	7.99	60.50	38.18
49.5m	45.78	25.35	8.71	8.77	2.60	2.48	2.76	1.77	0.80	0.82	0.07	0.09		4685.59	3144.93	2188.35	738.56	162.18	176.86	115.87	55.64	47.72	32.76	29.53	7.85	79.51	40.91
51m	44.28	25.49	9.21	9.52	2.59	2.53	2.73	1.76	0.81	0.94	0.06	0.09		4659.94	3207.61	2186.11	698.32	205.66	171.28	149.43	63.99	36.78	44.48	32.78	6.86	59.89	nd

Appendix 3: % elemental composition of the major elements (weight %) of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples as a function of depth based on XRF analysis

Sample ID	%Si	%Al	%Ca	%Na	%Fe	%Mg	%Ti	%K	%P	%Mn	%S
Fresh ash	23.77	13.51	6.40	1.63	1.58	1.13	1.07	0.79	0.31	0.04	0.01
surface	22.80	12.93	5.36	1.69	3.01	1.54	1.01	0.62	0.23	0.05	0.03
1.5m	21.86	12.44	6.78	1.82	4.29	1.43	1.05	0.64	0.25	0.05	0.04
3m	22.86	13.63	5.71	1.80	1.93	1.54	1.07	0.72	0.30	0.04	0.04
4.5m	20.46	12.27	7.11	1.91	2.81	1.53	1.09	0.83	0.30	0.05	0.05
6m	21.42	12.64	6.97	1.82	3.15	1.68	1.04	0.78	0.29	0.06	0.04
7.5m	21.65	13.35	6.35	2.03	2.01	1.79	1.06	0.77	0.31	0.06	0.04
9m	20.97	12.73	6.57	1.85	2.60	1.71	1.02	0.76	0.31	0.05	0.04
10.5m	20.30	12.35	6.48	1.94	2.90	1.65	1.02	0.82	0.30	0.06	0.04
12m	21.40	13.14	6.20	1.88	3.31	1.68	1.05	0.92	0.32	0.06	0.03
13.5m	21.77	13.13	6.12	1.89	2.25	1.63	1.10	0.94	0.33	0.05	0.04
15m	21.91	13.36	5.95	1.88	2.19	1.60	1.05	0.93	0.32	0.05	0.04
16.5m	21.31	13.18	6.73	1.94	2.40	1.59	1.10	0.93	0.34	0.05	0.05
18m	21.99	13.48	5.77	1.85	2.24	1.59	1.07	0.90	0.33	0.05	0.04
19.5m	21.21	13.32	5.83	1.86	2.69	1.59	1.06	0.91	0.34	0.05	0.04
21m	21.51	13.54	5.82	1.90	2.29	1.55	1.05	0.95	0.34	0.05	0.04
22.5m	21.49	13.18	5.97	1.86	2.36	1.57	1.08	0.87	0.33	0.05	0.04
24m	21.38	13.56	5.75	1.85	2.29	1.51	1.07	0.94	0.35	0.05	0.04
25.5m	22.00	13.48	5.52	1.85	2.00	1.50	1.06	0.97	0.32	0.05	0.04
27m	22.16	13.16	5.78	1.81	2.36	1.57	1.04	0.98	0.32	0.05	0.04
28.5m	21.38	12.97	5.93	1.83	3.29	1.55	1.02	0.93	0.32	0.05	0.04
30m	21.83	13.31	5.66	1.80	2.13	1.54	1.05	0.95	0.34	0.05	0.04
31.5m	21.69	13.08	5.89	1.86	2.57	1.54	1.05	0.95	0.31	0.05	0.04
33m	21.49	13.04	6.08	1.85	2.55	1.54	1.06	0.92	0.32	0.05	0.04
34.5m	21.84	12.98	5.85	1.80	2.58	1.62	1.06	0.97	0.31	0.05	0.04
36m	22.36	13.64	5.65	1.73	2.09	1.52	1.08	0.92	0.34	0.05	0.03
37.5m	21.50	12.80	5.77	1.72	1.95	1.55	1.02	0.98	0.31	0.05	0.03
39m	21.41	12.81	6.63	1.78	2.28	1.60	1.03	0.93	0.32	0.05	0.03
40.5m	22.18	13.28	5.89	1.81	1.85	1.64	1.04	0.95	0.32	0.05	0.03
42m	22.73	13.61	5.25	1.76	1.73	1.68	0.96	0.89	0.30	0.05	0.03
43.5m	22.18	13.60	6.06	1.88	1.50	1.65	1.08	0.87	0.34	0.05	0.03
45m	21.77	13.43	6.30	1.89	1.76	1.59	1.08	0.85	0.33	0.05	0.03
46.5m	21.47	13.25	5.81	1.86	1.94	1.68	1.04	0.81	0.33	0.05	0.04
48m	20.09	13.08	6.53	1.90	2.02	1.72	0.94	0.71	0.34	0.05	0.03
49.5m	21.40	13.42	6.22	1.84	1.82	1.66	1.06	0.66	0.36	0.05	0.04
51m	20.70	13.49	6.58	1.88	1.81	1.65	1.05	0.67	0.41	0.05	0.04

Appendix 4: Enrichment and depletion ratios of the major and trace elements in Secunda weathered fly ash core S2 samples with respect to Secunda fresh fly ash based on XRF analysis (> 1 = enrichment; < 1 = depletion)

