CHEMICAL, PHYSICAL AND MORPHOLOGICAL CHANGES IN WEATHERED COAL FLY ASH: A CASE STUDY OF BRINE IMPACTED WET ASH DUMP

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Abstract

Fly ash is the major waste material produced by power plants in the combustion of coal to generate electricity. The main constituents of fly ash are Si, Al, Fe and Ca with smaller amount of S, Mn, Na, K, and traces of many other elements such as Co, Cd, As, Se, Zn, Mo, Pb, B, Cu and Ni. Fly ash is usually disposed either by dry or wet disposal methods. These disposal methods have raised major environmental concerns due to the potential leaching of chemical species from the ash heap by ingress of rainfall and brine used to transport the fly ash to the dam. This study focuses on the changes in chemical composition, morphology and mineral phases due to weathering, of coal fly ash co-disposed with brine over 20 years at Sasol Secunda ash dump in Mpumalanga Province, South Africa. The design and operation of the Secunda ash dump presupposes that the ash dump may act as a sink for the salts which originated from chemicals used for normal operation in the plants. The majority of these salts come from the brines generated during desalination and raw water regeneration. The aim of this study is to ascertain if the ash dump could serve as a sustainable salt sink.

Samples were drawn along the depth of two drilled cores (S1 and S3) from the weathered Secunda ash dump and analysed in conjunction with the fresh (un-weathered) Secunda fly ash taken from the fly ash hoppers for comparative analysis. Scanning electron microscopy (SEM), X-ray diffractive (XRD) and X-ray fluorescence (XRF) spectrometry were employed to obtain a detailed morphological, mineralogical and bulk chemical composition of all the samples. Pore water analysis was used to determine the pH, EC and moisture content of fly ash samples. A five step sequential chemical extraction procedure was used to establish the geochemical association of particular elements with various mineral phases. The total acid digestion test was also used to determine the total elemental compositions of the Secunda fly ash samples.

The SEM results showed that the fly ashes consist of irregular and numerous spherically shaped particles. Changes (encrustations, etchings and corrosion) in the morphologies of the weathered ash particles were also observed. The XRD results revealed quartz, mullite, lime and calcite as the major mineral phases. Other minerals identified in very minor quantities in the drilled Secunda ash core that were dried prior to analysis were halite, kaolinite, nitratine, bassanite, microline. and hydrophitte. These phases may have formed during sample handling. XRF investigation revealed that the major oxides present in the dumped ash samples were SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, Na_2O, TiO_2 and the minor elements present were K_2O, P_2O_5, SO_3 and MnO. The sum of the mean values of the % composition of SiO_2, Al_2O_3, and Fe_2O_3 was 70.19 %, and 72.94 % for the two drilled ash core samples (S1 and S3) respectively, and 78.67 % for the fresh ash which shows the significant alteration of the Si, Al and Fe content in the ash matrix over time. The fly ash is classified as Class F using the ASTM C 618 standards. The loss on ignition (LOI) which is an indication of unburned carbon or organic content was 4.78 %, 13.45 % and 8.32 % for the fresh ash, drilled ash cores S1 and S3 respectively. The high LOI values for the drilled ash cores could indicate high hydrocarbon content in the ash dump because of co-disposal practises where hydrocarbon waste are included in the brine stream for disposal on the ash. While the ash samples from the surface appeared dry, moisture content (MC) analysis showed that there is considerable water entrained in the fly ash dump. The fresh ash MC was 1.8 % while core S1 ranged from 41.4 – 73.2 %; core S3 ranged from 21.7 – 76.4 %. The variations in the MC values can be attributed to uneven flow paths due to inconsistent placement conditions or variations in ambient weather conditions during placement. The fresh fly 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 the drilled ash core S1 (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. Core S3 (n=66) had pH of 11.04±0.09; EC was 0.99 ±0.03 and TDS was 0.57 ± 0.01. The changes in pH values can be attributed to the dissolution and flushing out from the dump basic alkaline oxides like CaO and MgO These variations in pH values shows that the fly ash is acidifying over time and metal mobility can be expected under these conditions. The large decrease of EC in the drilled ash cores S1 and S3 compared to the fresh ash indicated a major loss of ionic species over time in the ash dump.

The sequential extraction scheme revealed that the elements Al, Si, Ca, Mg, Ba, Sr, Fe, Mn, Na, K, As, Pb, Cr, Mo, Cu, Ni and Zn are present in Secunda fresh and weathered fly ash and are partitioned between the water soluble, exchangeable, carbonate, iron and manganese, and residual fractions of the coal fly ash. It also showed that the trace elements As, Pb, Cr, Mo, Cu, Ni and Zn do not show permanent association with particular mineral phases as a continuous partitioning between different mineral phases was observed in the weathered drilled core. Generally, all the elements had the highest concentration in the residual fraction. But it was evident that the labile phase (water soluble, exchangeable and carbonate fractions) had fairly high concentrations of Si (± 6.5 %), Al (± 6.5 %), Ca (±10 %), Mg (± 5.5 %), Ba (± 7.5 %), Sr (± 7.5 %), Na (± 12 %) and K (± 12 %) for the Secunda drilled ash core (S1 and S3) and fresh fly ash samples. This indicates that these species can leach easily upon water ingress and could pose a danger to the environment. Na and K had the highest concentrations leached out in the labile phase in all the ash samples. The amount of Na leached out of the drilled Secunda ash core in the labile phase was 13.21 % of 18584.26 mg/kg in the five geochemical phases of core S1; and 9.59 % of 11600.17 mg/kg in the five geochemical phases of core S3 while the fresh Secunda fly ash leached out 11.28 % of 16306.30 mg/kg of Na in the five geochemical phases.

This study provided significant insight into the pore water chemistry, morphology, mineralogy and chemical composition and the elemental distribution pattern of the major and trace elements in the Secunda fly ash and weathered drilled Secunda ash core S1 and S3. Though results from XRF analysis and the sequential extraction scheme shows that Na, K, S, Ca and Mg were slightly captured from the co-disposed brine by the Secunda fly ash, these species were however released in the labile phase. Hence there was no significant retention of these species in the ash dump. The amount of these species retained in the weathered ash were (0.26 % and 0.55 %) for Na, (0.02 % and 0.34 %) for K, (0.08 % and 0.06 %) for S, (0.94 % and 0.01 %) for Ca and (0.37 % and 0.96 %) for Mg in drilled ash cores S1 and S3 respectively. This poor retention of Na K, S, Ca and Mg which are major components of Sasol Secunda brine in the drilled ash cores S1 and S3 clearly shows the unsustainability of the Secunda fly ash dump as a salt sink.

Keywords

Coal fly ash

Coal combustion

Thermal power plants

Fly ash composition

Sequential extraction

Speciation

Leaching behaviour

Mineralogy

Major and trace elements

Declaration

I declare that "Chemical, physical and morphological changes in weathered coal fly ash: A case study of brine impacted wet ash dump" is my own work, has not been submitted before for any degree or examination in any other university, and that all the sources I have used or quoted have been indicated and acknowledged as complete references.

Full Name: Chuks Paul Eze November 2011

Signed…………………

Dedication

To Chukwuma, Isioma and Chukwuwatem, you are my reason for undertaking this journey

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List of Abbreviations

ASTM	American Society for Testing and Materials
EC	Electrical Conductivity
TDS	Total Dissolved Solids
IC	Ion Chromatography
ICP-OES	Inductively Coupled Plasma Optical Emission Spectrometry
XRF	X-ray Fluorescence
XRD	X-ray Diffraction
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy
PPM	Parts per million
LOI	Loss on ignition
CTL	Coal to a Liquid Fuel
LPG	Liquefied Petroleum Gas
NO_x,	Oxides of Nitrogen
SO_x	Oxides of Sulphur
BBL/D	Billion barrel per day

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Chapter One

Introduction

1 Introduction

The chapter introduces coal fly ash; its genesis, composition and properties are briefly overviewed in sections 1.1 and 1.2. Details of the area of study, research aims and objectives, research questions and approach are also presented in this chapter (sections 1.3 to 1.7). The scope and delimitations of this study is also presented in section 1.8. The chapter ends with a preview of the subsequent chapters in this thesis in section 1.9.

1.1 Coal fly ash

South Africa has an abundant coal reserve which is utilized in generating electricity and chemical production. South African Coal, Oil and Gas Corporation (Sasol), which is one of Africa's major producers of chemicals and liquid fuels, and the Electricity Supply Commission (Eskom), South African major power utility company, are amongst the biggest consumers of coal in South Africa (Bada and Potgieter-Vermaak, 2008). The Sasol-Syngas plants are located in Secunda in Mpumalanga province and Sasolburg in the Free State province. The Eskom coal fired power plants are located in the surrounding area of the coalfields in the northern part of the country (Gauteng, Mpumalanga, Limpopo and Free State). The major residue from this combustion plants is fly ash. Millions of tons of fly ash are produced each year from the combustion of coal to produce steam for the syngas processes in the Sasol plants and to generate electricity in the Eskom power plants. The management of this combustion waste is of major concern because of the huge amount that is produced annually and the environmental issues arising from its disposal.

Coal fly ash is a particulate waste product that results during the combustion of pulverised coal to generate electricity. This particulate matter which travels with the flue gas must be removed prior to releasing it up the stack and into the atmosphere to avoid pollution. The particulate (fly ash) that is removed from the flue gas either by electrostatic precipitators or bag filters is collected in hoppers. This major waste material (fly ash) produced from the combustion of coal has been defined as a "complex inorganic-organic mixture with distinctive poly-components, mixed and of variable composition containing closely linked and finely scattered solid, liquid, and gaseous components" (Vassilev and Vasssileva, 2007).

Fly ash is mainly disposed through either dry or wet disposal methods. In dry disposal, the fly ash is conditioned with brine and then transported by truck, chute or conveyor at the site and disposed by constructing a dry embankment; the ash heap is then irrigated with waste water for dust suppression. In wet disposal, the fly ash is transported as slurry through pipes and disposed of in impoundments that are called ash ponds or dams. The discharge water from the pond is collected and discharged into a river or a drain (Sushil et al., 2006). Various environmental risks are associated with fly ash disposal; these include air pollution and loss of arable land. Also soil and ground water contamination resulting from the leaching and mobilization of toxic elements and other non-degradable metals and chemical species from the ash dump. The leaching is due to the chemical interaction of the fly ash with air and percolating rain water or the water from the ash slurry or that is used for dust suppression (Vadapalli et al., 2010; Potgieter-Vermaak et al., 2005).

1.2 Properties and chemical composition of coal fly ash

The properties of fly ash depend on the physical and chemical properties of the coal origin, the coal particle size, the combustion process, and the type of ash collector used (Adriano et al., 1980). The minerals present in the coal dictates the elemental composition of the resultant fly ash. The mineralogy and crystallinity of the ash is also dictated by the boiler design and operation (Jankowski et al., 2006; Vassilev and Vasssileva, 2007; Sočo and Kalembkiewicz, 2009).

Although the chemical composition of fly ash from various sources varies, it still consists of the same basic chemical constituents but in different concentrations. The main constituents of fly ash are silica, aluminium, iron and calcium with smaller amount of sulphur, magnesium, alkalis, and traces of many other elements such as Co, Cd, As, Se, Zn, Mo, Pb, B, Cu and Ni (Cho et al., 2005). Several studies on the mineral phases of fly ash show that it consists mainly of aluminosilicate glass matrix in addition to crystalline mullite and quartz as the major mineral phases (Mattigod et al., 1990). Elements such as As, Na, Mg, K, Sr, B, Mo may occur as part of the crystalline phases within the aluminosilicate glass, or as coatings deposited on the surfaces of the individual particles by condensation of elements liberated from the coal into the furnace gases during combustion. The majority of the elements in fly ash are considered to occur in both inorganic and organic form, and each element has prevailing resemblance and link to some minerals and phases in coal. Thus an in depth understanding of their phase-mineralogical and chemical composition is required to fully understand the different characteristics associated with fly ash utilization and disposal (Fatoba, 2008; Gitari et al., 2008; Ward et al., 2009; Vassilev and Vassileva, 2006).

The weathering of coal fly ash results in the leaching and mobilisation of chemical species in the fly ash (Mattigod et al., 1990). The investigation of the mobility of potential pollutants (chemical species) due to ash leaching has been the focus of several studies in order to understand the factors that determine the mobility of chemical species from coal fly ash to the environment. The pattern of mobility of the species is important in evaluating the potential impacts of fly ash weathering on the environment. The potentially toxic chemical species leached from fly ash can contaminate soil, ground and surface water (Praharaj et al., 2002). Thus the study of ash leaching is significant in understanding the environmental impacts linked to the ash disposal methods and long term ash weathering patterns. The leaching behaviour of major and trace elements in fly ash varies with the properties of the ash such as pH of its leachate, its composition, the mineral phase association, the methods employed in studying the leaching process, and the distribution and form of the trace elements in the coal combustion by-products (Bhattacharyya et al., 2007).

1.3 Study Area

The Sasol complex in Secunda, South Africa operated by Sasol Synfuels (Pty) Ltd is the world’s largest commercial coal to liquids (CTL) facility and it utilizes low rank bituminous coal in its gasification and combustion process to produce synthesis gas and steam respectively. Sasol utilizes approximately 28 million tons of coal annually (70% of the coarse coal feedstock) for its gasification process at Sasol Synfuels in Secunda. The remaining (a finer coal fraction- 30%) is used in steam and electric power production. A mixture of coarse and fine ash particles is formed as a by-product of the gasification process and fly ash is the by-product of the combustion process (Matjie et al., 2005, Hlatshwayo et al., 2009). The Secunda ash dump core samples taken from the wet disposal ash dump which were used in this study are made up of 87% fly ash from the combustion of pulverized coal to produce steam and electric power and 13% fine ash from the gasification process (Pretorius, pers comm, 2010). The particle size of the fine ash being dumped ranges between 20 ≤ 50 µm. The ash was pumped to the ash dam as slurry of 5:1 water/ash ratio using the highly saline stream that was generated from the water treatment processes in the Secunda plant. The dump site was created in 1989 and dumping stopped in 2009. The oldest layer at the bottom of the Secunda dump is 21 years old as at the time of study (2010) and the most recent at the top being 1 year old.

Figure 1.3.1: Map of the study area (Secunda) in Mpumalanga province, South Africa. (http://www.bookinafrica. Com/travel-to-Secunda/)

Sasol Secunda was selected for this study because the plant employs the wet method for its ash disposal; the ash is transported in slurry form using high saline stream originating from the water treatment processes in the plant to pump the ash to the dump (Nyamhingura, 2009). Thus the saline effluent is co-disposed with the ash. The design and operation of this dam presupposes that the ash dump may act as a sink for the salts which originated from chemicals used for normal operation in the plants, with the majority of these salts coming from the brines generated during desalination and raw water regeneration.

This study analysed the chemical composition, morphological changes and the mineral phases of the weathered Secunda fly ash with a view to understand the changes in the chemical, physical and morphological properties of the ash dump that evolved from the weathering process over the years.

1.4 Problem statement

In South Africa millions of tons of fly ash are generated annually by coal-fired power plants in order to meet the large demand for industrial and domestic energy. In spite of the numerous environmental problems related with coal combustion, it will continue to be a major source of electrical power generation for many years to come. An estimated 36.7 million tons (www.eskom.co.za) of fly ash was produced in 2010 due to coal combustion in South Africa of which only about 1.8 million tons is utilized beneficially annually. The rest is disposed in ash dams or dry disposal sites which have led to various environmental issues owing to the leaching of toxic metals, and other chemical species from the ash dump by rainfall or groundwater (Gitari et al., 2008). The management of this combustion waste is of major concern and requires the proper understanding of the weathering characteristics of fly ash, because the huge amount that is disposed as waste cannot be separated from nature's weathering cycle. The weathering of fly ash results in changes in the physical, chemical and mineralogical properties of the ash. Some of these changes include the formation of secondary minerals (Yeheyis et al., 2009), decrease in the pH and EC values of the pore water (Ward et al., 2009, Baba et al., 2008, Gitari et al., 2009, Ugurlu, 2004) and reduction of soluble salt content (Brower, 1985) which may have significant effect on the leaching and mobilization of the fly ash species (Zevenbergen et al., 1999, Yeheyis et al., 2009). The changes in the chemical, physical, morphological properties and phase transformation studies are thus vital in predicting the environmental impact associated with fly ash disposal techniques and uses.

In the management of this combustion by-product the focus should not only be on the prevention of environmental pollution, but also on methods that can be used to produce or manufacture value-added products from stored fly ash. In order to achieve these objectives, an understanding of the quality and homogeneity of the ash would be required so as to achieve optimum utilization and effective disposal methods of fly ash. The chemical, physical, morphological properties mineral phase transformations of fly ash are the fundamental property that must be thoroughly investigated, because the accessibility and mobility of elements occurring in fly ashes depend on the physicochemical and mineralogical forms of the elements. Moreover the dangers linked to the disposal of coal fly ash in the natural environmental setting, with regards to the mobility and leachability of environmentally harmful species is mainly determined by the physicochemical conditions of the fly ash dump; the sum of leachable metal content in fly ash; and the distribution or mineralogical fractionation of metals (Jegadeesan et al., 2008).

The chemical compositions, leaching behaviour, utilization, and mineralogy analysis of South African fly ash have been the focus of numerous recent studies, (Fatoba, 2008, Gitari et al., 2008; Somerset et al., 2005; and Matjie et al., 2006). Most of these studies have been based on fresh ash samples without any relevant attention to the changes in the mineralogy and mobility of the major and trace species in the brine impacted fly ash that is stored in wet ash dumps over the long term. This study will focus on Sasol Secunda fly ash that was co-disposed with brine in order to ascertain whether the ash dump could serve as a sustainable salt sink. The purpose of co-disposing this ash with brine was originally aimed at using the ash as a sustainable salt sinking media. Parallel studies on Secunda's coal fresh ash will also be carried out for comparative purposes. The comparative analysis of the samples of fresh ash with that from the weathered drilled Secunda ash cores was to enable determination of the extent of the changes in the chemical, physical properties and mineral phase arising over time from weathering of the fly ash sample that was co-disposed with brine.

1.5 Aims and objectives of the study

The aims of this study are:-

1) To determine the effects of wet ash handling and of weathering on the chemical composition, morphological properties and mineralogical composition of coal fly ash

2) To determine the physiochemical forms in which species exists in the fresh and weathered coal fly ash

3) To evaluate the changes in these properties of the coal fly ash that was co-disposed with brine after some years of weathering.

Hence the specific objectives of this research are:-

- To characterize the fly ash samples (freshly sampled and samples from drilled ash cores S1 and S3) in order to determine the differences in chemical and mineralogical compositions between fresh fly ash and weathered brine impacted ash.

- To determine the physiochemical form and mineralogical phase association in which the mobile and stable components exist in the fresh fly ash and drilled core samples.

- To evaluate the amounts and mobility patterns of major and trace elements in the weathered ash core samples compared to fresh ash in order to understand the relative distributive weathering patterns of the various elements as a function of the depth profile of the cored ash dump.

- To analyse the changes in mineralogy of the weathered ash core samples compared to fresh ash in order to determine if the wet ash dump is actually a sustainable salt sink.

- To recommend appropriate good operational practices for the proper management of the wet ash handling and dumping systems.

1.6 Research Questions

This study intends to provide answer to the following questions;

- What are the major influences causing weathering and changes in the chemical composition of coal fly ash co-disposed with brine?

- What are the geochemical factors that control the mobilization of the constituents of the weathered fly ash?

- Can secondary mineral phases be formed in the weathered ash, are the amounts significant and are such secondary mineral phases stable?

- In what physiochemical forms or mineralogical association do the components of the ash exist?

- Can the wet disposed fly ash dump act as a sustainable salt sink to capture an excess salt load?

1.7 Research Approach

Several experiments involving morphological, spectroscopic and chemical characterizations and selective sequential extraction were carried out on the fresh Secunda fly ash and drilled ash core (S1 and S3) samples in order to achieve the objectives of this research. The research was approached by using the following specific techniques:

- Pore water analysis was used to determine the pH, EC and moisture content values in pore water along the depth of the two drilled Secunda ash cores S1 and S3 which had been chosen for investigation and results were compared with the fresh ash sample in order to determine the relative effect pH may have on readily soluble species.

- X-ray fluorescence (XRF) analysis was used to determine the elemental composition of the fresh Secunda fly ash and drilled ash core samples, to determine distributive patterns of weathering processes upon elemental composition.

- X-ray diffraction (XRD) analysis was used for the study of mineralogical phases and mineral composition of the fresh Secunda fly ash and drilled ash core samples, in order to determine the presence and abundance of any secondary mineral phases that may form due to mineralogical transformation over time.

- Scanning electron microscopy combined with energy dispersive X-ray spectrometry (SEM-EDX) was used to present detailed imaging information about the morphology and surface texture of individual particles, as well as qualitative elemental composition of samples. In order to characterize the morphological features in the fresh Secunda fly ash and drilled ash core samples.

- A five step sequential chemical extraction procedure modified from the proposed method of Tessier et al., (1979) was used in this study to establish the geochemical association of particular elements with various mineral phases.

- Total acid digestion test was used to determine the total elemental compositions of the fresh Secunda fly ash and drilled ash core samples S1 and S3, in order to draw comparisons and detect weathering patterns in the drilled core samples.

- The inductively coupled plasma - optical emission spectrometer (ICP-OES) was used in determining the concentrations of the major elements and trace elements in the leachates from the sequential extraction analysis and total acid digestion test.

1.8 Scope and delimitation

Extensive studies were done on the chemical composition and leaching behaviour of Sasol Secunda fresh fly ash (Fatoba, 2007), and weathered fly ash in a dry ash dumping system (Gitari et al., 2009). But, the effect of weathering of coal fly ash co-disposed with brine at the Sasol Secunda ash dam had not been studied. The characterization of the weathered fly ash co-disposed with brine in comparison with fresh fly ash was therefore investigated and sequential extraction experiments were conducted on the weathered ash core samples to understand and quantify the partitioning and mobility of elements in different mineral phases and determine the movement of metal species down the ash dump that had been placed using a wet ash handling system. The brine that was disposed at Sasol Secunda power station contains hydrocarbons. These organics have the potential to inhibit mineralization in the fly ash/brine dump. However, this study did not cover the effects of organics because of the large scope of the study.

1.9 Outline of the subsequent chapters

Besides this introductory chapter this thesis also consists of the following chapters:

Chapter 2: Literature review

Chapter two contains the review of different literature focusing on the composition, mineralogy, and uses of coal; a review of the chemical and physical properties of coal fly ash; types of fly ash, ash/water interaction chemistry and ash disposal techniques. The environmental impacts and utilization of fly ash are also overviewed.

Chapter 3: Sampling, experimental and analytical Methods

The outline of sampling, experimental and analytical methods used in this study to address the research objectives are presented in chapter 3. A detailed outline of the geophysics of the sampling site and how the Secunda fly ash samples were collected, stored and analysed are presented in this chapter.

Chapter 4: Characterization and pore water analysis

Chapter 4 presents and discusses the results obtained by applying the methods specified in chapter 3. In this chapter the results are presented of SEM/EDX, XRF and XRD characterization of the fresh fly ash and drilled cores samples; the results of the pore-water chemistry are presented, discussed and compared to that reported in literature and significant findings are highlighted.

Chapter 5: Mobility and partitioning patterns of elements

In this chapter the results obtained from the sequential extraction procedures are presented and discussed with a view to understanding and quantifying the liabilty and mobility patterns of the chemical species in the Secunda ash dam and geochemical association of particular elements is highlighted as a function of the weathering process.

Chapter 6: Conclusion

The conclusions reached from the investigation of the effects of co-disposing brine with fly ash are presented. The effect of weathering on the mobility of species in the fly ash dam is used to inform potential operational guidelines that may be needful in the future management of the ash dam and recommendations are made for future work.

Chapter Two

Literature Review

2 Introduction

The proper understanding of the chemical composition and structure of minerals in coal is necessary in order to comprehend the mineral transformation or agglomerate formation during its combustion or long term storage of ash after combustion (Van Dyk et al., 2009). Hence this chapter will first present a literature update on coal in section 2.1 before delving into the main study on coal fly ash in section 2.2 to 2.12. A brief overview of brine, its composition, and disposal is presented in section 2.13. The chapter ends with a summary of the major findings from the review of the literature.

2.1 Coal

Coal can be defined as a brown or black carbonaceous sedimentary rock (Snyman, 1989) that is derived mainly from plant remains that had undergone peatification and coalification (Teichmüller, 1989). It occurs naturally in seams or veins in sedimentary rocks and the seams thickness vary in different formations (Stranges, 2008).

Coal developed from the gathering and transformation of plant material that originated in swamps or other wet environments which decomposed to form layers of peat that were buried under layers of sediments over long periods of time. Under this increased pressure and ensuing higher temperatures the peat was transformed into coal (Daintith, 2004). The presence of certain plant components in coal and the presence of organic compounds that have similar structures to compounds that exist in plants attest that coal is formed from plants (Schobert, 1989).

Coal is an intricate combination of materials, and the combination can vary significantly from one formation or deposit to another. These differences result from the different types of vegetation from which the coal originated; the depths of burial, the temperatures and pressures at those depths; as well as the length of time the coal has been forming in the deposit (Carlsen et al., 1995). The characteristics of the precursor plant, the quantity of inorganic materials and the type, extent of the biochemical and geological processes that accounts for coal formation predetermines the chemical and physical characteristics of coal (Vassilev and Vassileva, 1997; Popovic et al., 2001).

Coal is one of the world's major important and rich energy sources. From its introduction as a fuel for heating and cooking, to its use in generating electricity and as a chemical feedstock, coal, along with crude oil and natural gas, has remained an important source of energy (http://www.chemistryexplained.com/Ce-Co/Coal.html). According to the Eskom report, the South African coal reserve is approximately 53 billion tons, and coal mining produces an average of 224 million tons of commercial coal yearly which accounts for South Africa being classified as the fifth largest coal producing country in the world (www.eskom.co.za). 25 % of this is sold internationally, while 53 % is used to generate electricity in South Africa, with the remainder supplied to various local industries. That Eskom is the 7th largest electricity generator in the world and Sasol has the world largest and only commercial coal to liquid fuel plant in Secunda South Africa (Mangena, 2009), portrays the important role that the coal reserve plays in the South African economy (www.eskom.co.za/live/content.php?category_id=121).

2.1.1 Coal Classification

Coal is usually classified according to type, rank and grade, Due to the extensive difference in the properties of coal, this system of classification is required to differentiate between coals that have similar properties. The difference in type, grade and rank are linked to the three stages of coal formation which results from the difference in the chemical composition of the coal precursor plant, and differences in diagenetic changes and level of metamorphism (Snyman, 1989). The varying amount of minerals in a coal deposit may also have a significant effect on its properties and classification as well as on the resultant ash after combustion.

The coal type is determined by the nature of the original plant material and its level of alteration during the diagenetic stage of coal formation. There are two recognized coal types, woody and sapropelic coal. Woody coals are formed from plants remains; and sapropelic coals are derived from algae, spores and finely divided plant materials (Daintith, 2004).

Coal rank shows the extent of coalification that has occurred for a particular coal. Coal rank is one of the major factors that determine the utilization characteristics of a given coal (Bend, 1992). The common ranks of coal are anthracite, bituminous, sub-bituminous, and lignite. Anthracite is low in volatile matter and mostly consists of carbon; bituminous coal contains significant amounts of volatile matter and typically exhibit swelling or caking properties when heated. Sub-bituminous is a younger coal and contains in addition to the volatile matter, significant amounts of moisture; and lignite is the youngest form of coal and is very high in moisture content resulting in a much lower heating value than the other types of coal. Since there is a continuous increase in carbon content with increasing maturation, and since greater degrees of maturation usually require longer times, the rank of a coal provides a qualitative indication of its age and carbon content (Schobert, 1989).

Coal grade is defined by the various impurities contained within the deposit, chemical composition, ash content, geological origin and age. These impurities include sediment and other non-organic matter (Boggs, 1995; Petrik et al., 2005). The mineral ash content, which is the amount of inorganic material that remains as residue after combustion of the coal is used to determine the grade; the higher the amount of inorganic residue, the lower the grade of the coal (Sellakumar and Conn, 1999).

South African coals are usually low grade with about 30 – 35% ash (Snyman and Botha, 1993). As a result of its fairly high clay mineral and quartz content (that results in high fusion temperatures), which is beneficial if the coal is to be used for steam-raising purposes, Sasol and Eskom, South Africa’s major coal consumers, are able to utilize these coals to produce steam for use in the production of liquid fuel and electricity generation respectively (Snyman and Botha, 1993).

2.1.2 Coal Composition and mineralogy

The rock called coal which originates from geological processes is composed of carbon, hydrogen, oxygen, silicon, aluminium, nitrogen, sulphur and iron as the major elements being greater than 1wt % respectively. The minor (1-0.1wt %) elements are calcium, potassium, magnesium, titanium, sodium, and occasionally phosphorus, manganese, barium, and strontium. The other recognised (<0.1wt %) elements in coal such as Hg, Zr, Zn, Cd, As, Pb, Mn, and Mo are mainly in trace concentrations (Vassilev and Vassileva, 1997; Ruch et al., 1998). Coal is an intricate heterogeneous mixture of organic matter, with a smaller amount of inorganic matter and fluids which occur in pores within and between the solid phases of the organic and inorganic matter. The elements found in coal may be present in both the organic and inorganic constituent and influences the rank of the coal (van Alphen, 2007); the volatile components in coal prior to mining are mainly moisture and methane.

The organic matter comprises mostly of non-crystalline constituents such as petrographic ingredients (lithotypes, microlithotype groups, and macerals), the lithotypes consist of clarain and vitrain while the microlithotypes are mostly clarite and vitrite (Vassilev et al., 1994). A wide range of macerals occur, but three main groups of macerals can be distinguished: the vitrinite group, the liptinite (or exinite) group, and the inertinite group, based on their general chemical, physical, optical, and technological properties (Falcon and Ham, 1988). The organic components are crucial in the coal classification (e.g. rank and type), and to its assessment in different beneficiations processes because all of the benefits derived from coal are derived essentially from the maceral constituents (Ward, 2002).

The inorganic matter in coal comprises different solid, liquid and gaseous phases of allothigenic (formed elsewhere than in the rock where it is found) or authigenic (formed or generated in the rock where it is found) origin. The inorganic matter can be described as having three categories of fundamentally different constituents, i.e. dissolved salts and other inorganic substances in the coal's pore water; inorganic elements integrated within the organic compounds of the coal macerals; and distinct inorganic particles representing exact mineral components (Ward, 2002). The mineral matter which forms part of the inorganic matter in coal and consists of different mineral species that are generally crystalline belong to the last category (Vassileva and Tascón, 2003). A vast variety of minerals are present in coals, with most of them occurring only sporadically or in trace amounts.

Studies of various coal literature reveals that the common inorganic minerals found in coal are quartz, aluminosilicate and clay minerals, carbonates minerals, disulphide and sulphate minerals, and feldspars (Ward, 2002; White and Case, 1990; Vassilev and Vassileva, 1996). Quartz (SiO2) has been reported as abundant in all coals. The generally reported clay minerals in coal are illite $[(OH)_4K_2(Si_6{\bullet}Al_2)Al_4O_{20}]$, kaolinite $[(OH)_8Si_4Al_4O_{10}]$, and interstratified illite/smectite. These minerals are the most commonly occurring constituent of coal and of the strata associated with the coal (Schweinfurth, S., 2002). Disulphide minerals are mainly pyrites (cubic FeS_2) and marcarsites (orthorhombic FeS_2), although sphalerite (ZnS) and galena (PbS) are found in significant quantities (Renton, 1986). The sulphate minerals are usually gypsum ($CaSO_4.2H_2O$), bassanite ($CaSO_4$.) and anhydrite (Renton, 1986). The most frequently reported carbonate minerals from the majority of the coals in the world are calcite ($CaCO_3$), dolomite ($CaCO_3{\bullet}MgCO_3$), ankerite ($2CaCO_3{\bullet}MgCO_3{\bullet}FeCO_3$) and siderite ($FeCO_3$). The occurrence, abundance and source of mineral matter which forms part of the inorganic matter in coal (Vassileva and Tascón, 2003), depend on the coal rank to a certain level.

There are several elements known to be of high toxicity in coal, most of them present in trace amounts (>0.1wt %). The increasing interest in the mode of occurrence and distribution of these trace elements in coal arises from environmental concerns in coal beneficiations processes and waste products (Gluskoter, 1975). During the coal combustion process, trace elements are partitioned between ash and vapour, this partitioning depends on the operating conditions, furnace design and the mode of occurrence of the trace elements (Martinez-Tarazona and Spears, 1996). Studies on occurrence and distribution of trace elements in coal showed that their affinities, which differ from one deposit to another have a significant impact on the behaviour of these elements during combustion (Querol et al., 1995).

2.1.3 Coal Combustion Process

Coal combustion in power plants provides approximately 42 % of the world's electricity (IEA, 2010) with China, United States of America (USA), India and Russia leading in the consumption of coal (www.nationmaster.com). Coal accounts for 79 % of total primary energy consumption in China. USA on the other hand generates 49 % from coal, while in South Africa, coal accounts for 92 % of its electricity (IEA, 2010). Since most use of coal lies with its combustion (Wagner, 2008) to generate electrical power, which subsequently leads to the generation of fly ash, it will be appropriate to understand the mineral transformations that occur in the coal combustion process since it dictates the physical and chemical properties of the fly ash remaining as combustion residue (Shirai et al., 2009).

Coal combustion is the generation of thermal energy due to the oxidation of the combustible constituents of coal in the presence of heat. An external heat source is initially required to start the process but the process is sustained by the continuing heat supplied by the highly exothermic oxidation process. During this combustion process which is a series of reactions involving oxidation and heat generation process the constituents of the coal are thermally altered. The organic matter is devolatilized into solid carbon-rich residues known as char or coke; that are also oxidized and consumed until it is depleted at elevated temperature (Falcon and Ham, 1986).

The coal rank and the petrographic composition of the organic constituent are the major factors determining the coal reactivity in combustion processes (Sharonova et al., (2008). The inorganic species are liberated and transformed into a complex mixture of solid, molten, and volatile species. Clay minerals are dehydrated and decomposed, while carbonates are calcined and sulphides are oxidized. Sulphates and chlorides are formed from the interactions between combustion gases and the alkali and alkali earth metals in either the maceral or mineral components. The trace metals that are usually volatilized during the combustion are consequently concentrated on the surface layer of the fly ash particles (Steenari et al., 1999).

These liberated and transformed inorganic species also give rise to slagging and fouling deposits, corrosion, pollution, and other problems. Although such problems are usually associated with the combustion of coal to produce electrical power, they are also common in coal gasification and liquefaction, coke making, and iron production (Huffman and Huggins, 1986). Vassileva and Vassilev, (2005), summarized the various physico-chemical processes occurring during coal combustion as oxidation and combustion of organic matter, transformation of mineral and inorganic solid phases, reactions between minerals and phases, and processes in solutions and melts.

2.1.4 Uses of Coal

The greatest use of coal lies with coal combustion in producing heat and generating electricity. Coal is also an important source of raw materials for manufacturing. Its destructive distillation (carbonization) produces hydrocarbon gases and coal tar, from which drugs, dyes, plastics, solvents, and numerous other organic chemicals can be synthesized.

2.1.4.1 Power Generation

Coal is used in power stations to generate electricity, which plays a very important role in human development. It lights houses, buildings, streets, provides domestic and industrial heat, and powers most equipment used in homes, offices and machinery in factories. The process of converting coal into electricity has multiple steps, Coal is first ground to a fine powder in a pulveriser, which increases the surface area and allows it to burn more quickly. The pulverized coal is then mixed with hot air and blown into the combustion chamber of a boiler where it is burnt at high temperature (1400^{o}C). The hot gases and heat energy produced converts water – in tubes lining the boiler – into steam. The high pressure steam is released into a turbine containing thousands of propeller-like blades. The steam pushes these blades causing the turbine shaft to rotate at high speed. A generator is mounted at one end of the turbine shaft and consists of carefully wound wire coils. Electricity is generated when these are rapidly rotated in a strong magnetic field. After passing through the turbine, the steam is condensed and returned to the boiler to be heated once again (World Coal Institute, 2009)

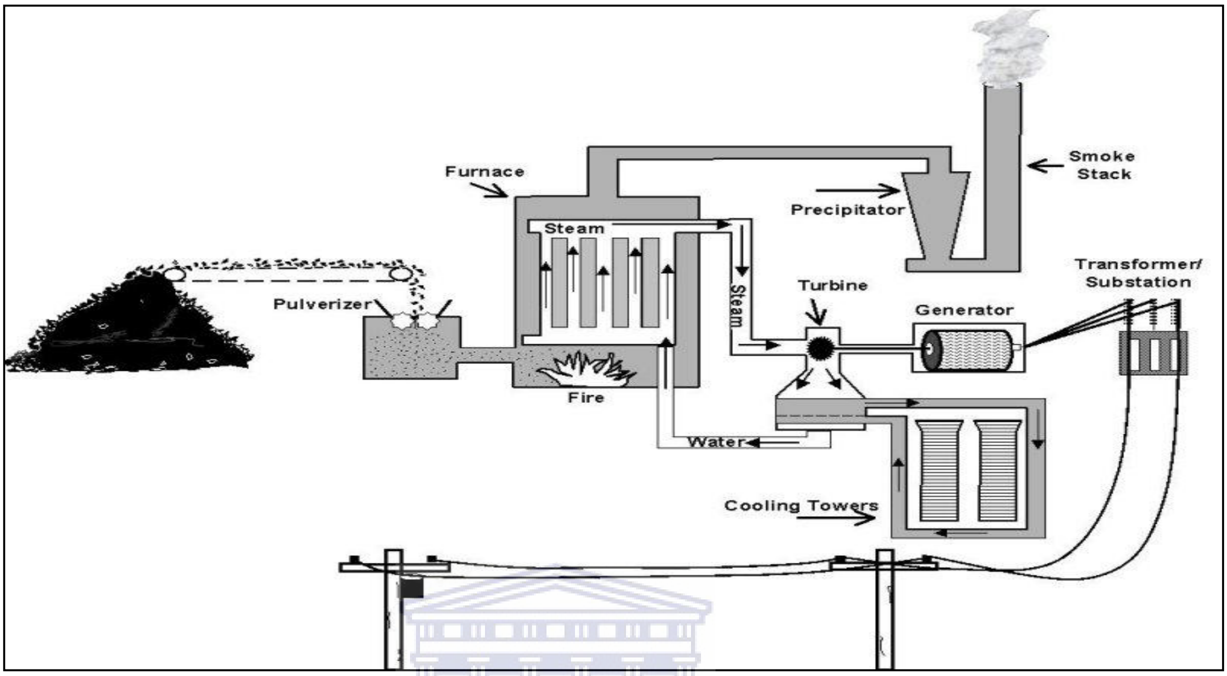


Figure 2.1.1: Electricity generation by conventional coal combustion (Kentucky Geological survey, KGS, 2006)

2.1.4.2 Production of synthetic gas

Coal liquefaction is the process of converting coal to a liquid fuel (CTL) thereby allowing coal to be used as a substitute for oil. This process is particularly appropriate to countries that depend greatly on oil imports and that have large domestic reserves of coal. Since 1955, South Africa has been producing coal-derived fuels and has the only commercial coal to liquids industry in operation today. South African energy company Sasol's CTL fuels have also being approved for utilization as aviation fuel. Currently around 30 % of the country's gasoline and diesel needs are produced from indigenous coal. The total capacity of the South African CTL operations now stands in excess of 160,000 bbl/d (World Coal Institute 2009). There are two different methods for converting coal into liquid fuels; direct liquefaction which requires creating a chemical reaction at high temperatures and then using hydrogen gas and a catalyst to produce a liquid fuel; and indirect liquefaction that gasifies the coal to form a 'syngas' (a mixture of hydrogen and carbon monoxide). Sasol uses the indirect method in the production of synthetic natural gas, and it involves several processes (Fischer–Tropsch) to convert the coal into gas. In a gasification process, coal can be used to produce synthesis gas ('syngas') by partial oxidation in the presence of oxygen and steam. The syngas is used as an intermediate reagent leading to different products (methanol, urea, pure hydrogen, dimethylether) according to the synthesis route chosen and above all to synthetic fuels by the Fischer-Tropsch reaction. In this case the product obtained is a wax containing a large amount of paraffin-type hydrocarbons with an extremely inconsistent number of carbon atoms. This wax has to undergo a hydro- cracking process to prepare mainly high quality diesel, and, in lesser amounts, liquefied petroleum gas (LPG) and petrol. High quality lubricating bases can also be obtained, depending on the method of operation of the hydrocracking plant. But this process is very expensive, and the production of synthesis gas from coal is highly insatiable in energy terms (Uses of coal: www.planete-energies.com/content/coal/uses).