Majors	SiO_2	Al_2O_3	CaO	Fe_2O_3	Na_2O	MgO	TiO_2	K_2O	P_2O_5	MnO	SO_3	Traces	Sr	Ba	Th	Zr	Ce	Y	Nb	As	Co	Pb	Ni	Rb	V	U
Fresh ash	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	nd
surface	0.96	0.96	0.84	1.90	1.04	1.37	0.95	0.79	0.75	1.24	2.28		0.82	0.70	0.81	0.91	0.61	0.90	0.96	0.78	1.05	1.48	1.05	2.15	5.73	
1.5m	0.92	0.92	1.06	2.71	1.11	1.27	0.98	0.81	0.80	1.40	3.33		0.85	0.71	0.84	0.97	0.99	0.95	0.90	1.17	1.19	1.20	1.62	2.01	5.48	
3m	0.96	1.01	0.89	1.22	1.10	1.37	1.00	0.92	0.96	1.09	2.87		0.97	0.88	0.97	0.94	0.92	1.02	1.14	0.86	0.76	1.41	1.18	nd	6.04	
4.5m	0.86	0.91	1.11	1.78	1.17	1.35	1.02	1.05	0.96	1.40	4.09		1.06	1.00	1.07	1.00	0.98	1.01	1.04	1.31	0.58	1.39	1.33	1.70	1.91	
6m	0.90	0.94	1.09	1.99	1.12	1.49	0.97	0.99	0.95	1.59	2.94		1.05	0.95	1.06	1.03	1.10	1.03	1.02	0.84	1.44	1.02	1.21	1.75	4.14	
7.5m	0.91	0.99	0.99	1.27	1.24	1.59	0.99	0.98	1.02	1.52	2.96		1.07	0.92	1.08	1.04	1.03	1.11	1.15	1.07	1.08	1.96	1.34	0.93	7.44	
9m	0.88	0.94	1.03	1.64	1.14	1.52	0.96	0.96	0.98	1.46	3.40		1.04	0.96	1.05	1.04	0.92	1.07	1.00	1.05	1.29	1.42	1.39	1.08	3.83	
10.5m	0.85	0.91	1.01	1.84	1.19	1.46	0.96	1.04	0.96	1.59	3.55		1.03	0.88	1.04	1.00	1.01	1.04	0.95	1.33	0.95	1.71	1.31	2.56	4.46	
12m	0.90	0.97	0.97	2.09	1.15	1.49	0.98	1.16	1.02	1.50	2.67		1.08	0.98	1.10	1.01	0.98	0.95	1.04	0.95	0.76	1.42	1.26	2.44	3.63	
13.5m	0.92	0.97	0.96	1.42	1.16	1.45	1.03	1.19	1.07	1.29	3.52		1.08	0.98	1.09	1.00	0.99	1.08	1.18	1.10	0.87	1.55	1.21	0.93	5.08	
15m	0.92	0.99	0.93	1.39	1.15	1.43	0.99	1.18	1.02	1.26	3.21		1.08	1.00	1.09	1.02	0.92	1.07	1.20	0.98	0.79	1.44	1.26	0.57	4.88	
16.5m	0.90	0.98	1.05	1.52	1.19	1.41	1.04	1.18	1.11	1.38	4.25		1.13	1.02	1.15	1.03	0.96	1.06	1.12	1.02	1.19	1.52	1.25	2.11	5.47	
18m	0.92	1.00	0.90	1.41	1.13	1.41	1.01	1.14	1.06	1.32	3.48		1.10	1.05	1.12	1.01	1.01	1.08	1.10	0.99	1.14	1.51	1.19	1.03	3.49	
19.5m	0.89	0.99	0.91	1.70	1.14	1.40	0.99	1.16	1.11	1.35	3.35		1.14	1.06	1.15	1.01	1.22	1.10	1.12	1.17	0.91	1.15	1.23	0.44	4.20	
21m	0.90	1.00	0.91	1.45	1.16	1.38	0.99	1.20	1.08	1.22	3.33		1.09	1.06	1.11	1.00	0.93	1.07	1.10	0.99	0.62	1.33	1.35	1.01	5.74	
22.5m	0.90	0.98	0.93	1.49	1.14	1.39	1.02	1.11	1.06	1.28	3.47		1.11	1.02	1.13	1.04	1.09	1.09	1.23	1.16	1.08	1.32	1.30	0.73	5.15	
24m	0.90	1.00	0.90	1.45	1.14	1.34	1.00	1.19	1.13	1.26	3.09		1.16	1.21	1.18	1.03	0.90	1.11	1.32	1.13	1.32	1.30	1.37	0.65	2.88	
25.5m	0.93	1.00	0.86	1.26	1.13	1.33	0.99	1.23	1.03	1.18	3.28		1.13	1.02	1.15	0.98	0.84	1.07	1.30	0.88	0.70	1.16	1.21	0.43	4.38	
27m	0.93	0.97	0.90	1.50	1.11	1.40	0.97	1.24	1.02	1.23	3.12		1.04	1.02	1.05	0.98	0.92	1.01	1.12	0.92	1.02	1.44	1.24	1.43	5.52	
28.5m	0.90	0.96	0.93	2.09	1.12	1.37	0.96	1.18	1.05	1.39	3.10		1.04	1.06	1.05	0.98	0.81	0.97	1.01	1.01	1.12	1.31	1.43	2.34	4.87	
30m	0.92	0.98	0.88	1.35	1.10	1.37	0.98	1.21	1.10	1.24	2.92		1.07	1.10	1.08	1.01	1.13	1.05	1.29	1.01	1.23	1.28	1.34	0.05	4.77	
31.5m	0.91	0.97	0.92	1.63	1.14	1.37	0.98	1.20	0.99	1.31	3.08		1.08	1.04	1.09	1.01	0.87	1.04	1.02	1.10	1.38	1.53	1.40	2.21	3.78	
33m	0.90	0.97	0.95	1.62	1.13	1.37	1.00	1.16	1.04	1.37	2.98		1.06	1.03	1.06	1.04	0.97	1.04	1.05	1.11	1.18	1.49	1.54	1.16	5.26	
34.5m	0.92	0.96	0.91	1.63	1.10	1.43	0.99	1.23	0.99	1.27	2.92		1.12	1.01	1.14	1.04	1.04	1.04	1.18	1.01	1.08	1.16	1.34	1.51	2.18	
36m	0.94	1.01	0.88	1.32	1.06	1.35	1.01	1.17	1.09	1.29	2.70		1.09	1.04	1.10	1.06	0.96	1.07	1.25	1.03	1.35	1.38	1.24	nd	4.06	
37.5m	0.90	0.95	0.90	1.23	1.05	1.37	0.96	1.24	1.01	1.20	2.67		1.13	1.04	1.14	1.05	1.06	1.08	1.14	1.11	0.79	1.44	1.24	0.67	5.45	
39m	0.90	0.95	1.04	1.44	1.09	1.42	0.96	1.18	1.04	1.46	2.67		1.06	1.03	1.07	1.05	1.07	1.03	0.96	1.09	0.85	1.07	1.23	2.00	2.42	
40.5m	0.93	0.98	0.92	1.17	1.11	1.46	0.98	1.21	1.04	1.25	2.76		1.07	1.02	1.08	1.02	0.97	1.07	1.19	0.70	0.79	0.88	1.28	0.67	6.51	
42m	0.96	1.01	0.82	1.09	1.08	1.49	0.90	1.13	0.96	1.25	2.24		1.04	1.04	1.04	1.01	1.02	1.03	1.20	0.66	1.28	1.04	1.21	0.51	3.91	
43.5m	0.93	1.01	0.95	0.95	1.15	1.46	1.01	1.10	1.10	1.25	2.76		1.23	1.16	1.26	1.04	0.91	1.12	1.19	0.79	0.60	1.07	1.30	1.09	4.14	
45m	0.92	0.99	0.98	1.12	1.16	1.40	1.02	1.08	1.08	1.34	2.64		1.13	1.10	1.15	1.05	0.92	1.04	1.18	0.97	0.78	1.37	1.35	2.77	5.52	
46.5m	0.90	0.98	1.02	1.22	1.14	1.49	0.97	1.03	1.07	1.27	2.83		1.11	1.11	1.12	1.05	1.06	1.06	1.11	0.84	0.75	1.17	1.33	1.22	4.02	
48m	0.84	0.97	1.02	1.28	1.16	1.52	0.88	0.89	1.09	1.26	2.77		1.24	1.19	1.26	1.03	1.01	1.15	1.18	0.90	1.13	1.24	1.42	0.49	3.93	
49.5m	0.90	0.99	0.97	1.15	1.13	1.48	1.00	0.84	1.15	1.37	3.02		1.13	1.14	1.14	1.11	0.92	1.13	1.06	0.91	1.46	1.18	1.31	0.48	5.16	
51m	0.87	1.00	1.03	1.15	1.15	1.46	0.99	0.85	1.32	1.27	2.87		1.12	1.17	1.14	1.05	1.16	1.10	1.37	1.04	1.12	1.60	1.45	0.42	3.89	

Appendix 5: Dry weight concentrations of the water soluble fraction leachates of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples as a function of depth (nd = not detected)