2.1.4.3 Production of iron and steel

Another important beneficiation of coal is in making coke for use in steel blast furnaces. Metallurgical coal (coking coal) is a vital ingredient in steel making process. The physical process of coking coal causes the coal to soften, liquefy, and then re-solidify into hard but porous lumps of carbon-rich material called "coke" when heated in the absence of air. When cooled, this material is quite strong and is used in the production of iron and steel. When iron and steel are made, coke is one of the constituents needed to properly heat the furnace (limestone and iron ore are two other constituents used). Gaseous by-products from coke ovens are also used. These include crude coal tar, light oils, and ammonia. Seventy per cent of steel production comes from iron made in blast furnaces using coal and coke (Kentucky Geological Survey, (KGS), 2006).

2.1.4.4 Coal & Cement

Cement is critical to the construction industry, concrete which is one of the key construction materials available today is formed by mixing cement with water, and gravel. By varying the mix of cement, sand and aggregate enables concrete to be used in a range of applications. The cement industry requires energy to produce cement and coal is an important source of the energy needed. Cement is produced from a mixture of calcium carbonate (generally in the form of limestone), silica, iron oxide and alumina. A high-temperature kiln, often fuelled by coal, heats the raw materials to a partial melt at 1450°C, transforming them chemically and physically into a substance known as clinker. This grey pebble-like material is made up of special compounds that give cement its binding properties. Clinker is mixed with gypsum and ground to a fine powder to make cement. Coal is used as an energy source in cement production. Large amounts of energy are required to produce cement. Kilns usually burn coal in the form of powder and consume around 450 g of coal for about 900 g of cement produced. Over 2.7 billion tons of cement was consumed globally in 2007. China's cement consumption alone reached over 1.3 billion tons (World Coal Institute, 2009).

2.2 Fly Ash

Coal fly ash is the major component of the waste material produced from the combustion of coal in all these processes. It is produced by power plants as a waste product from the combustion of pulverised coal to generate electricity and collected by the cleaning equipment of flue gas emissions by means of electrostatic precipitators, bag houses, or cyclone. Fly ash consists usually of spheres composed of crystalline matter and some residual carbon. The basic spherical shape indicates that particles were formed under un-crowded free-fall conditions and a relatively sudden cooling maintains the spherical shape (Saikia et al., 2006).

Fly ash is generated by coal-fired electric and steam generating plants. Usually, coal is pulverized and blown with air into the boiler's combustion chamber where it instantly ignites, the combustion generate heat and produces a molten mineral residue. Boiler tubes remove heat from the boiler resulting in the cooling the flue gas and hardening of the molten mineral residue to form ash. Bottom ash or slag (which are coarse ash particles), fall to the bottom of the combustion chamber, while the lighter fine ash particles (fly ash), remain suspended in the flue gas. To prevent the release of fly ash into the atmosphere, the fly ash is removed by particulate emission control devices, such as electrostatic precipitators or filter fabric baghouses (United States Department of Transportation - Federal Highway Administration).

Approximately 80 % of the solid residue from pulverised coal combustion is released as fly ash; the properties of fly ash depend on the physical and chemical properties of the coal source, the coal particle size, the combustion process, and the type of ash collector used. Fly ashes are produced at 1200 - 1700 °C and are generated from the various inorganic and organic constituent present in the feed coal. In bulk, fly ash can be considered as homogeneous, but on a micro scale, the individual particles vary in size, morphology, mineralogy and chemical composition. These variable physical and chemical properties of fly ash are attributed to the influence of the coal source, particle size, type of combustion process and moisture content (Jankowski et al., 2006; Vassilev and Vasssileva, 2007; Sočo and Kalembkiewicz, 2009).

Bulk fly ash is an agglomerate mainly of spherical particles, ranging from a micron up to tens of microns in diameter. Al and Si are the major elements present in fly ash. The fairly high proportions of Al, Si, Fe, S, Ca, Na, and K of the coal mineral matter and the high temperature attained during coal combustion in conventional power stations (1200-1600°C) account for the characteristic composition and mineralogy of fly ash: aluminosilicate glass (amorphous component) and high temperature crystalline phases such as mullite ($Al_6Si_2O_{13}$), quartz (SiO_2) and magnetite (Fe_3O_4). Fly ash particles are deemed to be highly contaminating because their high surface area gives rise to the enrichment of potentially toxic elements which condense during cooling of combustion gases (Querol et al., 1996).

In South Africa a huge amount of fly ash is generated every year from the use of low bituminous coal in the production of cheap electricity. About 36.7 MT of fly ash is generated each year in South Africa of which only 5.7% (www.eskom.co.za), is utilized in the production of cement and concrete. It has been shown that fly ash can also be used in the neutralization of acid mine drainage, soil amendment and synthesis of zeolites (Gitari et al., 2008; Basu et al., 2009; Vadapalli et al., 2010), but these processes are not applied at commercial bulk scale yet. A large proportion is still disposed of, in ponds or dry dumps with little regard to its impacts on the environment, in spite of the fact that this material may generate environmental problems through the leaching of toxic chemical species present in the ashes (Potgeiter-Vermaak et al., 2005; Levandowski and Kalkrenth, 2009). Irrespective of the many environmental problems linked to coal combustion it will continue to be a major source of energy for both domestic and industrial use for many years to come (Somerset et al.,2005). Worldwide China is currently the largest producer of fly ash followed by Russia and the United States (Sushil and Batra, 2006).

2.3 Fly Ash Classification

Fly ash can be classified into two types, class F (low lime) and class C (high lime) (ASTM C618), based on their silica, alumina and iron oxide content as shown in Table 2.3.1. Class F fly ash is produced by the combustion of anthracite and bituminous coal and class F has > 70% total of SiO_2^+, $Al_2O_3^+$, Fe_2O_3. Class F is pozzolanic in nature (hardening when reacted with $Ca(OH)_2$ and water). Class F fly ashes usually contain less than 5 % CaO. Combustion of sub bituminous and lignite coal typically produces class C fly ash. Class C fly ash has a higher alkali and sulphate content than class F. Class C has a sum of SiO_2, Al_2O_3, and Fe_2O_3 in the range of 50 – 70%, and contains a large proportion of CaO (10–35%). Also class C fly asg is both cementious (self-hardening when reacted with water) and pozzolanic (Basu et al., 2008; Vassilev and Vassileva, 2006).

Table 2.3.1 ASTM standards classification of fly ash (ASTM C 618, 1993)

	Class F	**Class C**
$SiO_2 + Al_2O_3 + Fe_2O_3$, min %	70	50
SO_3, max %	5	5
Moisture content, max %	3	3
LOI, max %	6	6
Available alkalis, as Na_2O, max %	1.5	1.5

The combustion of high rank bituminous and anthracite coals produces low calcium class F fly ashes that have pozzolanic properties. In contrast the combustion of low rank lignite and sub-bituminous coals produces high calcium class C fly ashes that are self-cementing and pozzolanic (Mattigod et al., 1990). Other chemical and physical requirements in this classification include contents of SO_3 (≥5.0%), moisture (≥3.0%), Na2O (≥1.5% optional), particle size (≥34% ± 5% on average value retained on 45 µm), and loss on ignition (LOI) (≥6.0% and up to 12% for Class F fly ashes based on performance) (Vassilev and Vassileva, 2007).

The classification of fly ashes into four chemical groups with respect to certain chemical and physical properties was recommended by the subcommittee of "Fly Ash Utilization" at the United Nations. The classifications are based on the SiO_2/Al_2O_3 ratio, on the granulometry and Blaine specific surface area (SSA) and on the content of free CaO of the fly ash. Based on the SiO_2/Al_2O_3 ratio the fly ash are categorised as: (1) Group I – silico-aluminate fly ashes with SiO_2/Al_2O_3 ratio ≥2 and CaO <15%; (2) Group II – alumino-silicate fly ashes with SiO_2/Al_2O_3 ratio <2, CaO <15%, and SO_3<3%; (3) Group III – limesulphate fly ashes with CaO >15% and SO3 >3%; and (4) Group IV – basic fly ashes with CaO >15% and SO3 <3%. Based on the granulometry and Blaine specific surface area (SSA), fly ashes were divided into (1) fine-grained fly ashes (<25% are >75 µm and SSA of >3.0 m^{-2} g^{-1}); (2) medium-grained fly ashes (40– 75% are <75 µm and SSA of 1.5–3.0 m^{-2} $g\text{-}^{1}$); (3) coarse-grained fly ashes (<40% are <75 µm and SSA of <1.5 cm^{-2} g^{-1}). According to the contents of free CaO, fly ashes were specified into: (1) inactive or very slightly active (<3.5%); (2) slightly active (3.5–7%); (3) active (7.0–14.0%); and (4) very active (>14%), (Vassilev and Vassileva, 2007).

Roy and Griffin (1982), proposed a system for classifying fly ash based on the contents of sialic (SiO_2 + Al_2O_3 + TiO_2); Ferric (Fe_2O_3 + MnO + SO_3 + P_2O_5); and calcic (CaO + MgO + Na_2O + K_2O). This system classifies fly ash into seven chemical categories, namely sialic, modic or ferrocalsialic, fersic or ferrosialic, calsialic, ferric, fercalsic or ferrocalsic, and calcic types. The modic or ferrocalsialic fly ash type has the sialic (SiO_2 + Al_2O_3 + TiO_2) component >48 - 88 %; calcic (CaO + MgO + Na_2O + K_2O) component between 0 - 29 %; and Ferric (Fe_2O_3 + MnO + SO_3 + P_2O_5) component between 0 - <23 %. The sialic fly ashes are generated from bituminous coals and, to a lesser extent, sub-bituminous coals, which are highly enriched in detrital mineralization. The Sialic fly ash shows maximum values of Si, Al, K, Ti, detrital/authigenic index (DAI), glass, quartz, and ettringite. This classification system could be used to help determine which utilization and recycling method might be best suited for a particular type of fly ash. Modic fly ashes may generally correlate with class F fly ashes as they meet the requirement of this group of fly ash according to the ASTM classification (Roy and Griffin, 1982).

2.4 Physical properties of fly ash

The morphology, particle size distribution and surface area of the fly ash are covered in this section.

2.4.1 Fly Ash Morphology

The morphology of fly ash particle describes the size, shape, or structure and surface properties of the particle and is determined by combustion temperature and cooling rate in the power plant (Kutchko and Kim, 2006). The study of the fly ash particle morphology is important in understanding the physical properties and leaching behaviour in terms of toxicology and environmental studies of the fly ash (Singh, 2005).

Fisher et al., (1978) used light microscopy to analyse fly ash particle morphology which they classified into eleven categories based on opacity, shape and type of inclusions.

1) Amorphous, non-opaque
2) Amorphous, opaque
3) Amorphous, mixed opaque and non-opaque
4) Rounded, vesicular, non-opaque
5) Rounded, vesicular, mixed opaque and non-opaque
6) Angular, lacy, opaque
7) Cenosphere (hollow sphere), non-opaque
8) Plerosphere (sphere filled with other spheres), non-opaque
9) Nonopaque, solid sphere
10) Opaque, sphere
11) Sphere with either surface or internal crystals, non-opaque

These also stated that the relative abundances of the eleven morphological particle categories within each size regime seem to rely on particle size. The majority of the particles in the finer fractions are spherical, glassy and mostly non-opaque showing complete melting of the silicate minerals in the coal particle. The minor opaque spheres are usually iron oxide particles like magnetite. Kutchko and Kim, (2006) also reported that the fly ash samples were comprised of over 50 % amorphous alumino-silicate spheres and a lower quantity of iron-rich spheres. The finest fraction is made up of 87 % non-opaque solid spheres and 7.9 % cenospheres whereas the coarsest fraction comprises of 26 % non-opaque solid spheres and 41 % cenospheres. Various morphological studies show that fly ash consists of a range of spherical and irregularly shaped particles of different sizes ranging from <1µm to >200 µm formed from the various physical and chemical reactions that occur during the coal combustion process. The combustion heat causes the inorganic minerals in coal to fluidise or volatilise or to react with oxygen; which during cooling, may form crystalline solids, spherical amorphous particles or condense as coating on particles. Agglomerated particles are produced due to high temperature sintering reactions; spherical amorphous particles are formed from the fast cooling in the post-combustion zone; hollow cenospheres result from the expansion of trapped volatile matter that can cause the particle to expand while plerospheres are hollow spheres incorporating fly ash spheres (Fisher et al., 1978; Seames 2003; Cho et al., 2005; Kutchko and Kim, 2006; Saikia et al., 2006).

The surfaces of particles are generally smooth in fly ash that has not weathered whereas in weathered fly ash the particle surfaces have features such as encrustations, corrosions and etching which may have resulted from leaching or formation of new mineral phases as a result of weathering (Praharaj et al., 2002; Yeheyis et al., 2009).

Fly ash colour is highly influenced by the mineral phase and is mostly determined by two components. The remaining unburned carbon resulting from incomplete combustion of coal is responsible for the grey and black colour; while iron oxide with its characteristics colour depending on oxidation state of iron is another important component in determining the colour of fly ash. Trivalent iron (i.e. Fe^{3+}) is brown, red, or yellow, while bivalent iron (i.e. Fe^{2+}) is grey or grey with a bluish tinge. Magnetite which contains both Fe^{3+} and Fe^{2+} is black and can be brown when finely dispersed (Raclavska et al., 2009).

2.4.2 Particle Size Distribution and Surface Area

Fly ash consists of a range of spherical and irregular shaped particles of different sizes; the alumino-silicate iron-rich spheres spherical particles are usually small in size (between 0.1 µm and 100 µm) whereas the irregular shaped particles which consist mostly of unburned carbon are larger (<1µm - >200 µm) (Styszko-Grochowiak et al., 2004; Potgieter-Vermaak et al., 2005; Cho et al., 2005). A number of related factors such as the size distribution of the coal particle and the accessory minerals, combustion conditions and the particulate emission control devices determine the particle size distribution of fly ash (Fisher, 1983). The size and distribution of these particles is the most important characteristic determining its reactivity. The smaller particles have greater specific surface area making a larger area susceptible to hydrolysis. The particle size distribution is important during interaction of fly ash with different solutions because it affects the mobilisation of any trace element on the surface (Mattigod et al., 1990; Iyer, 2002; Jankowski et al., 2006). The particle size distribution also plays a role in the concentrations of some elements in fly ash. Fisher et al.,(1977) reported that the concentrations of some elements are dependent on particle size while some are independent of particle size. The highest size dependence is exhibited by the most volatile elements (Cd, Zn, Se, As, Sb, W, Mo, Ga, Pb and V) or their oxides while the least volatile elements such as (examples of the elements) do not exhibit significant particle size dependence. Extension of vapour-phase condensation to the sub-micrometre regime and homogeneous nucleation were attributed to the particle size dependence of the trace elements in fly ash.

The size of the particle seems to have an effect on density variations in the fly ash. There is an inverse variation of apparent density with particle sizes which may be as a result of the higher relative abundance of cenosphere particles and lower relative abundance of solid, non-opaque spheres in coarse fractions (Fisher et al., 1978). The particle size of a material can be important in understanding the physical and chemical properties of fly ash and plays a very important role in the utilization and disposal of fly ash. If fly ash is to be considered as a partial replacement for cement a low bulk density is required to make it ideal as a lightweight building material (Ural, 2005). The particle-size distribution of fly ashes is also a vital factor for their use as pozzolans. ASTM 618C requires that 34% of the ash must remain on a 45 mm sieve on wet sieving.

2.5 Chemical properties of fly ash

The chemical composition of fly ash, the major, minor and trace elements and their partitioning in fly ash is reviewed in this section. The compositions of different South African fly ashes are also discussed.

2.5.1 Ash Composition

The proportion of major elements in fly ash can be determined with X-ray fluorescence spectrometry (XRF), while inductive coupled plasma-optical emission spectroscopy (ICP-OES) or inductive coupled plasma-mass spectrometry (ICP-MS) can determine the concentration of the minor and trace elements. Chemical constituents of fly ash mostly depend on the chemical composition of the coal the combustion conditions and removal effectiveness of air pollution control device (electrostatic precipitators or bag filters) used (Li et al., 2009; Goodarzi, 2006; Vassilev and Vassileva, 2007; Adriano et al., 1980). The knowledge of partitioning of elements in fly ash is important because the particle enriched surface almost dominates the chemical contents of its core. It is the surface layer that seems to define most of the important characteristics such as pH, leaching and mobilization properties of the fly ash. As stated earlier the surface area of the fly ash particle increases as its size decreases thus the particles have an unusually large surface area that are enriched with elements that are volatilized during coal combustion and are condensed at lower temperature on the fly ash particles. The partitioning of elements and their surface association in fly ash is controlled by the extent of vaporisation during the coal combustion process (Choi et al., 2002). Iyer, (2002) reported the partitioning of these elements resulting from volatilization as:

1) Elements in the coal are volatile to a significant extent in the combustion process. These include Mn, Ba, V, Co, Cr, Ni, Ln, Ga, Nd, As, Sb, Sn, Br, Zn, Se, Pb, Hg and S
2) Elements that appear to have a smaller fraction that is volatilized during combustion. These include Mg, Na, K, Mo, Ce, Rb, Cs and Nb
3) Elements that are either not volatilized or only show minor trends related to geochemistry of mineral matter. These include Si, Fe, Ca, Sr, La, Sm, Eu, Tb, Py, Yb, Y, Se, Zr, Ta, Na, Ag, and Zn (Iyer, 2002).

The chemical composition of fly ash comprises major (>1wt %), minor (1–0.1wt %), and trace (<0.1wt %) elements (Vassilev and Vassileva, 1996). Fly ashes from the four coal ranks (anthracite, bituminous, sub-bituminous, and lignite coals) differ in chemical composition as a result of the difference in the coal heating values, chemical composition, ash content, and geological origin. Though the chemical composition of fly ash varies, spectroscopic analysis of fly ashes shows they still consist of the same fundamental chemical elements but in different concentrations as shown in table 2 below.

Table 2.5.1 below, compares the chemical composition range of the major and minor elements reported as oxides for bituminous, sub-bituminous, and lignite coal fly ashes. Sub-bituminous, and lignite fly ashes have higher CaO and lower LOI (loss on ignition) than bituminous fly ash.

Table 2.5.1: Normal range of chemical composition for fly ash produced from different coal ranks (expressed as weight %) (http://cementconsultant.org/flyash.pdf)

Component	**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

Table 2.5.2 present the average trace elements composition in fly ash. The concentrations of these elements are higher in the fly ash than the original coal due the volatilization and condensation during and following the coal combustion process. A high concentration of these trace elements creates environmental problems in the utilization and disposal of fly ash. These elements may leach out and contaminate the soil, surface and ground water (Sushil, S and Batra, S, 2006).

Table 2.5.2: Average trace elemental composition for fly ash (El-Mogazi et al., 1988).

Element	**Concentration (mg/g)**	**Element**	**Concentration (mg/g)**
As	2.3 - 312	Pb	31 - 241
B	10 - 600	Mo	6.6 - 41
Cd	0.2 - 3.9	Ni	1.8 - 15
Cu	45 - 259	Se	1.2 - 17
Cr	43 - 259	Zn	15 - 406

Table 2.5.3 compares the chemical compositions of some South African fly ashes, Gitari et al., (2008) reported that SiO_2, Al_2O_3, CaO and Fe_2O_3 were the major oxides while MgO, Na_2O, K_2O, SO_3, P_2O_5 and Cr_2O_3 were the minor elements. The traces elements were Cu, Mo, Ni, Pb, Sr, Zn, Zr, Co, Cr, V and Ba. The variation in chemical composition of the fly ashes from the different power stations was observed and could be a reflection of the differences in the source of parent coal, the combustion processes and the ash handling methods of the power stations.

Table 2.5.3: Chemical composition of some South African coal fly ashes (Gitari et al., 2008)

	Arnot Fly Ash	**Matla Fly Ash**	**Tutuka Fly Ash**	**Secunda Fly Ash**
gkg $^{-1}$				
SiO_2	534	538	561.3	500.6
TiO_2	13.4	14.4	16.1	16.3
Al_2O_3	234	262	243	257.1
Fe_2O_3	47.2	34	47.2	27.3
MnO	0.6	0.5	0.4	0.5
MgO	26.7	24.8	19.3	24.6
CaO	84.3	85	64.4	86.7
Na_2O	3.5	4.9		
K_2O	4.9	8.6	8.3	7.5
P_2O_5	3.4	6	3.1	6.2
Cr_2O_3	0.3	0.3	0.5	0.4
SO_3				
mgkg $^{-1}$				
Cu	47.3	57.9	9	7
Mo	5.23	6.56		
Ni	93.4	58.2	96.5	83
Pb	56.4	29.1	45	30
Sr	1463.9	2056	1787	3391
Zn	57.3	25.4	37	24
Zr	488.1	536.1	405	476
Co	18.2	10.4	24	13
Cr	179.2	122.7	138.5	121
V	147.4	145.8	86.5	85.5
Ba	928	1559.2	1243	1955

2.6 Mineralogical properties of fly ash

The origin, types, composition of the various mineral phases that are present in fly ash are reviewed and discussed in this section.

2.6.1 Fly Ash Mineralogy

The mineral composition of fly ash is usually determined by X-ray diffraction (XRD) and depends on the minerals entrained in the coal and its combustion conditions. The major minerals groups in coal are aluminosilicates (clays), carbonates (calcite and dolomite), sulphides (pyrite), and silica (quartz). While minerals such as quartz may remain thermally unaltered during combustion clay minerals may be altered to form new minerals or phases (White and Case, 1990). The phase and mineral composition of fly ash generally consist of an inorganic component (90 %-99 %), an organic component (1 % - 9 %), and a fluid component (<0.5 %) The inorganic component is made up of amorphous (non-crystalline) matter (34% - 80%) and crystalline matter (17 % - 63 %) The organic component contains char materials while the fluid component comprised liquid, gas and gas-liquid inclusions that were associated with both inorganic and organic matter (Vassilev and Vassileva, 2005). Amorphous (glass) or crystalline structure of the fly ash particles depends on the rate of cooling of the fluidized coal minerals in the post combustion area. Rapid cooling of the fluidized minerals results in spherical glassy particles whereas crystalline structures are formed when the fluidized minerals cool gradually (Kim, 2002). The chemical reactions related to fly ash utilisation (cement and concrete or zeolite synthesis) and disposal (weathering) can be attributed to the amorphous (glass) components because of its large quantity and the disorderly character of the atoms involved. It is also the main matrix in the ash for adsorbed trace elements that may be released from the fly ash during its leaching process (Ward and French, 2006).

The mineral components in fly ash have natural or technogenic origin and they can be classified as original (primary) or newly formed (secondary and tertiary) minerals and phases. The primary are original coal minerals or phases that have not undergone phase transformations during coal combustion, such as some stable silicates, oxides, sulphates, phosphates, carbonates, and others with moderately high decomposition or melting temperatures; the secondary are new phases formed during coal combustion, i.e. various silicates, oxides, sulphates, carbonates, sulphides, glass, and char; and tertiary, which are new minerals or phases formed during fly ash transport and storage, such as portlandite, brucite, gypsum, Fe sulphate, calcite, dolomite, Fe and Al hydroxides, and amorphous material (Vassilev and Vassileva, 2005).

Moreno et al., (2005) reported that the major phases present in coal fly ashes from several power plants in Europe were aluminosilicate glass, mullite ($Al_6Si_2O_{13}$), quartz (SiO_2), magnetite (Fe_3O_4), anorthite/albite ($(Ca,Na)(Al,Si)_4O_8$), anhydrite ($CaSO_4$), ettringite ($3CaO\ Al_2O_3\ 3CaSO_4\ 32H_2O$), opaline ($SiO_2$), hematite ($Fe_2O_3$) and lime ($CaO$). Praharaj et al., (2002) reported that quartz, mullite, hematite and magnetite were the major phases. Ilmenite and anorthite were observed as likely minor phases in coal fly ashes from India. Ward et al., (2009) in their studies of fresh and weathered Australian fly ashes reported that the major phases were quartz, mullite, magnetite, and hematite together with a large quantity of glass component. Also probable traces of gypsum ($CaSO_4.2H_2O$) is shown in the fresh fly ash, Choi et al., (2002) in their studies of Korean fly ashes stated that the major phases present were mullite, quartz and iron oxide (hematite and magnetite). Nathan et al.,(1999) summarized the mineralogy of South African fly ash identified by XRD and FTIR spectroscopy as mullite ($Al_6Si_2O_{13}$) amorphous Fe-Al silicates, lime (CaO), quartz (SiO_2), Portlandite ($Ca(OH)_2$), anorthite ($Ca_2Al_2S_2iO_8$), hematite (Fe_2O_3), magnetite (Fe_3O_4) and anatase $(TiO)_2$. From the FTIR results and SEM analysis of single particles, they reported that the fly ash consists of an amorphous phase that is rich in Si with some Al and Fe, more than one calcium–aluminum silicate amorphous phase and amorphous silicate phases and mullite that usually contain some iron.

Mineralogical studies of fly ash sample reported by the various authors above, shows that though the major phases are similar, the different minerals indicate the variation in the fly ashes and their chemical compositions. The prominent major phases in all the studies are glass, mullite, quartz, magnetite and hematite. At high temperatures the aluminosilicate clay minerals lose water and melt to form glass which then dissociate into amorphous and crystalline aluminosilicate phases (Hurley and Schobert, 1993). Quartz is a major crystalline phase in fly ash. It exists as a hard mineral commonly found as cell and pore infillings in the organic matter of coal and is usually a primary mineral because it is mostly unaltered by the combustion process due to its high fusion temperature (Ward, 2009). Mullite is a secondary mineral because it does not exist in coal but is formed from the decomposition of kaolinite an aluminosilicate mineral in the coal (Koukouzas et al., 2009, White and Case, 1990). Magnetite and hematite are also secondary minerals. They are formed from the oxidation of pyrite and other iron bearing minerals in the coal (Hurley and Schobert, 1993).

2.7 Fly Ash Disposal

The inevitable waste from coal combustion is fly ash, after coal combustion in the thermal power plants the fly ash generated is usually disposed as waste. Fly ash disposal is of major concern globally because of the enormous quantity that is generated and the environmental issues arising from the disposal methods that are currently employed. Worldwide huge amounts of coal fly ash are generated in order to meet up with energy demands and about 70 % of fly ash is disposed as waste (Haynes, 2009). In 2009, China generated over 375 million tons of coal ash (Greenpeace, 2010). In 2008, the coal-fuelled electric power industry generated approximately 72.4 million tons of coal fly ash, in the USA (www.epa.). India is predicted to generate about 170 million tonnes per annum by 2012 (Sushil, and Batra, 2006). Currently in South Africa, Eskom generated nearly 36.7 million tons of fly ash in 2009 from coal combustion, of which only 5.7% was utilised beneficially (www.eskom.co.za) while Sasol produced about 4 million tonnes annually (Mahlaba et al., 2011)

Fly ash is mainly disposed through either dry or wet disposal methods. In dry disposal, the fly ash is conveyed by truck, chute or conveyor at the site and disposed by building a dry embankment (Bhat, and Lovell, 1996). The ash heap is then irrigated with brine for dust suppression. In wet disposal, the fly ash is mixed with water and transported as slurry through pipe and disposed in ash ponds or dams where over time the water is allowed to drain away. Various environmental risks such as air, surface water and groundwater pollution may be linked to disposed coal fly ash. Air pollution results from wind-blown ash dust from the ash dump (Dellantonio et al., 2010). Deposition of the air borne particulate material on surface water or soil may lead to the contamination of the surface water or soil. Also interaction with water used in the wet disposal method or from the atmosphere may result in the leaching of toxic metals which may also contaminate the underlying soil and ultimately the groundwater. The serious problems that arise from both ash disposal methods include the need for a large area of land for the construction of the dump or dam which will lead to reduction in arable land overtime. Also the construction of new dams and dumps to replace the old ones that are filled up is done at a great cost and further loss of arable land. Another problem is the vast amounts of water that is needed to turn the ash into slurry.

In South Africa coal fly ash is also disposed via the dry and dense slurry (wet) disposal methods. For instance Sasol synthetic fuel plant in Secunda uses the wet disposal method while Eskom, Tutuka power plant uses the dry disposal method. In Sasol Secunda, the ash from the flue gas collection system is accumulated in hoppers from where the ash is added to a stirring tank in which waste water (brine) is continuously added until a slurry with controlled density is attained. The slurry is then pumped through pipes to the ash dam where the ash particles quickly settle out and the ash-make up water is either drained away via a penstock to the clear ash effluent dam, or permeates through the ash dam and is collected in a toe drain. The ash-make up water goes to the clear ash effluent dam, where it mixes with other wastewaters and after settling is pumped back for treatment using reverse osmosis (RO) and electro dialysis reversal (EDR). The reject waste stream (highly concentrated and salt laden) from these treatment processes is again used for hydraulic transport of more ash from the hoppers (Pretorius, pers comm, 2010). In Tutuka power station, the fly ash from the precipitators is moistened with low amounts (about 16 %) of brine for dust suppression during conveyance and is transported to the ash dumps via conveyor belts for disposal. At the Tutuka ash dump, the freshly stacked ash is irrigated with brine (generated from water treatment plants) for dust suppression (Fatoba, 2008).

2.8 Environmental Effect of Fly Ash

Fly ash particles are diverse, inhomogeneous, have different morphologies and their chemical, physical and mineralogical properties depend on the chemical composition of the source coal and the combustion process (Mehra et al., 1998). After combustion the toxic trace elements in coal are left behind in higher concentrations in the coal fly ash (Gitari et al., 2003), thus disposal or storage sites should be monitored for accumulation of the toxics. The environmental impacts associated with coal fly ash include the loss of arable land, air pollution, soil and surface and ground water contamination.

Air pollution from coal thermal plants results from the emission of toxic gases (such as NO_x, SO_x and CO_2) and of fly ash particulates from the flue gas stacks into the atmosphere. The gaseous and particulate emissions from the stacks are controlled by devices such as scrubbers, mechanical and electrostatic precipitators. Although these devices have high efficiency rates, considerable amounts of these toxic gases and fly ash may be emitted into the surrounding environments. At the disposal or storage sites airborne fly ash particles are practically weightless and are easily dispersible by wind and scattered into the atmosphere as secondary dust pollution. The airborne particles can fall on surface water systems or soil and may also contaminate them over time. The long term storage of ash in ponds under wet conditions and humid climate may cause leaching of toxic metals from ash and contaminate the underlying soil and ultimately the groundwater system.

2.9 Beneficial Application of Fly Ash

One way of combating problems caused by fly ash is by optimizing the uses of fly ash so that it could become a valuable raw material. This can be achieved through precisely defining and controlling physical and chemical characteristics of fly ash; so that a uniform and reproducible material can be supplied for reuse (Foner et al., 1998). Some of the uses of fly ash are as follows:

2.9.1 Cement and Construction Industry

Fly ash is used in the construction industry in the making of cement or concrete because of its cementious and pozzolanic properties which improves the workability, durability and strength in hardened concrete (Jaturapitakkul et al., 2003). The loss on ignition (LOI), which is a measurement of the amount of unburned carbon remaining in the fly ash (Styszko-Grochowiak et al., 2004), is one of the most significant chemical properties of fly ash, especially as an indicator of suitability for use as a cement replacement in concrete. According to ASTMC618, a loss-on-ignition (LOI) greater than 6 % renders fly ash unusable for cement or concrete manufacture, because the presence of carbon can influence air entrainment which is an important property of concrete. Surfactants, or air entraining admixtures that are normally used in the formulation of concrete, can be adsorbed onto the surfaces of the porous residual carbon particles resulting in a reduced resistance of the concrete to freeze and thaw (Senneca, 2008).

Fly ashes can certainly be beneficially used in the concrete and construction industries. It is used as a partial replacement for Portland cement in concrete manufacture (Ahmaruzzaman, 2010) and used as a sand supplement in the manufacture of building bricks, blocks and pavers (Manz, 1997). It is also used as a replacement for the fine aggregate (sea sand or machine-ground sand) in concretes and mortars. In addition it is also used as a constituent of light-weight aerated concrete, especially for construction of insulating building blocks. These could replace many of the low fines concrete blocks used presently. Furthermore it is used as a constituent of "flowable fill" for filling trenches, and surrounding insulation in building basements, shelters, foundations etc. (Foner et al., 1999).

2.9.2 Treatment of Acid Mine Drainage (AMD)

Acid mine drainage (AMD) is formed when sulphide minerals, such as pyrite, found in association with the coal or overburden come into contact with oxygen and water during mining and oxidize. Sulphide minerals undergo further bacterially-catalysed oxidation reactions which accelerate acidity generation and increases Fe and sulphate concentrations in recipient water bodies. Acid mine drainage is characterized by high acidity (pH 2–4), high sulphate concentrations (1–20 gL^{-1}) and contains high concentration of heavy metals such as Fe, Mn, Al, Cu, Ca, Pb, Mg, Na and Ni (Gitari et al., 2008). Acid mine drainage, often at a pH 2 or less, that contains a wide range of heavy metals is a major source of ground and surface water pollution near abandoned mines (Dutta et al., 2009). Fly ash can be used in the treatment of acid mine drainage because it contains relative high concentrations of SiO_2, Al_2O_3 and CaO, which is considered as a liming agent to neutralise acid mine drainage. The neutralisation of acid mine drainage is usually attained by the addition of chemicals such as CaO, $Ca(OH)_2$, $CaCO_3$, NaOH and Na_2CO_3. The use of fly ash for acid mine drainage neutralisation, involves a process whereby the pH of the acid mine drainage is increased from 2–3 up to a neutral pH of 7, or even over pH 10. Fly ash contains considerable amounts of total alkalinity in the form of CaO, MgO, K_2O and Na_2O, thus increasing the neutralisation potential of fly ash. Calcium oxide (CaO) is formed in fly ash by the oxidation of calcium during coal combustion process in a coal-fired power station. Fly ash may therefore be a substitute for limestone or lime treatment in the neutralisation of acid mine drainage (Somerset et al., 2005).

2.9.3 Removal of Heavy Metals in Water Treatment

Heavy metals are among the most important pollutants in wastewater, and are becoming a severe public health problem due to the toxicity of some heavy metals. Removal of heavy metals and metalloids from aqueous solutions is usually carried out by a number of processes such as, chemical precipitation, solvent extraction, ion exchange, reverse osmosis or adsorption etc. Among these processes, the adsorption process may be a simple and effective technique for the removal of heavy metals from wastewater. Fly ash has been widely used as a low-cost adsorbent for the removal of heavy metal such as Ni, Cr, Pb, As, Cu, Cd and Hg from wastewaters. The major chemical composition of fly ash (alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon), and its physical properties such as porosity, particle size distribution and surface, highlights its potential as an adsorbent in waste water treatment (Cetin and Pehlivan, 2006).

Heavy metal adsorption on fly ash depends on the initial concentration of the heavy metal, contact time and pH. The initial concentration of heavy metal has a strong effect on the adsorption capacity of the fly ash. The adsorption capacity of fly ash depends on the surface activities, such as specific surface area available for solute surface interaction. In a certain pH range, most metal adsorption increased with increased pH up to a certain value, and then decreases with further increase in pH (Krishnan and Anirudhan, 2003).

Fly ash can be regenerated after the adsorption, using suitable reagents. Batabyal et al., 1995) reported the regeneration of the used saturated fly ash with 2% aqueous H_2O_2 solution. The regenerated fly ash was dried, cooled and used for further adsorption. The adsorption rate and equilibrium time were found to be the same as the fresh fly ash particles.