(mg/Kg)	Si	Al	Ca	Na	Fe	Mg	K	Sr	Ba	Mn	As	Zn	Pb	Ni	Mo	Cr	Cu
Fresh ash	1217.2648	495.5176	792.1067	1618.3001	5.6116	20.3371	355.2187	56.7234	5.5888	0.7970	1.5135	0.5893	0.2312	0.3391	0.4706	0.2580	0.0753
surface	1883.2838	202.5945	382.5584	678.3563	nd	241.2185	19.2068	27.8191	0.7965	nd	nd	nd	nd	0.0238	0.0725	0.0838	0.0334
1.5m	1981.5891	735.0675	501.3144	695.7754	16.1563	79.2257	49.4067	34.2958	5.8798	0.4731	0.0551	0.1048	0.0012	0.1080	nd	0.0363	0.0368
3m	1845.5310	331.2200	442.9089	880.2360	9.6907	177.8789	48.9556	36.9135	4.7679	1.1967	0.0375	0.2017	nd	0.0795	0.0848	0.1231	0.1438
4.5m	1868.2855	396.0581	473.9575	1073.6762	14.8224	78.4212	58.1109	42.5668	1.5956	1.1009	0.0750	0.0074	nd	0.1234	0.0083	0.1195	0.1121
6m	1843.7189	646.2795	381.8306	1305.8203	16.9881	54.4839	57.8340	31.9468	3.2973	0.7187	0.0424	0.3460	nd	0.0771	0.0530	0.1873	0.0249
7.5m	1864.6416	262.9134	398.4370	1145.8322	1.2538	273.7403	57.3547	36.6560	4.4154	0.4096	0.0196	0.0791	0.0007	nd	0.0267	0.1063	0.0807
9m	1931.4360	317.6035	386.7280	899.8945	6.0008	224.6389	47.3063	37.8880	6.6295	0.4071	nd	0.0480	nd	0.0157	nd	0.2678	0.0416
10.5m	1966.5641	305.5155	454.5549	1538.1122	21.6917	156.4058	71.9521	32.7218	3.7003	0.5979	0.0233	1.3660	0.0051	0.0630	0.0013	0.0818	0.1654
12m	2000.1788	301.9230	366.0545	1015.0375	nd	202.3032	46.1362	39.3024	5.2956	0.9952	0.0573	0.0735	0.0079	0.0154	0.0669	0.0831	0.0282
13.5m	1841.4424	176.9684	488.5596	1019.9885	40.2592	314.4723	44.5087	39.8944	1.2462	0.7337	0.0511	0.0479	nd	nd	0.0149	0.1331	0.1393
15m	1854.3933	246.2310	476.6155	974.8049	8.7119	183.3768	50.9701	40.9458	3.7554	0.3989	0.0581	0.0855	nd	0.1210	0.0084	0.0853	0.0259
16.5m	1822.2687	275.1350	573.8171	1131.3607	nd	139.3574	49.4347	45.1204	4.9930	0.7757	0.0788	0.0584	nd	nd	0.0312	0.1094	0.0140
18m	1874.9023	259.1733	531.6718	1072.9673	3.1367	114.7973	95.9338	44.5764	5.5326	0.6258	0.0459	0.1810	nd	0.0432	nd	0.3152	0.0296
19.5m	1899.1986	248.3111	467.9120	1233.4375	5.4268	85.8555	71.4404	43.3939	4.1262	0.4999	0.0436	nd	nd	0.0703	0.0547	0.2560	0.0238
21m	1849.3902	219.9236	494.1198	1279.2578	nd	157.4265	71.3582	41.7716	4.1625	0.6666	0.0741	0.0078	nd	0.0295	0.0252	0.0346	0.0401
22.5m	1947.0038	975.0263	643.8130	2407.3963	nd	nd	339.3058	49.4699	25.4263	0.9781	nd	nd	0.0433	0.8772	0.1727	0.0098	nd
24m	1005.2205	803.2245	526.1652	2465.3614	nd	nd	350.1876	38.3745	12.6664	1.0718	nd	nd	nd	1.0512	0.1276	0.0171	nd
25.5m	783.5400	560.7167	481.5893	2635.2816	nd	nd	323.9844	41.2103	16.5474	0.9124	nd	nd	nd	0.8560	0.2399	0.0104	nd
27m	924.1680	692.9082	476.9138	2230.2403	nd	nd	236.8408	36.2990	13.2131	0.8951	nd	nd	0.0274	0.7011	0.2066	0.0091	nd
28.5m	1735.9200	862.5885	588.0816	2710.3810	nd	139.6895	245.6604	40.1545	12.8871	0.8521	0.7116	nd	0.0387	0.8628	0.6948	0.0086	nd
30m	1795.9875	702.7584	596.2388	2511.1615	nd	355.3512	30.1596	35.4644	17.2784	0.8896	0.1224	nd	nd	1.0134	0.6072	0.0126	nd
31.5m	1361.2590	803.3535	551.5957	2043.0682	nd	233.6220	nd	26.5803	16.4859	0.8042	0.3244	nd	nd	0.9202	0.4250	0.0094	nd
33m	952.3695	652.7453	496.4320	3041.1007	nd	290.3397	70.7618	49.8443	27.7199	0.8258	0.8668	nd	nd	0.9681	0.9502	0.0095	nd
34.5m	1013.0468	990.2228	487.5466	2737.8187	nd	251.9768	108.6156	42.5879	16.9673	0.9617	0.4300	nd	nd	1.0569	0.4003	0.0100	nd
36m	1861.5255	1031.2110	nd	2289.9929	nd	198.8781	97.4468	40.2615	15.0520	1.0087	0.3336	nd	nd	1.1483	nd	0.0150	nd
37.5m	1281.8475	771.5543	55.1227	2472.8357	nd	230.1413	332.0577	40.7755	17.2983	0.9476	0.1709	nd	0.3048	0.9280	0.4451	0.0088	nd
39m	433.5660	799.8585	91.2325	2115.1754	nd	61.0963	415.0404	30.4248	23.7335	0.9317	0.1507	nd	0.2720	0.8876	0.1811	0.0075	nd
40.5m	346.6145	764.6775	50.1652	2393.3448	nd	192.4362	419.9946	36.4597	25.5868	1.0394	nd	nd	0.2575	1.0319	0.2714	0.0133	nd
42m	183.9287	503.1399	nd	2375.5200	nd	279.0318	509.5866	36.2320	16.1064	0.8686	0.1966	nd	0.2335	0.7829	0.1111	0.0067	nd
43.5m	201.9726	793.8870	20.7818	2378.4634	nd	191.8026	520.4250	45.8169	19.8724	0.8711	0.0291	nd	0.2297	0.7827	0.1493	0.0067	nd
45m	164.0448	764.8110	nd	2472.5114	nd	225.7746	578.4354	32.5074	27.1242	1.0036	0.0779	nd	0.1840	1.0586	0.5286	0.0065	nd
46.5m	205.4259	367.1910	1.4168	2309.3633	nd	296.1459	635.6682	24.0414	35.6739	0.6879	0.1343	nd	0.1811	0.8825	0.3640	0.0081	nd
48m	nd	nd	nd	nd	nd	nd	nd	25.8206	nd	nd	0.1230	nd	0.1721	0.0234	0.5091	nd	nd
49.5m	nd	nd	nd	nd	nd	nd	nd	29.2953	nd	nd	nd	nd	0.1477	0.0697	0.2291	nd	nd
51m	nd	nd	nd	nd	nd	nd	nd	22.3183	nd	nd	nd	nd	0.0947	nd	0.1023	nd	nd

Appendix 6: Dry weight concentrations of the exchangeable fraction leachates of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples as a function of depth (nd = not detected)

(mg/Kg)	Si	Al	Ca	Na	Fe	Mg	K	Sr	Ba	Mn	As	Zn	Pb	Ni	Mo	Cr	Cu
Fresh ash	47.8516	46.1993	1399.6360	14.4254	53.7878	251.1053	513.6119	45.6697	59.4311	0.6085	1.9268	0.7801	0.4510	0.8305	0.4624	0.4305	0.0297
surface	nd	nd	62.2392	nd	251.7386	nd	nd	41.5410	22.8851	nd	nd	0.2781	0.0721	0.4186	0.2803	nd	nd
1.5m	1061.5770	nd	440.1855	nd	nd	294.2681	32.6892	54.1190	22.3942	nd	0.1771	0.3944	0.1209	0.2114	0.5037	0.0199	0.0199
3m	527.3975	nd	479.3885	nd	nd	300.2963	38.7801	61.7974	24.2056	0.3129	0.0433	0.5384	0.1060	0.3127	0.1802	0.0706	0.0141
4.5m	494.1045	nd	715.7649	nd	nd	408.8063	27.1804	94.7765	40.9811	0.4607	nd	0.5021	0.2584	0.1722	0.1686	0.0901	0.0176
6m	368.2431	nd	507.3422	nd	nd	365.5159	48.2635	68.3283	25.9107	nd	0.0137	0.4146	0.1565	nd	0.1629	0.0157	0.0117
7.5m	329.6534	nd	468.9747	nd	nd	344.4397	32.9689	67.2877	24.5000	0.7029	nd	0.3915	0.1107	0.4723	0.5589	0.0984	0.0167
9m	310.7801	125.3565	464.1085	nd	nd	336.7895	272.9851	60.6232	22.8234	1.4283	0.7544	0.5318	0.2463	0.2197	0.4715	0.2533	0.0213
10.5m	1712.7795	180.1620	487.7555	nd	nd	212.1386	359.2060	55.1022	16.8273	1.5865	0.6900	0.7522	0.5752	1.0402	0.2310	0.5278	0.0055
12m	1327.3245	nd	435.9168	111.5573	315.2462	205.2126	278.2568	67.2979	20.4232	1.5107	0.3995	0.7847	0.0856	0.7587	0.0219	0.3485	0.0030
13.5m	460.2561	54.2096	413.3821	nd	225.7929	120.1545	287.7296	58.7356	22.3687	0.7353	0.6620	0.7171	0.4938	nd	0.1073	0.1985	0.0076
15m	486.4622	nd	555.9278	nd	nd	265.7916	201.2414	70.1706	26.2346	1.0189	0.4190	0.7689	0.5144	0.0509	0.3445	0.1184	0.0119
16.5m	304.0334	nd	538.5719	nd	nd	223.1507	279.7027	64.5159	26.3692	0.6318	0.3822	0.6899	0.2008	0.6361	0.0524	0.1097	0.0107
18m	783.5378	nd	493.0871	199.1489	nd	235.3230	229.2197	48.6401	9.2090	0.0613	0.3778	0.6760	0.3436	nd	nd	0.1230	0.0099
19.5m	nd	nd	496.4609	194.3427	nd	199.7138	nd	43.5102	1.8362	nd	0.2984	0.6040	nd	nd	nd	nd	nd
21m	nd	nd	484.8675	192.2454	nd	157.8323	24.8347	38.4710	0.6825	nd	0.5717	0.5431	nd	nd	nd	nd	nd
22.5m	nd	nd	412.9598	182.8380	nd	207.5679	nd	36.5776	nd	nd	0.2120	0.4843	nd	nd	nd	nd	nd
24m	nd	nd	478.1331	178.8422	nd	172.5743	6.6877	42.1213	6.6145	nd	0.1476	0.3773	nd	nd	nd	nd	nd
25.5m	nd	nd	380.3052	173.1486	nd	136.6958	9.2966	31.3777	nd	nd	0.0933	0.2765	nd	nd	nd	nd	nd
27m	1821.1455	nd	506.6001	195.1373	nd	245.0927	nd	42.3653	4.2935	nd	nd	0.6360	nd	0.0955	0.1543	nd	nd
28.5m	1033.4520	nd	572.9443	190.0604	nd	314.7066	54.9594	43.9805	8.4908	nd	nd	0.5646	nd	nd	0.1304	nd	nd
30m	724.6875	nd	441.4972	181.3217	nd	275.1579	nd	33.1455	2.0090	nd	nd	0.4999	nd	nd	nd	nd	nd
31.5m	455.4867	nd	466.8288	182.4498	nd	247.8175	nd	39.4257	3.4462	nd	nd	0.5104	nd	nd	0.1023	nd	nd
33m	212.9898	nd	430.8560	176.2098	nd	202.4953	nd	33.7133	1.7436	nd	nd	0.4790	nd	nd	0.1477	nd	nd
34.5m	383.2790	nd	421.3440	183.5349	nd	190.2479	54.4678	39.6097	nd	nd	nd	0.5157	nd	1.4261	0.4374	nd	nd
36m	1762.1280	nd	491.3959	195.4961	nd	290.0903	19.5451	43.6353	nd	nd	0.1668	0.6665	nd	0.5871	nd	nd	nd
37.5m	403.3667	nd	529.6288	194.9487	nd	277.0529	nd	49.4041	3.4321	nd	0.3833	0.6169	nd	0.3407	0.1939	nd	nd
39m	388.8308	nd	607.1938	193.2480	nd	342.3992	8.0313	51.2868	2.9059	nd	0.3388	0.6287	nd	0.2394	0.0423	nd	nd
40.5m	207.3350	nd	630.2588	192.2859	nd	377.4735	58.3169	52.3118	8.8439	nd	0.1095	0.6694	nd	1.4376	0.4664	nd	nd
42m	374.1660	nd	547.5295	188.7225	nd	352.8180	28.9893	48.0397	5.0792	nd	0.4765	0.5065	nd	0.6332	0.4791	nd	nd
43.5m	2050.4565	nd	673.9782	11.9524	127.9106	419.6804	252.7302	92.7022	52.3545	2.2408	0.1061	0.1214	0.2714	0.3439	0.3791	0.0841	0.0184
45m	48.9771	58.3493	598.5284	11.3688	134.5039	444.8122	239.3700	79.5655	47.5412	1.1242	nd	nd	0.2177	nd	nd	0.1135	0.0284
46.5m	nd	nd	632.2729	11.4722	40.8728	477.0511	216.7412	83.4356	65.5559	0.9147	0.0904	0.0717	0.0817	nd	0.2312	nd	0.0301
48m	nd	nd	794.2007	14.9059	114.1052	499.5016	262.5351	114.4664	80.8908	1.0855	0.1733	nd	nd	nd	0.1764	0.0143	0.0369
49.5m	nd	nd	526.7695	8.5579	399.4551	482.8284	183.4293	68.5355	72.7385	1.5481	0.5124	nd	0.2482	0.7698	0.0854	0.0664	0.0381
51m	nd	nd	764.7325	16.6611	152.7445	634.6818	272.2297	95.7131	83.2705	3.4665	0.2158	0.0830	0.0133	0.2959	0.4802	0.1778	0.0239

Appendix 7: Dry weight concentrations of the carbonate fraction leachates of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples as a function of depth (nd = not detected)