2.9.4 Soil Amendment

Fly ash is also used in agriculture as a soil amendment, in composting and as a source of nutrients for plants based on its chemical compositions and physical properties. Fly ash contains almost all the necessary plant nutrients i.e., macronutrients including P, K, Ca, Mg and S and micronutrients like Fe, Mn, Zn, Cu, Co, B and Mo, except organic carbon and nitrogen. It can replace lime, a costly amendment for acid soils; agricultural lime application contributes to global warming through emission of CO_2 to the atmosphere. Use of fly-ash instead of lime as soil ameliorant can reduce net CO_2emission and thereby lower global warming (Basu et al., 2007). According to Kishor et al., (2010), the beneficial and harmful effects of fly ash application to soil are as follow

Beneficial effects

(1) Improvement in soil texture; (2) reduction in the bulk density of soil; (3) improvement in the water holding capacity of the soil; (4) optimization of the soil pH value; (5) increases the soil buffering capacity; (6) improvement in the soil aeration, percolation and water retention in the treated zone (due to dominance of silt-size particles in fly ash); (7) reduction in crust formation; (8) provision of micro-nutrients like Fe, Zn, Cu, Mo, B etc.; (9) provision of macro-nutrients like K, P, Ca, etc.; (10) reduction in the consumption of soil ameliorants (fertilizers, lime); (11) fly ash can also be used for insecticidal purposes and (12) decreases the metal mobility and availability in soil, due to an increased pH.

Harmful effects

(1) High pH results in the reduction in bioavailability of some nutrients (generally from 8 to 12); (2) high salinity and (3) high content of phytotoxic elements, especially boron.

Fly ash may be suitable for use on agricultural land where food crops are produced, although potential trace element enrichment in plants from certain types of fly ash may make it more suitable for non-food chain end uses (Punshon et al., 2002).

2.10 Weathering of Fly Ash

The management of disposed or stored fly ash is of major concern due to its potential impact on the environment and sustainable management requires the proper understanding of the weathering characteristics of fly ash since the fly ash dump is continuously exposed to water, air and rainfall. Thus the disposed fly ash cannot be separated from nature's weathering cycle. Weathering can be described as the chemical or physical breakdown or deterioration of rocks, soil and their minerals at or close to the surface of the earth. Weathering of coal fly ash normally occurs when the fly ash has been exposed to atmospheric elements (air and water) for a long period of time (Gitari et al., 2009; Zevenbergen et al., 1999).

The weathering of fly ash results in changes in the physical, chemical and mineralogical properties. Some of these changes include the formation of secondary minerals (Yeheyis et al., 2009) followed by equally significant changes in physical properties; According to Gitari et al., (2009) the presence of water seems to accelerate the weathering and transformation of the ash components into new mineral phases. McCarthy et al (1997) reported that interaction of landfilled coal ashes with permeating surface or ground water, or merely extra moisture included before closure of a landfill over a long period of time, may lead to major changes in crystalline and amorphous phase groups together with a similar significant changes in physical properties. Decrease in the pH and EC values of the pore water (Ward et al., 2009; Baba et al., 2008; Gitari et al., 2009; Ugurlu, 2004). Zevenbergen et al., (1999) reported that weathering of fly ash may mobilize trace elements as well as reduce the high pH of fly ash due to uptake of CO_2 from atmosphere. Reduction in the pH value can also be attributed to the dissolution of basic alkaline oxides like CaO and MgO (Saikia et al., 2006). Reduction of soluble salt content (Brower, 1985), which may have significant effect on the leaching and mobilization of the fly ash species (Zevenbergen et al., 1999; Yeheyis et al., 2009).

The changes in the chemical, physical and morphological properties and phase transformation studies are vital in predicting the environmental impact associated with fly ash disposal techniques and uses. Some common weathering phenomenon of coal fly ashes includes hydration, carbonation, pozzolanic reactions, ettringnite formation, leaching and mobility of chemical species.

Hydration reactions of coal fly ash: Fly ash usually contains unhydrated lime (CaO) and anhydrite ($CaSO_4$). During weathering of fly ash the lime reacts to form portlandite, calcium hydroxide. ($Ca(OH)_2$), and anhydrite that quickly react to form calcium sulphate hemi-hydrate ($CaSO_4 \cdot 1/2H_2O$) and subsequently gypsum (Brouwers and Van Eijk)

(($CaSO_4 \cdot 2H_2O$), also called calcium sulphate dihydrate.

$CaO + H_2O \longrightarrow Ca(OH)_2$ (Portlandite or Hydrated Lime)

$CaSO_4 + 1/2H_2O \longrightarrow CaSO_4 \cdot 1/2H_2O$ (Calcium Sulphate Hemi-hydrate)

$CaSO_4 \cdot 1/2H_2O + 3/2H_2O \longrightarrow CaSO_4 \cdot 2H_2O$ (Gypsum or Calcium Sulphate Di-hydrate)

Carbonation reactions of coal fly ash: Calcite (calcium carbonate, $CaCO_3$) is formed by carbonation of the lime (CaO) via reaction with the carbon dioxide (CO_2) in ambient air and by hydrated lime reacting with the carbonate alkalinity equilibria system in the water in the content of the fly ash (Beeghly et al, 1995).

$CaO + CO_2 \longrightarrow CaCO_3$

$Ca(OH)_2 + CO_3^{2-} \longrightarrow CaCO_3 + 2\ OH^-$

Pozzolanic Reactions of coal fly ash: Pozzolanic reactions between lime (CaO) and the fly ash components (aluminum oxide, silica dioxide, and iron oxide) also consume free moisture and cause the fly ash to harden and gain strength. These reactions occur in a high pH environment and are common when Portland cement or lime is mixed with Class F coal fly ash (Beeghly et al, 1995). Calcium silicate hydrate, calcium aluminate hydrates, and calcium aluminiumferro hydrates are formed. These reactions form glassy or non-crystalline (amorphous) phases characteristic of hydrated portland cement.

Silica dioxide:

$SiO_2 + Ca(OH)_2 + H_2O \longrightarrow CaO\text{-}SiO_2\text{-}H_2O$

calcium silicate hydrate

Alumina:

$A1_2O_3 + Ca(OH)_2 + 2H_2O \longrightarrow CaO\text{-}Al_2O_3\text{-}Ca(OH)_2\text{-}H_2O$

alumina: calcium aluminaiehydrates

Iron oxide:

$Fe_2O_3 + A1_2O_3 + Ca(OH)_2 + H_2O \longrightarrow Ca(OH)_2\text{-}\ Al_2O_3\text{-}Fe_2O_3\text{-}H_2O$

calcium aliunino-ferro hydrates

The changes in the pH can be attributed to the dissolution of basic alkaline oxides like CaO and MgO since the final pH value of ash is generally dependent on the relative contents and dissolutions of alkaline contributing oxides present in the waste (Saikia et al., 2006).

2.11 Leaching Process of Fly Ash

Fly ash is an intricate mixture of various minerals that are linked to high amounts of toxic elements which may be leached during disposal or utilisation in different environmental conditions. Leaching can be described as the loss of soluble substances by the action of a percolating liquid. When fly ash comes into contact with an aqueous media some components will dissolve to a greater or lesser degree and become mobile, the outcome of this interaction is known as the leachate (Zandi and Russell, 2007).The main aqueous media in contact with disposed fly ashes are the infiltrating rainwater, the slurry water used to transport the fly ash from the plant to the dump, and the waste water used for dust control in the ash dump (Nyamhingura, 2009).

Though fly ashes vary in terms of physical and chemical characteristics, they usually consist of aluminosilicate glassy particles with surfaces that are enriched with trace elements such as As, B, Ca, Cr, Mg and Sr as a result of condensation reactions during combustion. Elements such as K, Pb and many of the other trace elements are distributed throughout the particle and are not preferentially concentrated (Zandi and Russell, 2007). The surface associated fraction might dominate the leachate chemistry during the early stage of fly ash disposal in contact with water. However, as leaching progresses, further weathering of the aluminosilicate glass matrix would release the elements incorporated within the glass particle (Choi et al., 2002). The major chemical processes involved in fly ash leaching are: constituent solubility; metal complexation; sorption; dissolution of primary solids and precipitation of secondary solids; redox, sorption and hydrolysis reactions (Zandi and Russell, 2007; Jankowski et al., 2006).

The leaching behaviour of the trace elements in coal fly ash depends on the properties of the fly ash samples and the types and concentrations of constituents in the system with which they may interact. An understanding of the chemical behaviour of the coal fly ash elements in water, and their interactions with other components in the system is required to evaluate the impacts of environmental conditions on the release of trace elements (Bhattacharyya et al., 2007; Praharaj et al., 2002). According to Jones (1995) coal fly ash leaching test are generally carried out for the following reasons:

1) To assess compliance with regulatory standards for coal fly ash disposal.
2) To ascertain the highest amount of contaminants that can be leached from coal fly ash.
3) To evaluate the possible concentration of solutes in the supernatant of a wet disposal system.

4) To determine the concentration versus time profile for solutes extracted from coal fly ash.
5) To assess the effect of the leaching chemical condition on the leaching of elements from coal fly ash.
6) To acquire thermodynamic and kinetic parameters for input into predictive computer models.

Leaching tests usually entail the contacting of the waste material with a liquid to establish which constituent will be leached by the liquid and released to the environment.

Generally leaching tests can be categorized as extraction leaching tests and dynamic leaching tests. Extraction or batch leaching tests involves combining a specific amount of the solid material and the extraction liquid (leachant) for a given period of time. The leachate which is the product of the combination is then filtered and the supernatant is stored for further analysis. While dynamic or column tests entail continuous flowing of the leachant across the solid material. In batch leaching test the contact time (test period) is deemed long enough to achieve chemical equilibrium. The liquid to solid ratios employed in the test provide an accelerated leaching relative to the real leaching ensuing from disposed fly ash coming in contact with an aqueous media. Batch leaching tests when compared to column leaching tests are easier, more repeatable and have relatively low cost (Zandi and Russell, 2007; Steenari et al., 1999).

The leaching behaviour of major and trace elements in fly ash varies with the properties of the fly ash such as temperature, pH, composition, mineralogy morphology, particle size distribution and the methods employed in studying the leaching process; also the phases with which these elements are associated with and distribution in the fly ash can influence their leachability (Baba et al., 2007; Saikia et al., 2006; Jankowski et al., 2006; Wang et al., 1999). According to Gitari et al., (2009) neutralization and chemical weathering has been identified as the main leaching processes of coal fly ash. The rate of dissolution and leaching of species from fly ash is influenced by the pH of the leachate which depends on the composition of the coal fly ash. The pH values of solutions developed during the leaching process appear to be related to the acidity or alkalinity of the original fly ashes which in turn depends on the CaO or MgO content of the ash. Baba et al., (2007) reported that the effects of pH on leachability has been studied and documented but the effect of temperature has not yet been fully studied, though pH and temperature have a great influence on the seepage of heavy metal into water resources. They studied the transfer of heavy metals from fresh (unweathered) fly ash to water with standard experimental methods at different pH and temperature conditions and found that metals leaches from coal fly ash at concentrations inversely proportional to the leachate pH and temperatures. They concluded that the metal leaching (As, Cd, Co, total Cr, Cr^{6+}, Cu, Ni, Pb, Se and Zn) increases with decreasing pH. Temperatures beyond 30 °C stabilize element concentrations of Cd, Cr, Pb, As and Cr (VI) irrespective of the pH of the system.

The leaching behaviour of coal fly ash is also influenced by its mineralogical compositions because the liberation of species from solid wastes in aqueous solutions depends on the mineral forms of the species present in the solid state (Jankowski et al., 2006). In coal fly ash the leachability of toxic species usually depends on their speciation and the type of the host phases. The morphology of the coal fly ash particles has an effect on its leachability. The occurrence of a non-porous uninterrupted outer surface and a dense particle interior can limit heavy metal leachability from the combustion residues. Particle size distributions in conjunction with specific surface area of the material also provide information on potential interactions between the material and the aqueous solutions (Saikia et al., 2006).

Example of some leaching tests are the DIN-S4 (German leach test), acid neutralization capacity test (ANC), toxicity characteristic leaching protocol (TCLP), serial batch leaching procedure (SBLP), synthetic groundwater leaching procedure (SGLP), mine water leaching procedure (MWLP), 3TIER integrated framework leaching protocol (3TIER) (Fatoba, 2008, Kim and Hesbach, 2009).

2.12 Mobility of Species in Fly Ash

The mobility of potential pollutants (chemical species) due to ash leaching has been the focus of broad research as understanding the factors that determine environmental mobility of species from coal fly ash is important in evaluating the potential impacts of fly ash on the environment and developing novel methods to control the species leaching from fly ash. Apart from Si, Al and Fe, fly ash may also be rich in potentially mobile major elements such as Ca, Mg, Na and K, and in minor elements, such as P and B. A number of metals and metalloids (such as Cd, As, Se, Pb, Ni, Cu, Cr, Co, Mo, Be) present as carbonates, oxides, hydroxides and sulphates, may also occur in trace concentrations (Gómez et al. 2007). The elements that are adsorbed on the particle surfaces are much more easily mobilized into solution during fly ash-water interaction. The leachability of these elements is closely related to the phases with which they are associated, as well as to the pH and other aspects of the leaching environment (Jankowski et al., 2006)

A significant factor in the mobility of particular elements in emplaced ashes is the pH developed within the relevant ash-water system. Fly ash, especially ash with an alkaline pH, also has a relatively strong buffering capacity, and tends to retain its natural pH value to a significant extent even if placed in a contrasting pH environment (Jankowski et al., 2006). Fly ash varies from acidic to alkaline depending on the chemical composition of the source coal, those with high proportions of Ca and Mg, for example, in relation to those of absorbed sulphates ions, may develop a very alkaline pH (11-12) on contact with water; while the ones that do not have significant concentrations of Ca and Mg in relation to the sulphate content, characteristically develop acid pH values (about 4-5) (Ward et al., 2009). Studies have shown that the mobility of many species in fly ash also varies with the ash disposal method and that the difference in species mobility is largely attributed to the changes in the pH of the ash water system. Analysis of leachate water from ash ponds reveals that alkalinity and acidity controlled the extractability of elements like As, B, Be, Cd, Cr, Cu, F, Mo, Se, V and Zn. Aqueous extracts of an acidic fly ash contained concentrations of Cd, Co, Cu, Mn, Ni, Zn, As, B, Be, Cd, F, Mo, Se and V (Ward et al., 2009; R.Iyer, 2002).

The mobility of trace elements from coal fly ashes also depends on the element concentration and mode of occurrence, studies have shown (Alborés et al., 2000; Kalembkiewicz et al., 2008) that mobility and biological availability of trace metals in solid waste materials like coal fly ash depend not only on their total concentration but also on the physicochemical forms in which they occur. It is now widely recognized that the toxicity and the mobility of these pollutants depend strongly on their specific chemical forms and on their binding state (Gleyzes et al., 2002). Hence, identification of the main binding states and phase associations of trace elements in solid waste samples helps in understanding geochemical processes in order to evaluate the remobilization potential and the risks induced (Gleyzes et al., 2002).

Several studies have acknowledged that the mobilization of various elements in coal fly ash are controlled by factors such as precipitation/dissolution, complex formation, adsorption/desorption and redox reactions (Matigod et al., 1990). Leaching tests are used to explain the mobility of certain elements in soils, industrial wastes and other materials, as well as in ionic speciation (Querol et al., 1996). Speciation which provides information about the chemical association form of a certain metal is often needed in the modelling and prediction of dissolution processes. For this reason it is important to evaluate the speciation of particulate metals, speciation refers to the partitioning of metal among the various mineral forms in which they may exist.

Chemical speciation can be defined as the process of determining and recognizing specific chemical species or binding forms; it allows discerning the availability and mobility of metals in solid waste samples in order to understand their chemical behaviour and fate. Thus, some useful environmental guidelines for handling potential toxic hazards can be developed (Huang et al., 2007). Chemical speciation is of interest in environmental analytical chemistry because the behaviour of trace elements in natural systems depends on the forms, as well as the amounts, which are present (Kalembkiewicz et al., 2008).

In this study, the environmental mobility of chemical species in the Secunda coal fly ash co-disposed with brine shall be investigated by means of sequential extraction. Chemical extraction techniques such as sequential extraction have been employed to determine the geochemical association of metals in fly ash and also provide a reasonable estimate of metal availability under environmentally relevant conditions. These particulate materials are subjected to sequential extraction so metal mobility can be characterised (Jegadasaan et al., 2008; Karlfeldt and Steenari. 2007).

2.12.1 Sequential Extraction

Sequential extraction is an analytical method that sequentially chemically leaches metals from soil, sludge or sediments. It is a process widely used to fractionate chemical species in solids materials into several groups of different leachability which is usually applied in determining the distribution of metals in different phases. It has been recently applied to solid waste like municipal solid waste incinerator (MWSI) bottom ash and fly ash (Bruder-Hubscher et al., 2007; Wan et al 2006) and coal fly ash (Jegadasaan et al., 2008). Sequential extraction results can give detailed information about origin, mode of occurrence, bioavailability, potential mobilizability, and transport of the metals in natural environments (Tessier et al., 1979). It is therefore widely used as a tool for the study of source and fate of metals in many solid materials such as soil, sludge, sediment and solid waste (Shiowatana et al., 2001). Sequential extraction procedures involve subjecting a given solid sample (soil, sediment, sludge, bottom ash or fly ash) to a sequence of increasingly strong leachant reagents possessing different chemical properties (acidity, redox potential, or complexing properties) under specified conditions (Nirel and Morel, 1990; Tokalioglu et al., 2005). Several sequential extraction methods were developed during the ‘70s and ‘80s, the idea behind their development was that the consecutive use of selective reagents (single or mixtures), could stepwise release the metals associated with a specific bottom fractions, like carbonates, oxyhydroxides, sulphides, organic material or those present in a very labile (exchangeable-adsorbed) or non-labile (crystalline) form. Usually, extraction liquids that are suitable to dissolve specific mineral phases are selected (Baeyens et al., 2003).

The limitations associated with sequential extraction procedures include non-selectivity of the extractants, re-adsorption among phases during the extraction, extraction being highly affected by the operating conditions and difficulty of comparing results from different methods (Gleyzes et al., 2002). Sample collection, preparation and storage can also lead to changes in chemical speciation and thus cause misinterpretation of results. The disturbance of equilibrium conditions, particularly during sample collection can be a major source of error. Thus these procedures are said to be operational and do not provide a true picture of the forms of trace metals. Being operationally defined procedures, sequential extractions unavoidably give results that depend on the extraction factors such as type, concentration, and pH of each reagent, sample weight to extractant volume ratios, extraction times and temperatures, methods of shaking and phase separation, etc. (Shiowatana et al., 2000).