(mg/Kg)	Si	Al	Ca	Na	Fe	Mg	K	Sr	Ba	Mn	As	Zn	Pb	Ni	Mo	Cr	Cu
Fresh ash	12439.0015	9860.4704	3927.9430	207.3014	189.7011	202.1612	147.4679	113.6613	111.8444	17.2027	2.8991	0.7812	3.8444	1.2743	0.6361	0.7785	0.4812
surface	3519.9480	6365.7975	490.5855	4.4764	286.7613	132.4348	32.9974	66.8065	157.8502	14.1017	nd	0.0667	2.4313	0.1035	3.0616	0.9510	0.1002
1.5m	6975.1230	7769.3085	889.8210	2.9535	521.0693	268.1062	28.9752	113.1302	155.4427	22.5092	0.1448	0.4501	2.1488	0.0943	3.2106	0.7709	0.2688
3m	14394.8400	10326.0600	1256.5118	4.5292	353.6739	325.0884	38.1579	183.5746	185.4033	32.7914	3.4184	0.1353	1.4787	0.1712	1.7282	1.0697	0.3343
4.5m	13787.7000	10392.0450	1668.5213	3.3301	585.1485	384.7633	63.4413	238.9384	214.1202	41.4629	2.0321	0.1184	0.5009	0.3559	3.5238	0.8068	0.2108
6m	11270.8710	8924.7000	1468.8893	3.6674	351.2536	329.8100	46.2586	194.9711	197.4263	42.1333	nd	0.2926	1.2607	0.5526	3.8085	0.3890	0.3315
7.5m	9101.9820	7615.7235	1667.4758	90.4246	nd	225.6316	65.7536	130.1972	110.6351	33.4977	nd	1.3295	2.3186	0.4646	nd	0.2418	0.4494
9m	9776.8170	8803.2990	1658.0775	91.4400	171.0691	292.0109	57.8796	154.6784	164.7546	35.1065	0.8053	1.1300	1.4018	0.2213	nd	0.4618	0.1828
10.5m	10869.8340	9050.2905	1750.1963	90.2459	146.4994	278.0459	59.2057	132.8254	134.4096	38.3052	nd	1.2402	0.6019	0.4653	nd	0.3077	0.4109
12m	7859.4510	7505.7465	1395.6450	88.3660	75.3625	209.0500	44.7651	133.3878	162.0677	23.5501	nd	0.9800	2.5209	0.3804	nd	0.2741	0.3373
13.5m	10537.5000	8734.5555	1390.4340	82.7766	103.3708	191.0454	15.7111	134.2346	115.7361	20.4138	nd	0.9511	0.9917	0.1491	nd	0.0428	0.2866
15m	19522.5750	10610.6265	1328.2530	84.7801	240.4091	210.7791	91.2378	157.2037	129.6581	29.1365	1.6012	nd	0.2397	0.2788	2.4966	0.2208	0.2773
16.5m	20384.1900	12446.8800	1685.3340	85.7346	352.4958	271.1709	60.0466	184.4929	152.2445	34.8436	nd	nd	1.3225	0.2486	1.5984	0.4192	0.1668
18m	13775.4900	9750.3330	1082.4683	88.6024	107.7010	177.8532	43.1941	137.3987	116.7446	21.4634	nd	nd	1.3712	0.5517	2.5671	0.2975	0.2570
19.5m	14107.2600	10035.7215	1232.1863	85.6734	113.3887	199.6617	57.2886	156.4453	153.5925	24.6739	nd	nd	1.6110	0.5417	1.7629	0.2230	0.4747
21m	18356.2200	11542.2300	1588.2150	85.7875	174.6918	222.2069	63.2937	189.2152	186.9630	30.9656	nd	nd	0.6050	0.3800	2.5766	0.2121	0.3276
22.5m	16162.8300	11293.9200	1406.3363	92.1686	220.9588	210.9610	72.7651	172.2419	195.7730	29.7261	1.0720	0.0892	0.6771	0.6634	2.3836	0.2632	0.3226
24m	19418.1000	10018.4700	1537.0830	88.5126	nd	176.0258	75.2684	173.3605	194.0156	26.8489	nd	0.1192	nd	0.4443	4.1024	0.5374	0.2092
25.5m	15094.7400	9847.9215	1272.2565	90.6012	nd	141.9908	52.6176	129.2458	94.6372	20.4213	0.9596	nd	0.9677	0.5804	1.4779	0.4121	0.1131
27m	12310.0800	9340.8510	1098.5685	85.8941	nd	150.3638	55.9229	118.5222	107.5300	20.5328	1.7801	nd	0.0050	0.8485	6.0947	0.4483	0.1385
28.5m	16310.1600	10615.0200	1382.9010	85.5355	nd	198.5080	51.7343	126.5973	125.3467	25.2997	1.1110	nd	nd	0.5715	1.5618	0.2082	0.3742
30m	11506.3500	8395.6125	1119.5460	83.7682	nd	157.5869	27.1142	112.9810	109.8035	21.1349	2.2579	nd	1.7804	0.5576	3.5940	0.2755	0.1839
31.5m	18115.0200	9611.2515	1251.9405	89.2488	nd	173.3638	50.9077	128.1299	133.7474	24.6200	7.4237	nd	nd	0.5130	3.7180	0.3213	0.2041
33m	17601.3000	10025.0670	1567.7280	85.4719	nd	222.1414	54.7026	168.5413	171.5822	28.5327	5.2068	0.1997	0.9276	0.8507	1.9524	0.3573	0.1215
34.5m	11963.2200	8950.4445	1239.1508	85.4009	nd	170.6804	55.6938	127.3239	115.8038	21.8993	6.7067	0.1187	0.4724	0.7553	3.8648	nd	nd
36m	10303.6110	7965.3540	1114.3155	84.7481	nd	163.8218	48.8867	124.1808	96.9603	22.1195	6.0403	0.0614	2.6608	0.6684	2.2842	0.2432	nd
37.5m	14905.9800	9607.8435	1617.1530	91.3207	nd	237.6032	75.7325	203.9375	152.9502	30.9599	7.3344	0.2283	1.9654	0.7716	2.7774	0.1980	0.0300
39m	18583.1700	11519.7750	1983.3255	83.7512	nd	342.8918	53.2860	217.9607	191.7164	41.9291	3.2750	0.0572	1.2886	0.8806	2.6739	0.2753	nd
40.5m	18239.9400	9052.7295	1333.3283	86.3611	nd	206.9617	33.4753	151.2883	126.2190	17.4223	2.9302	nd	1.7213	0.0798	2.7591	0.3222	nd
42m	11462.0400	8608.7415	1056.7208	84.4901	nd	179.1682	16.7065	115.5387	109.2153	17.1724	2.9995	nd	nd	nd	0.3036	nd	nd
43.5m	8970.4920	7447.6965	1437.8985	83.7949	nd	153.7633	32.8224	170.8201	128.9075	13.8150	3.1312	nd	0.1968	nd	0.4647	0.3065	0.3050
45m	11562.0810	8802.0720	1634.9063	86.3076	nd	197.8192	45.1915	179.2595	133.2904	16.1148	0.8242	nd	1.1561	nd	nd	0.2867	0.0900
46.5m	8833.2900	7881.0075	1217.3655	83.9398	nd	158.5101	9.6886	138.2241	113.8436	12.5221	1.5406	nd	1.3914	nd	0.0673	0.1443	nd
48m	10666.8000	7655.2590	2289.0308	83.2330	nd	191.8371	37.5626	252.5542	145.2065	27.0331	2.5076	nd	0.4237	0.6037	nd	0.2597	0.0713
49.5m	15627.7800	8929.8615	1430.9693	83.8634	nd	205.0062	73.2822	165.3080	145.5516	27.0284	nd	0.0633	0.7692	0.6994	nd	0.0721	0.1658
51m	17062.9500	9546.1620	2092.1963	82.4845	nd	228.1650	88.3784	230.2798	190.2884	33.0027	nd	0.1313	nd	0.5883	0.4595	0.2158	0.4010

Appendix 8: Dry weight concentrations of the iron and manganese (Fe & Mn) fraction leachates of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples as a function of depth (nd = not detected)

(mg/Kg)	Si	Al	Ca	Na	Fe	Mg	K	Sr	Ba	Mn	As	Zn	Pb	Ni	Mo	Cr	Cu
Fresh ash	13545.8853	8328.4515	2152.9513	404.4528	1996.2282	653.3296	98.0310	262.5286	138.7168	40.5087	1.9568	1.6524	0.4125	0.9744	0.5525	0.6828	0.3743
surface	7562.3048	8809.1685	1109.4953	50.8171	1138.9950	977.2753	37.3746	31.1070	32.3384	41.8137	1.3378	1.6730	nd	0.0144	nd	0.8539	0.0791
1.5m	7426.8653	9279.3750	1012.0410	39.9780	1306.9995	706.8728	36.1094	34.3775	42.8229	40.1721	2.6388	1.5128	nd	0.3610	2.5148	0.0303	0.1967
3m	5159.4375	9142.4310	1014.0728	52.6210	1256.5115	606.9571	54.6457	71.7924	45.7455	24.6572	0.8044	1.8197	nd	0.2828	4.2389	0.1322	0.2844
4.5m	5583.9945	8878.7160	1048.2773	49.5367	1202.9745	738.4351	47.3709	82.6578	43.9893	39.0746	1.5741	1.8610	0.2041	0.3514	0.2636	0.2163	0.3681
6m	5111.6835	8658.0009	1061.9876	37.7908	1286.9315	551.4896	36.6790	74.4529	33.6369	36.2674	1.4684	1.1439	nd	0.0747	2.2330	0.4046	0.0470
7.5m	15666.5565	9546.1365	928.2690	49.5768	1102.9952	738.0042	36.9592	149.7518	59.1225	26.6464	2.4903	1.6780	0.0182	1.0225	4.0202	0.2786	0.1686
9m	10366.5398	9680.8425	1045.4063	51.9295	1244.3040	760.0499	50.2945	104.5804	54.4245	29.3366	0.3958	1.5968	nd	0.6143	0.1918	0.3433	0.1729
10.5m	10512.5790	9953.6040	1056.5145	48.8763	1134.1235	629.7296	33.7732	194.9483	65.0980	23.9423	1.7676	1.9907	nd	0.8040	3.0943	nd	0.0419
12m	9409.0553	9776.0115	969.2393	51.1418	1178.7368	674.2271	41.1134	162.1384	68.3821	24.2730	1.9781	1.6464	0.1680	0.6667	nd	0.0266	0.1478
13.5m	9101.4263	9454.1985	959.8680	60.2785	1093.5939	576.8110	36.8123	154.2599	79.4607	16.2434	2.3541	1.8371	0.0836	0.8000	0.2810	0.2384	nd
15m	5842.9611	8614.7759	869.6093	48.7566	1006.2651	612.2777	32.4669	77.9417	40.2703	17.8949	1.0827	1.1821	nd	0.7320	1.5236	0.9591	0.0633
16.5m	16929.3443	9813.6240	1122.9255	48.5005	1183.8870	586.3694	55.1622	196.8446	71.9819	19.1385	2.3733	1.3804	0.3565	0.8367	4.4408	0.8447	0.2299
18m	9373.9275	9540.8265	1016.0460	47.6859	1183.0200	559.1523	50.7145	143.5462	61.0531	17.8981	1.3496	1.8940	0.3608	0.7459	3.3472	0.4500	0.0537
19.5m	8619.4395	9322.9770	1077.6578	60.4215	1082.1452	573.1237	44.3055	173.6359	70.8128	20.3159	2.7906	2.2525	0.2445	1.1464	3.0168	0.2695	0.2849
21m	8526.7560	9971.5575	1126.5975	62.7194	1190.7108	652.2890	67.8863	178.8859	75.5361	15.8530	1.7884	1.7546	nd	1.1814	1.2243	1.0641	0.1295
22.5m	7223.2334	8958.0429	1123.2304	46.7512	1237.1551	756.0656	67.9446	90.0143	38.6543	17.3969	2.3080	0.9866	nd	0.5547	1.5076	0.2948	0.0337
24m	10811.7345	10060.0725	904.1085	46.1948	1175.3328	663.9955	77.1234	192.8299	99.9867	14.3424	3.9059	1.9951	0.2580	1.1650	5.0089	1.0867	0.0854
25.5m	20820.0825	10513.2975	1006.7805	46.5268	1178.9250	631.7972	57.3268	284.9411	101.9547	27.0433	2.9709	1.8622	0.2006	0.5508	2.1848	0.5083	0.2170
27m	9443.6160	9205.6335	1110.8025	52.8624	1093.7622	614.6474	59.0513	140.6693	66.3171	29.8640	1.7367	1.1337	nd	0.4605	0.3934	0.9918	0.4094
28.5m	10187.2470	9802.7415	1070.1675	48.6625	1214.3370	623.6112	50.7425	181.7954	84.3648	31.9975	2.4838	1.3161	0.1579	0.5616	3.1865	0.1316	0.2037
30m	10799.0295	9837.5310	965.8643	51.5139	1159.0952	635.3039	90.3081	153.2195	63.7273	30.1813	0.7220	2.3765	0.4045	0.6588	5.1811	0.2859	0.2778
31.5m	10572.5970	9758.9040	1093.5225	54.5325	1145.9547	642.7831	69.0992	175.4744	70.9519	27.5254	2.6127	1.1460	0.1274	0.4153	2.8647	0.0629	0.1811
33m	8198.7990	9000.8685	1149.9795	48.6524	1071.6032	830.1331	82.6221	147.2837	63.2567	45.6546	2.9500	1.5731	0.1781	0.8096	1.3488	0.4745	0.2136
34.5m	10119.2858	9988.6110	1065.9218	46.1393	1155.4713	718.8746	83.0213	236.2227	66.9956	32.2309	2.3072	1.6926	0.5959	0.4648	nd	nd	0.2293
36m	8347.2060	9313.9575	1074.3503	39.7923	1149.6347	664.2153	58.1314	66.8836	39.9107	28.4431	2.3200	2.0390	0.1548	0.6079	nd	0.5156	0.1499
37.5m	8251.1625	9194.4450	1121.1458	40.0610	1111.9974	644.7578	73.9050	147.3143	56.2013	27.6224	2.1517	2.0748	0.0444	0.4906	0.7693	0.3999	0.1674
39m	6323.8232	9040.1738	1191.8273	44.1452	1123.3330	765.4659	41.1586	73.2092	43.6206	39.3706	0.8700	1.2677	0.0567	0.2793	0.1568	nd	0.2631
40.5m	8360.3310	9290.8890	1034.6153	37.0204	1103.9691	770.3790	39.2621	101.4417	47.3764	27.5427	3.2487	1.6555	0.1406	0.8040	2.2557	0.3769	0.2485
42m	12414.8063	10473.4245	1043.9910	40.4857	1403.5050	676.1815	52.2718	95.3396	48.6601	30.5284	1.4399	1.5239	0.1748	0.8468	0.1677	0.5363	0.2411
43.5m	15259.3403	9066.0660	1082.4840	45.5150	1010.4320	878.5541	23.2213	179.0166	58.0024	38.0385	1.1288	1.5999	0.3476	0.3300	3.4217	nd	0.3833
45m	9304.8218	9457.2570	1168.2135	46.4922	1194.6071	935.8893	26.6990	142.0328	49.9786	37.3839	1.7138	2.3287	0.2075	0.5071	2.7630	nd	0.4259
46.5m	8693.3385	8940.6870	1021.6305	37.4986	1065.7986	872.2408	34.6546	118.6159	47.6763	33.6545	1.9469	1.7997	0.2288	0.2936	5.2949	nd	0.4754
48m	14404.5720	10637.5320	1074.7305	47.6103	1722.5475	1061.7629	67.4216	170.1782	51.3863	37.5673	nd	2.0840	0.0690	0.3488	2.6288	nd	0.3389
49.5m	7790.0393	8917.2150	1023.3225	37.7513	1126.2812	902.1926	40.4959	66.2617	31.4907	43.2818	nd	1.8929	0.9561	0.5770	3.0904	nd	0.3315
51m	9340.5953	9633.8295	1135.1858	45.9769	1080.0644	941.2188	38.7395	152.8141	58.2790	40.7582	nd	2.1774	0.6353	0.5199	1.0326	nd	0.3549

Appendix 9: Dry weight concentrations of the residual fraction of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples as a function of depth