The sequential extraction procedures adapted by Tessier et al., (1979) and the Community Bureau of Reference (BCR) are the most commonly used procedures (Shiowatana et al., 2001). The procedure developed by Tessier et al., (1979) assumes that the chemical behaviour of a certain element is related to five fractions namely exchangeable, carbonate, Fe/Mn sulphide and the residual fractions. The exchangeable fraction relates to the form of metals that can be released by simply changing the ionic strength of the medium. The metal content bound to carbonates is sensitive to changes in pH and can become mobilised when pH is decreased. The metal fraction bound to Fe–Mn oxides and organic matter can be mobilised with increasing reducing or oxidising conditions in the environment. The metal fractions associated with the residual fraction (e.g. silicate) are not expected to be released in solution over a reasonable time span under the conditions normally encountered in nature (Tessier et al., 1979). The BCR three-step sequential extraction procedure was developed by the Standards, Measurements and Testing Programme (formerly BCR) of the European Commission. The procedure was modified by a group of European experts in order to create an accepted protocol that could be used and the results easily reproduced. The BCR consists or the following three steps namely extraction A, exchangeable and weak-acid soluble fraction; extraction B, reducible fraction; extraction C, oxidisable fraction, the residue from extraction C is digested with aqua regia (extraction D) (Gleyzes et al., 2002).

2.13 Brine

Brines are saline effluents that are a direct consequence of the drive to recover water through desalination process. They are defined as waters saturated or nearly saturated with salt and are commonly considered to be those waters more concentrated in dissolved materials than sea water (35 g of dissolved constituents per kg of sea water) (Muriithi, 2009).). Brine can contain salt concentration more than five times greater than the salt content of average sea water. At 15.5 ºC (60 ºF) saturated brine is 26.4 % salt by weight, at 0 ºC (32 ºF) brine can only hold 23.3 % salt (McCaffrey et al., 1987).

Desalination is the term used to describe the process of removal of salts from water. This process uses saline feed water, usually obtained from the ocean or ground water or that can originate due to human activities to produce two streams of water, fresh water and waste water (saline effluents) also known as brine (Abdul-Wahab and Al-Weshahi, 2009). This waste water (saline effluent) from the desalination process contains high concentrations of salts and residues of chemicals that were used in the purification process together with the by-products resulting from the process (Mohamed et al., 2005). Desalination can be achieved by using a number of techniques such as membrane technologies (reverse osmosis (RO), nanofiltration (NF), ultrafiltration, and microfiltration); distillation processes (thermal technologies such as multi-stage flush (MSF) and vapour compression (VC)); and chemical approaches (ion exchange) (Younos and Tulou, 2005).

Brines contain various cations and anions depending on their origins, and generally contain Ca, Mg, Na, K, Br, Fe, SiO_2, Cl^-, NH_3, CO_3^{2-}, NO_3, SO_4, Fl^-, trace elements and have a pH of approximately 7.5. Some brines may also contain heavy metals and even organic contaminants (Nyamhingura, 2009). According to Mooketsi et al., (2007), Sasol Synfuels brines consist of the following components: Na (2% - 4.4 %), Cl (5 %), SO_4 (5 %), Ca (0.12 %), K (0.38 %), Mg (0.059 %), ions and trace elements such as Fe, Mn, Cr, V, Ti, P, Si and Al. Nyamhingura, (2009) in his study of brines from two different power plant (Eskom, Tutuka and Sasol, Secunda), confirmed that brine composition and concentration is highly variable at South African power utilities and processes such as reverse osmosis, contact with ash and CO_2 ingress can have an impact upon the overall brine quality and concentration.

The Sasol synthetic fuel plant in Secunda is situated in the interior of South Africa in water sensitive catchment areas, where the re-use and recycling of water are compulsory (Menghistu, 2010). Hence it was decided in the 1980's to design it as a zero effluent discharge complex (Muntingh et al., 2009). Large quantities of water are utilized in producing steam for gasification; process heating; electricity generation and for general process cooling. Both Reverse Osmosis (RO) and Electro-Dialysis Reversal (EDR) are the water treatment process utilized at the plant (Nyamhingura, 2009). Although the re-use and recycling of the water significantly cuts down the volumes of effluent, still huge amounts of saline/salty effluents (brine) remains that have to be disposed. The brines (saline/salty effluents) evolve from the desalination, demineralization and evaporation processes that are employed for optimum utilization, upgrading and re-use of the various industrial effluents (Mooketsi et al., 2007).

Brines generated in industrial applications such as power generation are pollutants which must be disposed of safely in a manner that protects the environment and abides by the principles of sustainable development. Although much progress into desalination techniques has been made over the past decade at Sasol synthetic fuel plant in Secunda, concentrated saline effluents still present a major challenge in finding sustainable treatment and disposal methods (Muntingh et al., 2009).

2.13.1 Brine Disposal

Brine is deemed a waste by-product of the desalination processes that cannot be reprocessed and that must be disposed safely. In coastal regions, disposal of brine water can be accomplished by discharging into the neighbouring body of seawater. In land areas brine from desalination plants is disposed into a surface impoundment (unlined pits). The selection of a suitable brine disposal method is influenced by several factors such as: amount of concentrate; constituents of concentrate; physical or geographical location of the discharge point of the concentrate; availability of receiving site; permissibility of the option; public acceptance; capital and operating costs; ability for the facility to be expanded; and economics of the recovered product (Mickley et al., 1993). The impacts of its disposal on the environment are usually underestimated, irrespective of the high concentrations of its constituents. A good example is the pollution of ground water resources that may arise from the improper surface disposal of brine (Wahab and Al-Weshahi, 2009).

Brine management methods currently used in desalination plants include: deep injection wells; irrigation systems; evaporation ponds; freeze crystallization; salt recovery/harvesting systems (or salt harvesting); direct discharge of the brine at the coastline; discharging the brines by a long pipe far into the sea; discharging the brines via the outlet of the power station’s cooling water; direct discharge to waste water treatment plants; power generation (methods of energy recovery); aquaculture; and value adding (on-site hypochlorite generation) (Wahab and Al-Weshahi, 2009).

2.13.2 Brine Disposal at Sasol, Secunda

Brine handling and disposal is a difficult and complex challenge. Currently in the Sasol plant in Secunda, the bulk of the brine is co-disposed with the ash residue in the ash dam (Muntingh et al., 2009). The brine and the ash are mixed to form pumpable slurry (with 20 % solids) which is pumped into ash dams. The ash settles in the dam and the brine percolates into clear effluent dams where the salty water is recycled. The cementing properties (pozzolanic properties) of the ash are assumed to enable the salts in the brine to be encapsulated and bound in the ash preventing rapid leaching of the salts, a practice that has not yet been proven to be sustainable. According to Menghistu, (2010), pozzolanic reactions are not possible within the wet ash dams because wet ash dams are normally saturated with water so that carbon dioxide cannot permeate through, and carbon dioxide is vital for pozzololanic reactions to occur. The wet ash dams only have a few millimetre thick layers of pozzolanic material on its surface which is formed from atmospheric carbon dioxide. Hence the co-disposal of coal fly ash and brine may have adverse effects on the environment due to the accumulation of salts within the ash system and its subsequent leaching.

2.14 Conclusion

Coal is one of the world's major important and rich energy sources and is mostly combusted to generate electrical power, which subsequently leads to the production of fly ash, a particulate waste product that result during the combustion of pulverised coal. The bulk of the fly ash produced globally is disposed as waste and only a minor fraction are beneficially reused. Various environmental risks are associated with fly ash disposal, these include air pollution, loss of arable land and surface and ground water contamination due to the leaching and mobilization of non-degradable toxic metals, and other chemical species from the ash dump by rainfall or groundwater. The management of this combustion waste is of major concern and requires the proper understanding of the weathering characteristics of fly ash because the huge amount that is disposed as waste cannot be separated from nature’s weathering cycle. The weathering of fly ash results in changes in the physical, chemical and mineralogical properties. Some of these changes may include the formation of secondary minerals, decrease in the pH and EC values of the pore water and leaching of soluble salt content. This may have significant effects on the leaching and mobilization of the fly ash species. Thus evaluating changes in the chemical, physical and morphological properties and phase transformation studies of fly ash during long term storage are vital in predicting the environmental impact associated with fly ash disposal techniques and uses.

Several methods including X-ray Fluorescence (XRF) analysis, X-ray Diffraction (XRD) analysis, Scanning Electron Microscope and Energy Dispersive X-ray spectrometry (SEM-EDS), have been used to determine and characterize, the morphology, chemical and mineralogical composition and phases of the fresh and weathered fly ash. Also sequential chemical extraction has been used to understand, evaluate and determine the various mineral phases with which the elements were associated. These studies were usually based on fly ash samples that were stored or disposed using different methods. But no study has tried comparing the fresh fly ash to that of a wet ash dam that was co-disposed with brine a saline effluent in order to understand the effect of the co-disposed brine on the physical and chemical properties of the fly ash over time; the effect of the co-disposed brine on the weathering of the fly ash and the sustainability of the fly ash and brine co-disposal dump as a salt sink.

The main focus of this study is therefore to determine if the fly ash dump is a sustainable salt sink when brine is co-disposed upon it. This aim shall be achieved through study of the effects of weathering on the chemical, morphological properties and mineralogical composition coal fly ash that was co-disposed with brine. This sequential extraction scheme will be employed as it has been shown to provide understanding of the elemental partitioning in both the fresh and weathered fly ash. This will play a vital role in predicting the environmental impact associated with fly ash disposal techniques and beneficiations and in determining the sustainability of the ash dam as a salt sink.

Chapter Three

Materials and Methods

3 Introduction

The previous chapter reviewed the literature concerning coal and fly ash with a specific focus on weathering. This chapter describes the sampling methods used in this study in section 3.1. The experimental methodology and analytical methods used in this study are presented in sections 3.2 and 3.3 respectively.

3.1 Sampling of Fly ash from Secunda Ash Dam

The fresh fly ash and weathered fly ash Samples used in this study were collected from the Sasol-Syngas plants located in Secunda in Mpumalanga province of South Africa. The fresh Secunda fly ash sample that was used in this study was collected directly from the hoppers at SASOL (Secunda) in South Africa. The fly ash samples were kept in plastic containers which were tightly closed to prevent ingress of air, and stored at room temperature for subsequent analysis. The weathered Secunda fly ash were obtained from the fine ash dam according to the following procedure

3.1.1 Procedure

A combination of air flush coring and standard percussion drilling was used to drill the cores from the ash dump. An initial starter hole was drilled (215 mm diameter) using air percussion drilling through the overburden to the top of the ash. The air flush coring technique was then used to drill to the bottom of the ash dump. Standard air percussion of 165 mm diameter was used to drill into the underlying bedrock. Large diameter vertical boreholes were drilled in the ash dump to extract samples from different depths for evaluation. The drilling technique produced 165 mm diameter cores from which approximately 100-200 gram of fly ash sample was taken from the core inside the air flush core barrel at 1.5 meter sampling intervals. A sample of ash was 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 (30cm) 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. During the coring process of S1, the drilling stopped at 22.5 meters due to an unknown obstruction in the dump that prevented the auger from proceeding further. S3 coring stopped at 31.5 meters.

3.1.2 Storage of Samples

The fly ash samples extracted from the drilled Secunda cores S1 and S3 and hoppers were stored in sealed plastic containers that were labelled accordingly, in a dark cool cupboard far away from any heat source, direct sunlight and fluctuating temperatures.

3.1.3 Storage of Leachates for Analysis

After pore water analysis, total acid digestion and sequential extraction of drilled core samples as described in section 3.2.3, 3.2.4 and 3.2.5 were carried out in the laboratory. The samples from the extracts of the fly ashes were taken after being filtered through a 0.45 μm cellouse nitrate membrane filter paper. The samples for anion analysis were kept in the refrigerator at 4 °C while the samples for cation analysis were acidified with concentrated HNO3 before storage in the refrigerator at 4 °C. The samples were analysed for anions using ion chromatography (IC) and for cations using inductively coupled plasma - optical emission spectrometer (ICP-OES).

3.2 Methodology

The experimental procedures used in this study to extract species from the fly ash samples are moisture content determination; pore-water chemistry; total acid digestion and sequential extraction. The list of reagents used is given in Table 3.1

List of reagents used

Table 3.1 below presents the name, source, catalogue number and purity of the reagents that were used in this study.

Table 3.2.1: List of reagents used

Reagent	Name	Source	Catalogue No.	% Purity
$HClO_4$	Perchloric acid	Merck	100519	60
HF	Hydrofluoric acid	Merck	100334	48
HNO_3	Nitric acid	Merck	100443	65
CH_3COONH_4	Ammonium Acetate	Merck	101116	98
NH_2OHCl	Hydroxylamine Hydrochloride	Merck	104611	99
HCl	Hydrochloric acid	Merck	101514	32
H_2BO_3	Boric acid	Merck	100162	99.5

3.2.1 Preparation of reagents

The preparation of the chemical used in the sequential extraction tests are described below

1 M Ammonium acetate (NH_4AC)

77.09 g of ammonium acetate was weighed into a 1 L volumetric flask. Ultrapure water was added to dissolve the salt. After the complete dissolution of the salt, the solution was made up to the1L mark with ultrapure water and mixed.

1 M Acetic acid (CH_3COOH)

57.47 cm3 of acetic acid was measured into a 1 L volumetric flask containing ultrapure water. More ultrapure water was added and the diluted acid was shaken and made up to the 1 L mark with ultrapure water and mixed.

0.025 M Nitric acid (HNO_3)

2.1 cm3 of concentrated HNO_3 was accurately measured and added into a 1 L volumetric flask containing ultrapure water. More ultrapure water was added to the diluted HNO_3 and the diluted acid was shaken and made up to the 1 L mark with ultrapure water and mixed.

0.25 M Hydroxylamine hydrochloride (NH_2OHCl)

17.37 g hydroxylamine hydrochloride (NH_2OHCl) was weighed into 1 L volumetric flask. Ultrapure water was added to dissolve the salt. After the complete dissolution of the salt, the solution was made up to I L mark with ultrapure water and mixed.

3.2.2 Moisture Content Determination

Moisture content is the quantity of water contained in a material such as soils, sewage, sludge and rocks, expressed in percentage by weight of water in the mass. The moisture content influences the physical properties of a material such as weight, density, electrical conductivity and more. Two methods are usually employed in the determination of the moisture content. These are the thermo-gravimetric method and the loss on drying technique. The loss on drying technique was employed in this study. This was carried out by drying pre-weighed samples of the fresh ash as well as pre-weighed samples taken at 1.5 m intervals down the drilled Secunda ash columns S1 and S3 at 105 ºC for 24 hours. The sample was then allowed to cool down and weighed again. The percentage moisture content was then calculated from the difference in weight of the sample (www.deldot.gov/information/). Moisture content was calculated as follows:

$$\%\ \text{moisture} = \frac{\text{Change in weight of sample after drying}}{\text{Weight of sample after drying}} \times 100$$

3.2.3 Pore-Water Chemistry

The pore water chemistry of the ash samples was done to determine the amount of cations and anions that are soluble after fly ash had been interacted with neutral water. The alkalinity or acidity of the fly ash was also obtained from this experiment. For the determination, a 1:10 ratio of core: water was used. 10 grams of each of the Secunda ash core S1 and S3 samples that had been taken at 1.5 m intervals down the profile of the ash dump were used. Samples were weighed and each put in a polyethylene flask and suspended in 100 mL of ultra-pure water. The mixture was then agitated thoroughly for 30 min and allowed to settle for 15 min. The pH and electrical conductivity (EC) and total dissolved solids (TDS) of the supernatant were recorded with a Hanna HI 991301 pH meter with portable pH/EC/TDS/Temperature probe. The pH meter was calibrated before use with a buffer solution of pH 4.0 and 7.0. The filtrate was set aside for analysis of anions using ion chromatography. Triplicate analysis was carried out in each case. The solution was filtered through a 45 µm membrane filter paper. There after the supernatant was collected and analysed for anions (SO_4^{2-} and Cl^-) present using a Dionex ICS-16000 ion chromatograph (IC) with an Ion Pac AS14A column and AG14-4 mm guard column.

3.2.4 Total Acid Digestion

The digestant for total acid digestion of the solid ash samples selected included $HClO_4$: HF: HNO_3 mixed in the ratio of 3:3:1. The digested solutions are similar to those used in a previous study by the authors Smeda and Zyrnicki, (2002) and Mester et al., (1999). Perchloric acid ($HClO_4$) is commonly used as oxidants for the digestion. In general, perchloric acid has high strength of oxidation.

0.5 g of the drilled ash Secunda core S1 and S3 samples taken at a depth interval of 1 m was weighed into a Teflon cup. 7 mL of combined acid ($HClO_4$: HF: HNO_3) mixed in the ratio of 3:3:1 respectively was added. The Parr bomb the Teflon cup was sealed and heated to 180 °C for 3 hours in an oven. It was removed from the oven and allowed to cool down. The sample was allowed to cool after which 35 mL of H_3BO_3 was added in order to neutralize the excess HF and made up to 100 mL with ultra-pure water (ELGA Pure lab UHQ). The solution obtained was analysed for major and trace species with ICP-OES. The procedure was triplicated for each sample.

3.2.5 Sequential Extraction Procedure

Sequential extraction is an analytical method that sequentially chemically leaches elements out of the various mineralogical fractions present in soil, sludge or sediments. It has been recently applied to solid waste such as municipal solid waste incinerator (MWSI) bottom ash and fly ash and coal fly ash (Bruder-Hubscher et al, 2002). Sequential extraction results can give detailed information about origin, mode of occurrence, bioavailability, potential mobilizability, and transport of the metals in natural environments. It is therefore widely used as a tool for the study of the source and fate of elements in many solid materials such as soil, sludge, sediment and solid waste. Sequential extraction procedures involve subjecting a given solid sample to a sequence of increasingly strong reagents possessing different chemical properties (acidity, redox potential, or complexing properties) under specified conditions. These extractions are intended to replicate the different possible natural and anthropogenic modifications of environmental conditions. The five-step sequential extraction applied in this study is described below. The extraction method was a modified form of the method proposed by Tessier et al, (1979), (steps 2, 3, 4 and 5). The modification consisted of a water soluble extraction step which was added in this study. First, a water soluble fraction extraction was executed followed by exchangeable fraction extraction, carbonate fraction extraction, iron manganese fraction extraction and residual fraction extraction. The metals extracted were analysed for using inductively coupled plasma - optical emission spectrometer (ICP-OES). The detailed procedures are as follows:

Step 1: Water soluble fractions

1 g of the ash samples taken directly from the ash core samples at various intervals in the ash horizon was weighed into 50 mL centrifuge tubes and 45 mL of ultra-pure water (H2O) was added. The samples were then shaken at room temperature for 1 hour with a mechanical shaker. The procedure was repeated to give triplicate samples. The solution was allowed to settle down for 1 hour. The mixture was centrifuged at 6000 rpm for 20 minutes and the supernatant filtered through a 42 µm pore nucleopore membrane. The remaining solid portion was carefully decanted into a 100 mL plastic clear bottle to reduce weight loss. 42 mL of filtered supernatant was recovered. 10 mL of the supernatant solution was measured into a standard volumetric flask and made up to 100 mL with ultra-pure water (ELGA Pure lab UHQ). The solution obtained was set aside for analysis of major and trace species with ICP-MS. The solid residue remaining after the extraction was quantitatively recovered and kept in a refrigerated condition for the next extraction method.

Step 2: Exchangeable fractions (Extraction at pH 7)

45 mL of the 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. The mixture was then centrifuged at 6000 rpm for 20 minutes and filtered through a 42 µm pore nucleopore membrane. The solid portion was decanted into a 100 mL plastic clear bottle quantitatively to avoid weight loss. 44 mL of filtered supernatant was recovered. 10 mL of the supernatant solution was measured into a standard volumetric flask and made up to 100 mL with ultra-pure water (ELGA Pure lab UHQ). The solution obtained was set aside for analysis of major and trace species with ICP-OES. The residue recovered from this step was kept in a refrigerated condition to avoid contamination.

Step 3: Carbonate fractions (Extraction at pH 5)

45 mL of 1M ammonium acetate buffer solution at pH 5 was added to the 0.97 g of solid residue recovered from step 2. 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 42 µm pore nucleopore membrane. The solid portion was quantitatively decanted into 100 mL plastic clear bottle to avoid weight loss. 45 mL of supernatant was recovered. 10 mL of the supernatant solution was measured into a standard volumetric flask and make up to 100 mL with deionised water (ultra-pure water generated with ELGA Pure lab UHQ instrument). The solution obtained was set aside for analysis major and trace species with ICP-OES. The residue recovered from this step was kept in a refrigerated condition.

Step 4: Fe and Mn fractions

45 mL of hydroxylamine hydrochloride (0.25M) in nitric acid (0.025 M) solution was added to the 0.94 g of solid residue recovered from step 3. 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 42 µm nucleopore membrane. The solid portion was quantitatively decanted into a 100 mL plastic clear bottle carefully to avoid weight loss. 44 mL of filtered supernatant were recovered. 10 mL of the supernatant solution was measured into a standard volumetric flask and made up to 100 mL with ultra-pure water (ELGA Pure lab UHQ). The solution obtained was set aside for analysis of major and trace species with ICP-OES. The solid residue recovered from this extraction step was kept in a refrigerated condition

Step 5: Residual fractions

The solid residue recovered from step 4 was rinsed with ultra-pure water and quantitatively transferred to a crucible, oven dried at 105 ºC and weighed. 0.90 g of dried sample was carefully transferred into the Teflon cup of a Parr bomb. 14 mL of the combined acid ($HClO_4$: HF: HNO_3) mixed in the ratio of 3:3:1 respectively was added and the Teflon cup placed in a Parr bomb, sealed and heated to 180 °C for 3 hours in an oven. It was removed from the oven and allowed to cool down. After cooling, the solution was diluted with 40 mL of 1% HCl and then filtered through a 42 µm pore nucleopore membrane. 10 mL of the solution was measured into standard volumetric flask and made up to 100 mL with ultra-pure water (ELGA Pure lab UHQ). The solution obtained was set aside for analysis of major and trace species with ICP-OES. Dry weight concentration of the analytes for this residual fraction was calculated using the dilution factor and the weight of the solid residue used in the digestion.

3.3 Analytical Methods

The analytical techniques used in this study was the measurement of pH, Electrical Conductivity (EC), the Total Dissolved Solids (TDS), XRF, XRD, SEM/EDX, IC and ICP – OES.

3.3.1 pH Measurement

The pH of a solution is a measure of the hydrogen ion [H+] concentration in the solution which defines the acidity or alkalinity of the solution. pH analysis is one of the most common analytical tests carried out on any liquid sample including water and wastewater. It is measured on a continuous scale from 0 - 14. The scale is logarithmic. The pH value of a given solution is a measure of the activity of the hydrogen ion (H^+) in that solution. pH measurement involves comparing the potential of solutions with unknown hydrogen ion [H^+] to a known reference potential (Berndt, H, 1991). This is done when the indicating electrode, which is sensitive to the hydrogen ion, develops a potential directly related to the hydrogen concentration in the solution, and the reference electrode provides a stable potential against which the indicating electrode can be compared. The pH meter converts the potential (voltage) ratio between a reference half-cell and an indicating half-cell to pH values. In acidic or alkaline solutions, the voltage on the outer membrane surface changes proportionally to changes in [H^+]. The pH meter detects the change in potential and determines [H^+] of the unknown sample (Fatoba, 2007).

Procedure

The pH of all the samples in this sample in this study was measured, using a Hanna 991 301 pH meter with portable pH/EC/TDS/Temperature probe. The pH meter was calibrated before use with buffer solutions of pH 4.0 and 7.0. The measurements were done at room temperature.

3.3.2 Electrical Conductivity

Electrical conductivity (EC) is related to the concentration of ionized substances in a water sample, and is a measure of the ability of a water sample to convey an electrical current (www.rrcap.unep.org). Conductivity is used to measure the total concentration of inorganic substances in water which depends on the presence, mobility and valence of the species in solution. Conductivity is measured by a probe that applies voltage between two electrodes, spaced a known distance apart, and records the decrease in voltage. This decrease reflects the resistance of the water, which is then converted to conductivity. Thus, conductivity is the inverse of resistance and is measured as the amount of conductance over a certain distance. EC is normally measured in mScm-1 or µScm-1or in µmohmscm-1 (1mScm-1 = 1000 µmohmscm-1).

Procedure

The electrical conductivity (EC) measurements of the samples were measured, using a Hanna 991 301 pH meter with portable pH/EC/TDS/Temperature probe. The pH meter was calibrated beforehand and the measurements were done at room temperature.

3.3.3 Total Dissolved Solids

The measurement of total dissolved solids (TDS) is an expression of the combined content of all inorganic and organic substances contained in a liquid which are present in a molecular, ionized or micro-granular (colloidal) suspended form (Fatoba, 2007). Electrical conductivity of water is directly related to the concentration of dissolved ionized solids in the water. Ions from the dissolved solids in water create the ability for that water to conduct an electrical current, which can be measured using a conventional conductivity meter (Theimer et al., 1994). A TDS meter is based on the electrical conductivity (EC) of water. Pure H2O has virtually zero conductivity. Conductivity is usually about 100 times the total cations or anions expressed as equivalents. TDS is calculated by converting the EC by a factor of 0.5 to 1.0 times the EC, depending upon the levels. Typically, the higher the level of EC, the higher the conversion factor to determine the TDS. While a TDS meter is based on conductivity, TDS and conductivity are not the same thing.

Procedure

The total dissolved solids (TDS) of the samples in this study were measured by using a Hanna 991 301 pH meter with portable pH/EC/TDS/Temperature probe. The pH meter was calibrated beforehand and the measurements were done at room temperature.

3.3.4 Bulk Chemical Composition Analysis (XRF)

X-ray Fluorescence (XRF) spectroscopy is generally used for the qualitative and quantitative elemental analysis of solid environmental, geological, biological, industrial and other samples. XRF is a better multi-element analytical technique when compared to other techniques such as, Inductively Coupled Plasma Spectroscopy (ICPS) which requires dissolution procedures that are generally time consuming and can induce losses of some volatile elements (As, Pb, Se, Sb and Zn); and Neutron Activation Analysis (NAA) which is expensive and not widely available. XRF has the advantage of being non-destructive, fast and cost-effective. It also afford a reasonably uniform detection limit across a large portion of the periodic table and is applicable to a wide range of concentrations, from a 100% to few parts per million. Its disadvantages are that analyses are normally limited to elements heavier than fluorine and that a large amount of sample is required for analysis due to the sample preparation method (Brown and Milton, 2005).

Procedure

The bulk chemical compositions of the drilled Secunda ash core S1 and S3 samples were determined with X-ray fluorescence spectrometry (XRF) A PW1480 x-ray fluorescence spectrometer using a Rhodium Tube as the x-ray source was used. The samples for XRF analysis were taken at intervals of 1.5 m along the depth of the drilled cores S1 and S3 from Sasol-Synfuels-Secunda. The core ash samples were oven-dried at 100 °C for 12 hours to determine the adsorbed water prior to analysis, and milled to a uniform size grained powder. The powder samples were then mixed with a binder (ratio of 1: 9 in grams of at a ratio of 2: 9 (2 g binder and 9 g sample). The powder mixture was then pelletized at a pressure 15 Kbars. Loss on ignition (LOI) experiment was performed prior to major element analysis and for accuracy of the analytical results. Elements reported as mass % oxides were converted to mass % of the elements using element conversion software downloaded at www.marscigrp.org/elconv.html. The technique reports concentration as % oxides for major elements and ppm (mg/kg) for minor and trace elements.

3.3.5 Mineralogical analysis (XRD)

X-ray diffraction (XRD) is an analytical technique which uses the diffraction pattern produced by bombarding a single crystal with X-rays to determine the phase identity and crystal structure. The diffraction pattern is recorded and then analyzed or "solved" to reveal the nature of the crystal (Wicks et al., 1995). This technique is widely used in chemistry and biochemistry to determine the structures of an immense variety of molecules, including inorganic compounds, DNA, and proteins. When single crystals are not available, related techniques such as powder diffraction or thin film x-ray diffraction coupled with lattice refinement alogrithms such as Rietveld refinement may be used to extract similar, though less complete, information about the nature of the crystal. The atomic spacing in the crystal lattice can be determined using Bragg's law ($n\lambda=2d\sin\theta$) (Scrivener et al. 2004). The electrons that surround the atoms, rather than the atomic nuclei themselves, are the entities that physically interact with the incoming X-ray photons. If the angles of incidence (θ) and the wavelenght (λ) are known, the spacing d of the reflecting atomic planes can be determined using the above equation. The lattice spacing is characteristic of the mineral, thus, the X-ray diffraction method can be used for the identification of minerals and for the analysis of mixtures of minerals.

Procedure

The mineralogical identity and phase purity of the fly ash samples were determined by XRD. A D8 ADVANCE from BRUKER AXS instrument equipped with a pw3830 X-ray generator operated at 40 kV and 40 mA was used. The ash samples were oven-dried at 105°C for 12 hours to remove the adsorbed water. The samples were pressed into rectangular aluminium sample holders using an alcohol wiped spatula and then clipped into the instrument sample holder. The representative samples for different depths and ages were step-scanned from 12 to 80 ° 2Θ scale at intervals of 0.02 ° and counted for 0.5 seconds per step.

3.3.6 Morphological Analysis (SEM)

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface. The SEM uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens. The signals that are derived from electron-sample interactions reveal information about the sample (Thomas and Gai, 2004). Due to the manner in which the image is created, SEM images have a characteristic three-dimensional appearance and are useful for judging the surface structure and morphology (texture), chemical composition, and crystalline structure and orientation of materials making up the sample of the sample. The SEM is routinely used to generate high-resolution images of shapes of objects and to show spatial variations in chemical compositions. It is also widely used to identify phases based on qualitative chemical analysis and/or crystalline structure. Precise measurement of very small features and objects down to 50 nm in size is also accomplished using the SEM. Specimen preparation includes drying the sample in the oven at 100 °C and making it conductive, if it is not already. Photographs are taken at a very slow rate of scan in order to capture greater resolution. SEM is typically used to examine the external structure of objects that are as varied as biological specimens, rocks, metals, ceramics and almost anything that can be observed in a dissecting light microscope (http://serc.carleton.edu/research_education/geochemsheets/techniques/SEM.html).

Scanning electron microscopy examines structure by bombarding the specimen with a scanning beam of electrons and then collecting slow moving secondary electrons that the specimen generates (Thomas and Gai, 2004). These are collected, amplified, and displayed on a cathode ray tube. The electron beam and the cathode ray tube scan synchronously so that an image of the surface of the specimen is formed.

Detection of secondary electrons

The most common imaging mode monitors low energy (<50 eV) secondary electrons. Due to their low energy, these electrons originate within a few nanometers from the surface. The electrons are detected by a scintillator-photomultiplier device and the resulting signal is rendered into a two-dimensional intensity distribution that can be viewed and saved as a digital image. This process relies on a raster-scanned primary beam. The brightness of the signal depends on the number of secondary electrons reaching the detector. If the beam enters the sample perpendicular to the surface, then the activated region is uniform about the axis of the beam and a certain number of electrons escape from within the sample. As the angle of incidence increases, the "escape" distance of one side of the beam will decrease, and more secondary electrons will be emitted. Thus steep surfaces and edges tend to be brighter than flat surfaces, which results in images with a well-defined, three-dimensional appearance. Using this technique, resolutions less than 1 nm are possible.

Procedure

The scanning electron microscope / electron dispersive x-ray spectroscopy (SEM / EDX) analysis was carried out with an Nova Nano SEM 230, equipped with an Oxford X- max detector and Inca software was used for the elemental analysis by EDS. The fly ash samples were oven-dried at 105 °C for 12 hours in preparation for the analysis. The dried samples were sprinkled on special glue mixed with carbon graphite. Each sample was then mounted into specimen holders and the morphology (texture) and chemistry of the samples were analysed from backscattered electron as well as secondary electron images.

3.3.7 Ion Chromatography (IC)

Ion chromatography is a form of liquid chromatography that uses ion-exchange resins to separate atomic or molecular ions based on their interaction with the resin. Its greatest utility is for analysis of anions for which there are no other rapid analytical methods. It is used for water chemistry analysis. Ion chromatographs are able to measure concentrations of major anions, such as fluoride, chloride, nitrate, nitrite, and sulphate, as well as major cations such as lithium, sodium, ammonium, potassium, calcium, and magnesium in the parts-per-billion (ppb) range depending on column condition. Concentrations of organic acids can also be measured through ion chromatography. Most ion-exchange separations are done with pumps and metal columns. The column packings for ion chromatography consist of ion-exchange functional groups bonded to inert polymeric particles. For cation separation the cation-exchange resin is usually a sulfonic or carboxylic acid, and for anion separation the anion-exchange resin is usually a quaternary ammonium group.

Ion chromatography, measures concentrations of ionic species by separating them based on their interaction with a resin. Ionic species separate differently depending on species type and size (www.lycos.com/info/ion.html). Sample solutions pass through a pressurized chromatographic column where ions are absorbed by column constituents. As an ion extraction liquid, known as eluent, runs through the column, the absorbed ions begin separating from the column. The retention time of different species determines the ionic concentrations in the sample. Total concentration of ions in solution can be detected qualitatively by measuring the conductivity of the solution.

In ion chromatography, the mobile phase contains ions that create a background conductivity, making it difficult to measure the conductivity due only to the analyte ions as they exit the column. This problem can be greatly reduced by selectively removing the mobile phase ions after the analytical column and before the detector. This is done by converting the mobile phase ions to a neutral form or removing them with an eluent suppressor, which consists of an ion-exchange column or membrane (www.files.chem.vt.edu/chem-ed/sep/lc/ion-chro.html). For cation analysis, the mobile phase is often HCl or HNO3, which can be neutralized by an eluent suppressor that supplies OH-. The Cl- or NO3- is either retained or removed by the suppressor column or membrane. The same principle holds for anion analysis. The mobile phase is often NaOH or NaHCO3, and the eluent suppressor supplies H+ to neutralize the anion and retain or remove the Na+.

Some typical applications of ion chromatography include drinking water analysis for pollution and other constituents; determination of water chemistries in aquatic ecosystems; determination of sugar and salt content in foods; Isolation of select proteins (www.lycos.com/info/ion.html).

Procedure

The leachates of the fly ashes were filtered through a 0.45 µm membrane filter to remove suspended solids and then diluted with de-mineralized water to obtain EC values of between 50 and 100 µS/cm. SO_4^{2-}, Cl^-, NO_3^- and PO_4^{3-} were analysed in the leachates using a DionexICS-16000 ion chromatograph with an Ion Pac AS14A column and AG14-4 mm guard column.

3.3.8 Inductively Coupled Plasma - Optical emission spectrometry (ICP-OES)

The inductively coupled plasma - optical emission spectrometer (ICP-OES) is used to determine concentrations of a wide range of elements in solution. ICP - OES is one of the most widely used analytical techniques for measuring concentrations of major, minor and trace elements. It is a robust analytical method capable of providing analyses for a wide range of elements in a diversity of sample matrices. ICP-OES makes use of the fact that the atoms of elements can take up energy from an inductively coupled plasma, are thereby excited, and fall back into their ground state again emitting a characteristic radiation (Meynen et al. 2009). The identification of this radiation permits the qualitative analysis of a sample. A quantitative determination takes place on the basis of the proportionality of radiation intensity and element concentration in calibration and analysis samples. In ICP-OES analysis, the liquid sample is introduced into the inductively generated argon plasma through a nebulizer system and excited. The spectrum emitted is transferred into a spectrometer where it is decomposed into the individual wavelengths and evaluated. The intensities of the spectral lines are measured by CID semiconductor detectors. Calibration is effected with multi-element solutions mixed from standard solutions.

In ICP-OES, the sample is subjected to temperatures high enough to cause not only dissociation into atoms but to cause significant amounts of collisional excitation (and ionization) of the sample atoms to take place. Once the atoms or ions are in their excited states, they can decay to lower states through thermal or radiative (emission) energy transition. In OES, the intensity of the light emitted at specific wavelengths is measured and used to determine the concentrations of the elements of interest.

Procedure

All the aqueous samples taken in this study were filtered through a 0.45 µm membrane filter to remove suspended solids and then diluted with de-mineralized water to obtain EC values of between 50 and 100 µScm-1. Major, minor and trace elements were analysed using ICP-OES (Varian Liberty II).

Chapter Four

Characterisation and Pore Water Analysis

4 Introduction

The results of the pore water chemistry, morphological, chemical and mineralogical composition of the Secunda fresh fly ash taken from the hoppers and samples taken from the drilled cores S1 and S3 of the 20 years old Secunda brine impacted fly ash dump are presented and discussed this chapter. Section 4.1 presents and discusses the chemical composition of the fresh fly ash and the core samples while the results of the morphological analysis (SEM-EDS data) are presented and discussed in section 4.2. The mineralogical composition of the fresh fly ash and the drilled core samples are presented and discussed in section 4.3. The pore water chemistry of the fresh fly ash and drilled core samples is presented and discussed in section 4.4. This chapter ends with a summary of the comparative bulk chemistry and mineralogy of the fresh fly ash and the drilled cores S1 and S3 from Sasol Synfuels-Secunda ash dam in section 4.5. The sequential extraction results will be presented and discussed in chapter five.

4.1 Sampling of Fly ash from Secunda Ash Dam

The Secunda fly ash used in this study was made up of 87% fly ash from the combustion of pulverised coal to produce steam and electric power and 13% fine ash from the gasification process. The size of the fine ash ranges between 20 ≤50 μm. The fine ash was pumped as slurry of 5:1 water/ash ratio using the high saline stream that was generated from the water treatment processes in the plant. The dump site was created in 1989 and dumping stopped in 2009. The oldest layer at the bottom was 21 years old at the time of sampling (2010) and the youngest at the top was 1 year old. The geophysics electrical resistivity survey profile (Figure 4.1.1), shows the position of the two cores drilled at the fly ash dump. S1 was drilled at 960 m (Latitude 26.560411, longitude 29.119348), and S3 was at 600 m (Latitude 26.557826, longitude 29.118943). During the coring process of S1, the drilling stopped at 22.5 meters due to an unknown obstruction in the dump that prevented the auger from proceeding further, while S3 coring stopped at 31.5 meters. The fly ash samples that were taken from the core were collected at 1.5 meter intervals.