(mg/Kg)	Si	Al	Ca	Na	Fe	Mg	K	Sr	Ba	Mn	As	Zn	Pb	Ni	Mo	Cr	Cu
Fresh ash	195613.5667	113902.9880	54462.2233	14021.8163	13453.2740	7423.6653	6788.1239	3367.9922	2202.8843	365.1453	51.3572	21.9040	21.6953	18.1943	14.8981	8.6000	8.3937
surface	168873.7828	106297.1852	69611.8315	15926.4719	23856.8519	13958.6778	6646.3630	3907.2000	1800.2452	404.4500	17.7634	67.3733	27.8883	25.2627	6.5397	9.9066	5.8994
1.5m	197612.2222	110881.0370	84554.6296	15673.1963	32878.7546	14393.5519	5681.8778	3894.5667	2163.1081	434.2469	32.9736	61.9641	31.5646	26.9295	5.6155	5.1256	6.5062
3m	193002.2222	107424.7253	49241.8889	17270.0630	16823.4444	14135.0300	7682.9185	3556.4615	1996.5576	429.7463	31.6964	56.9237	35.2138	31.2418	11.2010	9.3855	5.9723
4.5m	199709.0580	115507.6667	58977.0741	15476.6300	35513.4444	14456.8222	8202.6030	4101.8356	2748.8593	443.8074	37.4771	22.6103	44.6159	31.5332	9.3794	12.0002	5.4754
6m	191591.1111	112930.9630	56810.0362	17062.5074	29797.2222	14276.9222	7879.2556	4097.6356	2393.1037	538.9885	46.5820	42.0610	33.1837	26.4478	13.8690	9.2738	6.6697
7.5m	214770.0000	102543.6996	52587.8481	17227.3926	17056.5185	13533.7626	7192.9259	3693.4067	2286.1293	564.1489	44.9795	30.5751	49.6919	18.4989	19.8332	7.4501	3.3199
9m	197521.4815	114616.3333	58048.3704	15691.6926	22017.5556	14124.0072	6627.5407	3893.9248	2623.8519	466.5800	45.4516	33.8780	57.3138	27.4937	10.2820	9.9546	3.6678
10.5m	225415.1515	114598.2197	58405.6296	16280.9407	21368.6447	14484.8037	6470.2630	3720.9144	2144.3052	528.7085	25.7547	33.0203	40.0465	24.9621	8.3389	3.0346	2.8356
12m	197764.0741	106238.3333	60172.7407	17054.7625	24830.8148	14246.4370	7098.1311	3894.2033	2189.0721	450.2585	29.2883	29.4455	30.6459	29.9185	8.3389	5.7138	4.2494
13.5m	183713.3333	101247.3408	58609.4444	15736.2259	17612.1111	14040.2407	8282.0852	4013.2896	2449.5419	468.1281	25.4659	35.4652	26.6449	26.1790	7.1541	6.1031	5.3015
15m	183125.1852	101302.0370	53533.5581	16851.8741	15962.1852	13749.4103	8915.2333	3815.7263	2308.6215	399.9192	13.3416	34.0021	23.9694	27.2696	11.9199	3.7031	5.5538
16.5m	179127.0370	101807.0741	54545.0741	16127.3444	16598.7407	14202.2889	8242.4815	3775.4732	2127.2911	412.6689	57.7496	48.5772	20.5716	37.5151	8.6895	13.3375	5.5851
18m	182544.4444	99767.1481	50896.7556	17795.7481	13439.5880	12850.6611	7611.2778	3667.1563	1967.2478	412.1681	9.0079	12.6388	17.5347	19.9307	5.4119	9.6259	2.4903
19.5m	176500.3663	104488.9513	47318.5185	14304.5341	18932.2963	13022.0933	7323.7481	3685.5167	2052.3015	296.2789	10.2823	57.2377	17.6450	27.8784	4.4265	7.6672	2.3118
21m	175694.0741	102986.0741	44472.9630	14033.9000	19856.5926	13270.2104	7077.6000	3594.2452	2042.4881	310.8481	44.9750	49.7594	22.0014	23.0547	16.4982	6.3387	3.1760
22.5m	184432.5926	109901.3333	47438.0861	13992.9519	16758.0370	13188.1944	6915.0623	3555.6426	2352.8543	335.9148	66.6416	44.2120	31.7138	24.9664	5.1581	10.2314	2.2884
24m	184051.4815	103851.6296	47203.6630	12797.5389	16815.1481	12979.1796	7070.7852	3656.5429	2430.3207	365.9915	50.7833	49.3195	19.3909	24.8342	10.4043	9.4355	1.9395
25.5m	182727.4074	98138.5556	45615.1741	15638.3295	16907.6779	13589.3617	7679.4963	3707.7996	2620.2681	314.8225	54.0165	40.8378	60.3331	26.3157	20.4016	7.2495	2.6914
27m	183771.1111	102692.0599	49796.9185	14617.7333	19564.8519	13107.4474	7117.7963	3753.1837	2473.6774	427.9659	48.2946	48.4396	51.6583	28.4115	24.9125	11.9335	2.6082
28.5m	182182.4176	101373.0000	48592.2407	14576.0630	28559.5556	13105.7515	7643.3963	3966.6056	2443.1146	387.0459	38.5636	50.9017	49.6279	38.8069	17.5008	9.6030	3.8867
30m	184350.0000	101241.7407	43920.2407	14757.2593	17384.9259	13195.9719	8079.8333	3755.3019	2330.0507	503.7291	52.4152	64.9780	41.7661	30.3244	22.8907	7.8791	3.0158
31.5m	198508.5185	103574.6067	46999.0074	14504.4593	18927.2963	12986.4967	8306.8185	3719.3126	2365.2115	390.7396	90.7631	37.4880	44.4905	25.5903	23.3389	8.1156	2.1570
33m	197922.5926	102772.3333	50733.3704	16082.6037	22396.8148	13374.5470	8102.0147	3760.4396	2422.9785	411.1430	109.9322	38.6263	26.0393	30.7285	17.1240	11.7261	2.7108
34.5m	196202.9630	101339.2222	49724.8889	14676.4481	25026.8148	13415.3300	8184.8926	3824.8459	2301.1781	445.5239	110.1961	43.1598	57.8123	20.9954	17.9336	9.9939	1.7679
36m	191113.3333	97397.7963	43831.8427	14968.1407	18481.0000	13049.2804	7661.2963	3767.9422	2332.6730	443.2063	103.7377	43.2035	37.8253	22.9916	24.4316	13.6614	1.4802
37.5m	181562.5926	97729.7378	49945.4852	14551.6222	19157.0881	13296.1712	8177.5926	3795.2230	2491.9067	404.3567	98.9544	20.3114	20.2235	25.9410	21.7314	10.4032	1.8846
39m	177253.7037	97383.4556	49891.1370	14708.5296	22587.4815	13080.1600	6991.3407	3948.1237	2425.0926	424.0767	39.5005	28.6092	36.6343	19.8380	22.4188	6.6368	1.9334
40.5m	173757.7778	96652.4638	51697.6704	15348.2967	19236.9630	13172.7078	6839.8696	3899.9274	2785.5152	506.7267	90.4519	38.4996	23.9498	14.5170	10.1034	9.8754	1.8740
42m	158528.0899	97014.1852	47836.9259	14788.1444	15568.0000	13094.3474	7129.7259	3798.9052	2195.2711	548.5919	95.7930	34.2166	25.4419	23.1239	12.7170	13.8477	1.0880
43.5m	157963.8148	101441.3333	47722.5407	14497.7333	15374.5556	13177.3663	7647.1926	4205.8996	3046.6341	341.7700	77.1258	40.9631	9.8704	21.8302	13.4030	2.8410	2.4857
45m	153160.1852	104858.2963	53554.1852	15040.9963	19855.2593	13743.9159	8873.1667	5026.3519	2903.4593	435.2904	48.3115	34.6285	8.4989	15.7756	5.3884	3.1958	1.9383
46.5m	151013.3333	97944.1935	52474.8704	14291.0599	17713.1522	13224.1315	7021.5985	3684.7330	2160.5693	509.5944	38.5270	31.1069	10.7453	21.1115	5.3920	2.5031	2.1898
48m	151102.6217	99699.0741	47695.0741	13859.2444	17970.0370	13018.5526	6047.5926	3654.9825	2063.1763	382.9181	30.8356	50.0253	44.1006	21.6117	4.4989	2.5742	1.8774
49.5m	138658.8889	95275.9259	45833.7926	13701.6148	12948.7778	12843.7322	5406.4519	3664.8430	2180.3422	366.4189	26.9673	31.4520	7.5271	16.7514	3.8119	1.3031	2.1928
51m	130970.0000	96144.8148	46496.9074	14008.0815	13971.2593	12828.6285	5048.2785	3651.8847	2116.4622	326.9107	5.9750	23.9119	6.3209	19.0520	2.5039	1.9483	1.1690

Appendix 10: Dry weight concentrations of the total metal content of Secunda fresh fly ash and Secunda weathered fly ash core S2 samples as a function of depth

(mg/Kg)	Si	Al	Ca	Na	Fe	Mg	K	Sr	Ba	Mn	As	Zn	Pb	Ni	Mo	Cr	Cu
Fresh ash	230180.6667	134015.2800	64096.7333	16543.3133	15874.4400	8757.2533	7986.7340	3961.9673	2603.3933	429.5827	60.2032	25.7694	26.9863	22.0309	17.5272	11.2738	9.9698
surface	211644.6667	113425.7200	73803.2000	19243.3133	25208.6000	15557.2533	8741.0807	4267.2640	2032.6107	568.1527	21.1728	83.6785	30.3207	30.5685	10.9655	10.2188	7.8959
1.5m	212136.0000	129115.7333	89596.7333	18613.6133	40820.6000	15449.7067	7666.5390	4167.9273	2352.5920	614.6880	41.0819	88.9390	35.7847	33.1670	6.4542	6.3267	7.5982
3m	200757.3333	117637.4667	55200.8733	17798.8387	20151.3933	16709.2000	8472.9173	3658.7360	2290.3633	458.9800	38.9545	66.0106	41.8094	42.3739	13.7148	10.6406	6.4551
4.5m	227745.3333	133661.6667	82324.9333	16331.4667	36794.2667	15255.2587	8610.4373	4916.6533	3087.1600	623.9693	42.2159	28.6393	51.7966	43.3403	15.6373	14.9069	6.0158
6m	220806.6667	117540.5467	68090.1333	26769.9200	32815.7333	17154.4800	9167.3953	4376.0847	2660.6967	661.3460	56.9435	47.4108	36.9845	31.2453	19.6321	12.5593	7.5514
7.5m	236408.0000	125720.6667	60239.5933	20144.2067	18051.9467	16005.3467	8205.1747	3888.9453	2629.4367	605.2113	66.4395	39.2160	56.6212	24.8977	35.0555	8.9795	6.6534
9m	226067.3333	138136.4000	68349.9333	16030.1747	24053.4000	15083.2953	7274.1440	4148.5433	2811.6200	505.8807	55.5101	42.4678	77.8361	35.9123	11.4350	10.4076	7.0176
10.5m	231398.0000	135009.4667	65450.0000	16514.5933	24900.6000	15878.3933	9759.7533	3946.9587	2447.1753	541.2927	27.3631	40.9161	47.0413	28.7769	11.1839	3.7834	6.9025
12m	203250.8667	158165.2000	68253.8000	25474.7200	27723.4667	15308.9707	9787.7720	4700.6080	2829.2067	421.1293	34.3464	34.1710	33.4969	38.2746	11.7711	6.9427	6.1812
13.5m	223315.2667	147183.3000	73240.3333	18307.5000	19415.3400	16817.9960	12241.0600	5107.5200	3312.1133	491.4640	30.2491	44.6775	30.0934	31.3248	10.5562	7.1310	6.7254
15m	213913.0000	131685.2533	56807.3533	19350.6333	19163.8000	16851.8600	9541.9467	4958.6660	3081.1467	411.1320	15.2913	45.9400	26.3593	31.9640	17.6408	4.5461	7.1146
16.5m	190010.2667	126683.8000	59955.6667	17204.4067	19365.3733	16534.6620	9219.7293	4383.2880	2614.9740	434.9020	61.2602	53.5961	23.6469	40.2846	25.4706	14.1554	7.6441
18m	205012.8667	121220.2667	54035.2933	19891.8600	16601.1400	16296.9593	8810.4373	3852.9820	2237.2553	437.8953	11.4443	30.0089	22.4033	23.2595	6.9954	10.5168	2.7503
19.5m	193591.0667	138115.4467	51794.4600	15706.3940	21425.6600	16478.1727	8625.0773	4161.3380	2453.6160	367.9940	12.6632	70.2223	22.9141	31.0474	5.4332	9.0507	2.7422
21m	211168.4667	152963.4467	45988.8333	15234.9880	20049.3733	16844.9000	8619.7173	3894.5167	2738.3600	411.8840	74.5941	60.9235	24.4453	36.6878	21.5249	7.3859	4.2205
22.5m	206618.8667	142504.8667	49642.9000	14446.8390	18110.6467	16623.2467	8252.7173	3602.7540	2590.5667	376.0067	75.5841	50.2620	39.3669	39.5451	5.6580	11.7127	2.8831
24m	198211.8667	122205.7200	52382.6333	13900.0000	18507.2533	16586.3253	8010.4373	4186.6713	3025.8467	382.2267	67.3969	53.2282	26.9990	33.6756	11.9516	12.0980	2.2208
25.5m	216847.9333	144774.9800	47082.4733	18431.2800	19837.8000	16321.3153	7797.3173	4591.5867	3002.1267	498.4887	94.4302	48.3083	69.9513	34.7988	30.0950	7.8379	3.3535
27m	213240.0000	116907.7067	51363.3800	16602.4400	20527.3467	15987.5100	7472.9573	4199.5047	2887.1667	521.1813	51.5959	55.2109	59.4202	33.8110	39.3249	13.2583	4.6906
28.5m	203477.3333	126282.6000	59882.7333	16039.6040	32466.0667	15562.1947	7886.3020	5523.4933	3320.9400	660.5867	41.8924	60.1985	59.3264	44.1327	25.3759	10.3893	5.7129
30m	206774.7333	131652.8133	45379.2200	17407.6400	19546.7867	15597.6867	8252.9773	4147.6453	2930.7747	527.1467	68.3130	70.0303	54.0810	36.2873	40.2082	10.1690	4.7818
31.5m	203247.5333	126130.0067	56522.5600	15034.0730	22142.7133	15809.6067	8615.7360	4635.4847	2852.0593	416.9760	99.5930	43.4492	48.0177	32.4406	29.2626	12.5456	2.7422
33m	201736.4000	118998.5333	69892.4667	16160.5200	23421.7200	16368.3773	8827.2110	6135.5400	3023.2867	440.6987	119.3461	45.8072	37.8379	37.7403	46.3259	14.0178	3.0925
34.5m	207172.5333	126244.4867	53286.3000	18764.7067	33829.4667	16907.3067	8816.8590	5001.4433	2698.7893	428.4013	121.2487	53.1423	72.1507	26.6199	44.3993	10.2112	2.9076
36m	229041.2667	115111.1800	45762.4533	16582.2467	21930.3067	15824.5200	8782.0680	3975.1680	2566.4533	365.4167	130.0995	53.6379	41.8560	30.2572	36.5899	16.2935	3.2986
37.5m	216232.1333	127987.0000	55786.4400	14962.5387	21526.4000	15621.1120	8640.1600	4542.5900	2935.1467	526.7600	105.8754	45.4876	26.8667	33.2245	24.1393	16.7971	2.7918
39m	210581.8000	130622.2667	60929.0000	15125.7060	27113.7000	15418.5093	7226.2130	4717.0067	2644.3720	620.5247	45.9076	31.4666	40.5834	23.5309	23.6082	8.0522	2.3305
40.5m	212188.6667	127667.0000	57766.6333	17309.6300	21339.3267	15619.1713	7096.7260	4450.5967	2929.0467	566.8660	109.8586	46.7668	28.6630	18.9822	15.1310	15.8690	2.9078
42m	220649.5333	118875.5267	49506.8533	16085.1800	18774.3000	15059.0533	7354.3900	3942.6153	2614.4687	562.5200	103.2306	42.4605	31.3044	29.8784	14.1817	20.8082	3.0067
43.5m	208352.9333	153721.0467	49259.2133	15034.4000	17204.2133	15064.8587	7891.0360	5019.8667	3344.2800	557.7033	90.6806	50.8914	12.5713	28.2425	14.1047	15.5102	2.8801
45m	201440.4667	144301.7600	79989.2667	15924.9947	21308.0067	15113.6867	9349.8013	6269.7547	3290.9467	574.9067	81.3155	44.5305	9.3683	20.2517	12.5171	10.0318	3.2586
46.5m	198768.1333	166642.3333	75577.6667	17666.7493	23526.9933	16050.9013	8356.7060	6431.2633	3639.6200	571.5967	44.1408	47.4164	12.5659	27.5092	9.4086	4.1123	2.8411
48m	200859.6000	129231.8667	58739.2667	18551.8793	30073.3333	16443.9513	8019.1637	4684.3200	2938.2400	689.2780	58.1852	63.8132	12.0451	26.2142	7.6747	3.6794	3.0707
49.5m	208984.9333	120824.4000	52454.5533	16068.7320	19208.1733	15070.3567	7796.1573	4171.8873	2718.8333	521.5273	59.1057	33.9021	10.6180	22.8284	5.1600	2.7225	3.1582
51m	200337.7333	129808.8000	56560.4533	15139.5174	29132.0000	14909.0007	7225.0773	4441.1113	3107.6867	657.9387	9.6973	48.4749	10.2387	20.9312	3.1931	2.3850	3.8173

Appendix 11: Calculations showing an estimate of the total amount of brine and the estimated content of Na salt that may have passed through Secunda ash dam over the 20 year period

	Base (m)	Top (m)	Mean (m)
Length of Secunda ash dam	1018.95	848.86	933.91
Width of Secunda ash dam	586.85	401.21	494.03
Height of Secunda ash dam			51.00

Total volume of ash disposed at Secunda ash dam over 20 year period = (933.91 m x 494.03 m x 51 m) = **23,530,357.42 m³**

NB: Slurry consists of 5:1 brine: ash ratio

Therefore total volume of brine that went through Secunda ash dam over 20 year period = 23,530,357.42 m³ x 5 = **117,651,787.11 m³**

Since 1 m³ = 1000 L

Total volume of brine that went through Secunda ash dam over 20 year period in litres = 117,651,787.11 m³ x 1000= **117,651,787,111.50 L**

Therefore, approximately **117.65 billion litres of brine** went through Secunda dam in its entire lifetime.

NB: Na concentration in Secunda brine samples = 2355.53 mg/L which means 1 L of Secunda brine contains 2355.53 mg of Na

Therefore dry weight Na content (in mg) in 117.65 billion litres of Secunda brine = (117,651,787,111.50 x 2355.53) = **277,132,314,094,752.00 mg**

Since 1 kg = 1,000,000 mg

Therefore dry weight Na content (in kg) in 117.65 billion litres of Secunda brine = 277,132,314,094,752.00 /1,000,000 = **277,132, 314.09 kg**

which means 277,132,314.09 kg of Na went through Secunda dam in its entire lifetime

Approximately **277 million kg of Na** went through Secunda dam in its entire lifetime

Note: The estimates were done on the assumption that brine was the only feed stream used in ash transportation. The ash dam has a broad base and a narrower top section hence the calculation showing the mean length and the mean width.

Appendix 12: The overall total salt capture capacity of Secunda ash dam calculated using data obtained from the total metal content (TMC) analysis determined by acid digestion and ICP-OES analysis

Element	Fresh ash content (weight %)	Weathered ash content (weight %)	Difference* (salt capture capacity) (weight %)
Si	47.50	44.27	-3.23
Al	27.65	27.67	0.02
Ca	13.23	12.62	-0.61
Fe	3.28	4.96	1.68
Na	3.41	3.65	0.24
Mg	1.81	3.35	1.54
K	1.65	1.78	0.13
Sr	0.82	0.96	0.14
Ba	0.54	0.59	0.05
Others**	0.12	0.15	0.03
Overall total salt capture capacity of Secunda ash dam			**-0.01**

*Difference = Weathered ash content (weight %) - Fresh ash content (weight %)

**Others: As, Cr, Cu, Mn, Mo, Ni, Pb and Zn