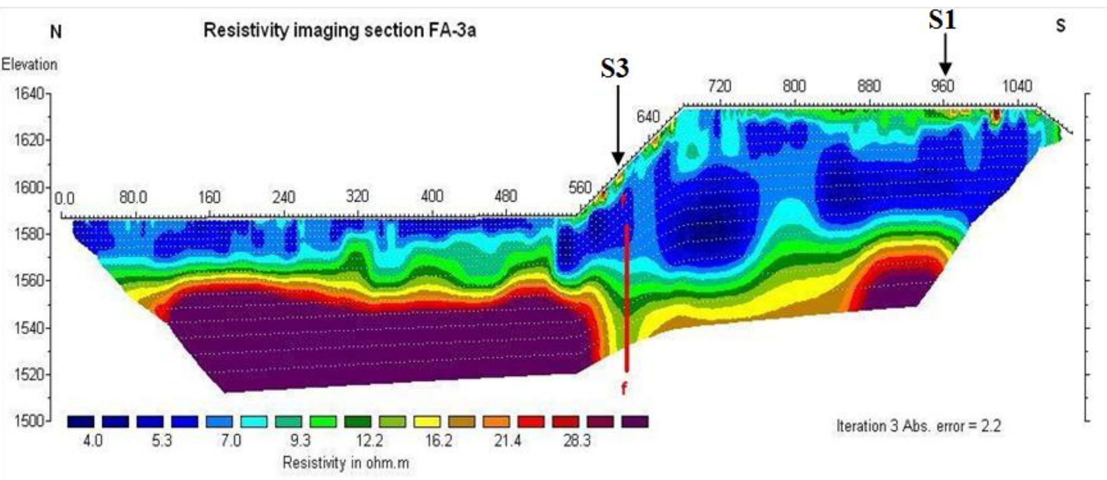


Figure 4.1.1: Resistivity mapping of Secunda ash dump showing sites for cores S1 and S3.

4.2 pH, EC, TDS and moisture profile

Figures 4.2.1 to 4.2.8 show the pH, EC (Electrical Conductivity), TDS (total dissolved solid) profiles and MC (moisture content) of the extracted pore water of the two drilled cores (S1 and S3) as a function of depth.

4.2.1 pH

Figures 4.2.1 to 4.2.2 show the pH profile of the extracted pore water of the fresh fly ash and two drilled cores (S1 and S3) as a function of depth.

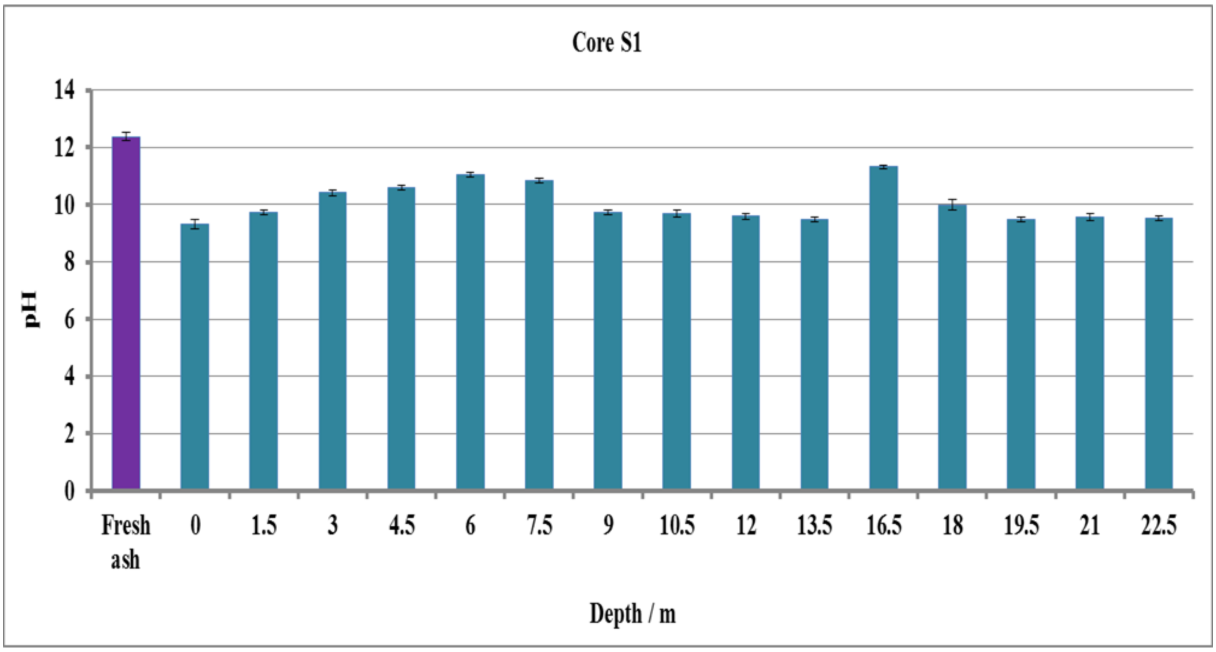


Figure 4.2.1: pH profile of Secunda fresh fly ash and weathered drilled core S1 [number of determinations for fresh ash and S1 are 3 and 30 respectively]

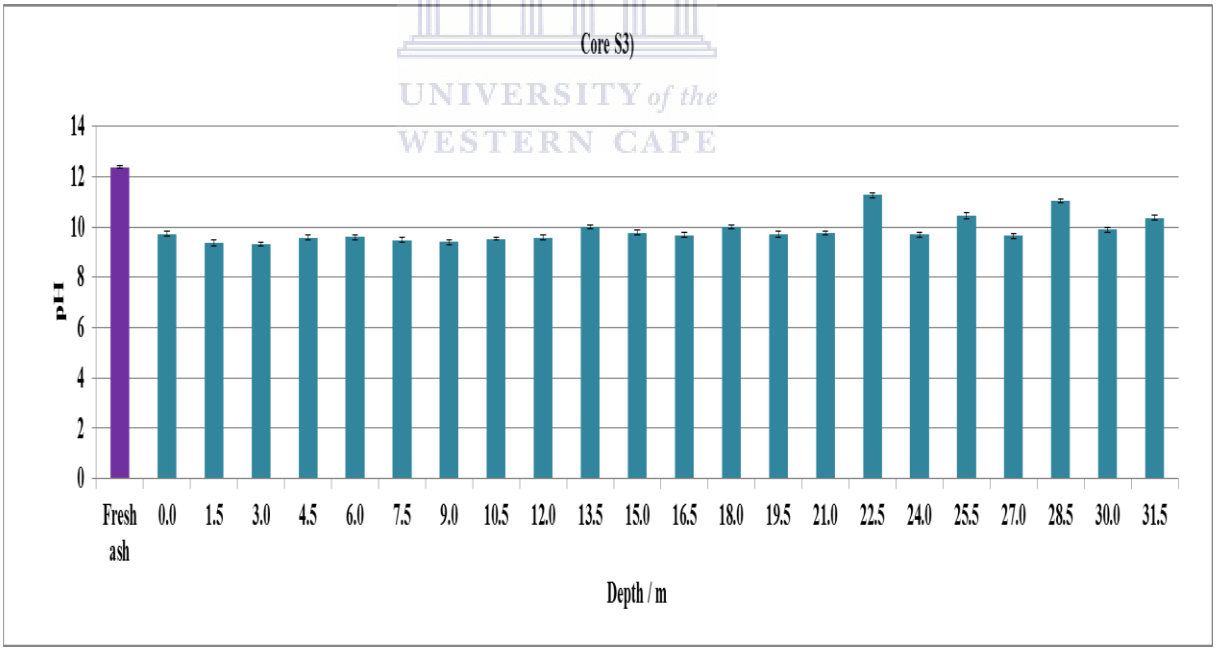


Figure 4.2.2: pH profile of Secunda fresh fly ash and weathered drilled core S3 [number of determinations for fresh ash and S3 are 3 and 44 respectively]

The pH analysis (Figure 4.2.1 and 4.2.2) shows that the fresh Secunda fly ash sample had a pH value of 12.38. For the drilled Secunda ash core sample from core S1, the pH values ranged from 9.33 at the surface to 11.32 at 16.5 m depth and 9.52 at 22.5 m depth (Figure 4.2.1). In the drilled ash core sample S3, the pH values were between 9.32 at 3 m depth and 11.27 at 22.5 m depth, 9.64 at depth 27 m and from 11.02 at 28.5 m to 10.36 m at 31.5 m (Figure 4.2.2). The pH values show that the fresh Secunda fly ash and drilled ash core samples are alkaline. However the pH analysis of the drilled ash cores shows significant decrease in pH from 12.38 in fresh ash compared to a range of 9.33–11.32 in S1 and 9.32–11.27 in S3 showing weathering and inconsistency or inhomogeneity in the ash dump.

The change in pH values in the drilled Secunda ash core samples is attributed to the transformation or loss of CaO and MgO over time resulting from the interactions of the ash and brine as well as with the atmospheric CO_2 and percolating rain water, The changes in pH values can be attributed to the dissolution and flushing out from the dump basic alkaline oxides like CaO and MgO since the final pH value of ash is generally dependent on the relative contents and dissolutions of alkaline materials present in the waste (Saikia et al., 2006).

The variations in the pH values along the depth of the ash cores indicate that there are different weathering zones within the dump. This fluctuation of pH is expected to have an effect on the mobility of the chemical species in the fly ash. For drilled ash core S1, the pH values of the pore water indicates that there are three weathering zones along the depth. These zones are from surface to 9m having a pH trend of 9.33–9.73 being the zone of greatest weathering; 10 to 16.5 m having a pH trend of 9.67–11.32; and 18 to 22.5 m with a pH trend of 9.98–9.52 For drilled ash core S3 the weathering zones are Surface to 4.5 m having a pH trend of 9.71-9.57; 6 to 9 m having a pH trend of 9.59-9.40; 10.5 to 12 m having a pH trend of 9.53-9.58; 13.5 to 16.5 m having a pH trend of 10.00-9.67, 18 to 22.5 m having a pH trend of 10.11-11.27; and 23.5 to 31.5 m with a pH trend of 9.70-10.36. These variations in pH values shows that the fly ash is acidifying over time and metal mobility can be expected under these conditions.

4.2.2 EC (Electrical Conductivity)

Figures 4.2.3 to 4.2.4 present The EC profile of the extracted pore water of the fresh fly ash and two drilled ash cores (S1 and S3) as a function of depth.

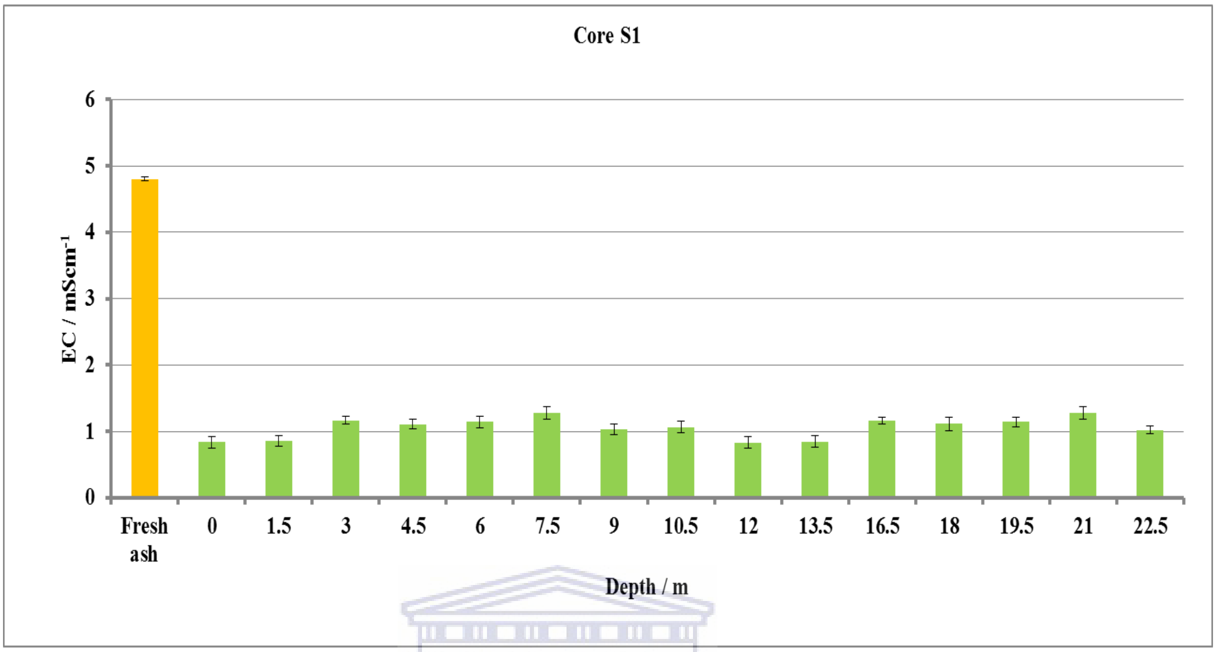


Figure 4.2.3: EC profile of Secunda fresh fly ash and weathered drilled ash core S1 [number of determinations for fresh ash and S1 are 3 and 30 respectively]

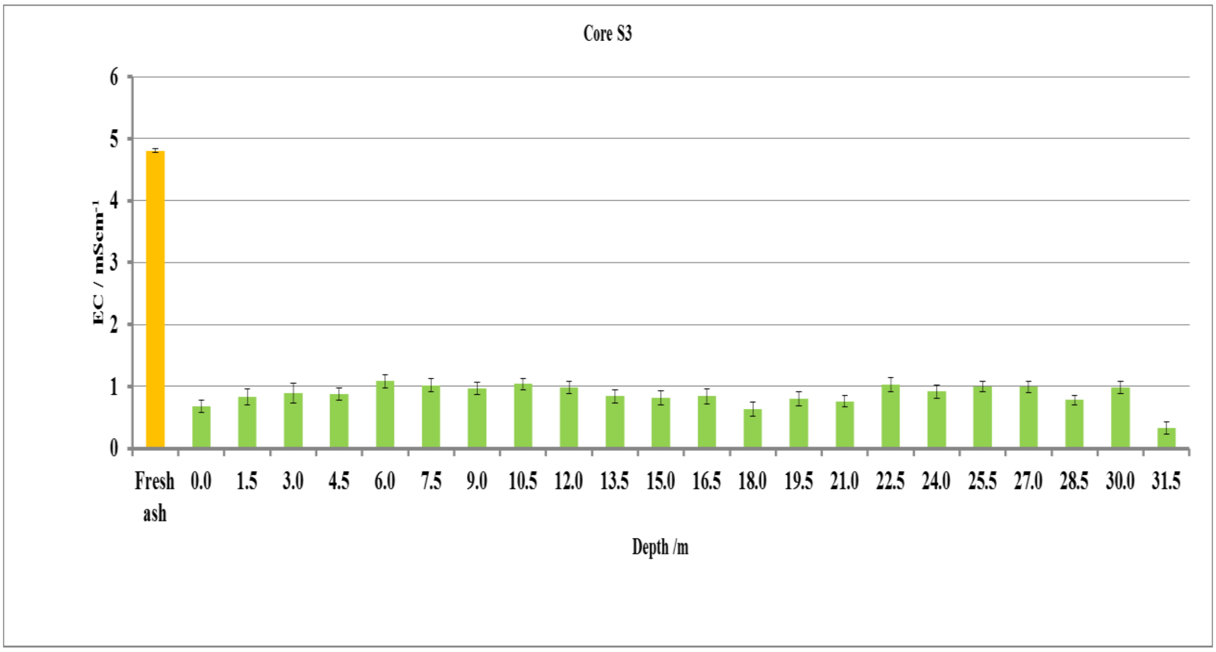


Figure 4.2.4: EC profile of Secunda fresh fly ash and weathered drilled ash core S3 [number of determinations for fresh ash and S3 are 3 and 44 respectively]

The EC (Electrical Conductivity) value (Figure 4.2.3 and 4.2.4) of the fresh Secunda fly ash sample was observed to be 4.92 mS/cm (milli Siemens per centimetre). For the drilled Secunda ash core S1, the EC values were between 0.83 mS/cm at the surface and 22.5 m, and 1.28 mS/cm at 7.5 m (Figure 4.2.3) while for the drilled Secunda ash core S3, the EC values range from 0.32-1.08 mS/cm with the minimum value at 31.5 m depth and maximum EC at 6 m depth (Figure 4.2.4). High values of EC indicate the release of more ionisable species from the ash into the pore water of the ash at those depths while lower values imply that lesser amount of ions are present, indicating mobilisation into other chemical forms or depletion over time to the ground water through leaching.

4.2.3 TDS (total dissolved solid)

Figures 4.2.5 to 4.2.6 show The TDS profile of the extracted pore water of the fresh fly ash and two drilled ash cores (S1 and S3) as a function of depth.

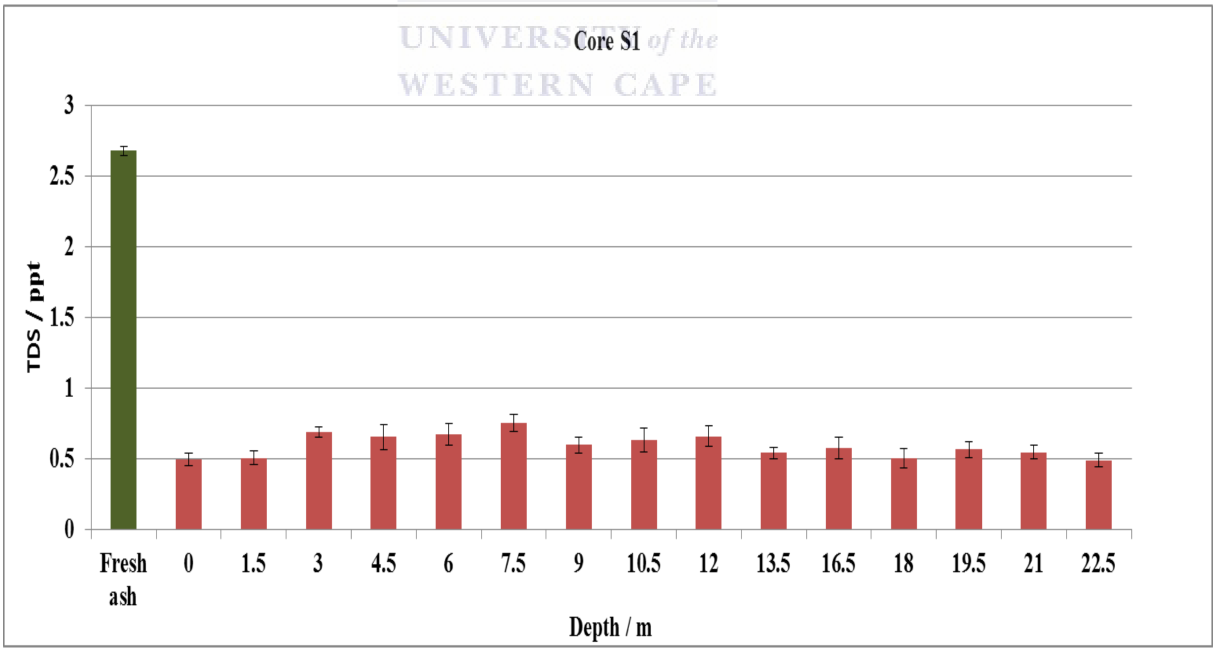


Figure 4.2.5: TDS profile of Secunda fresh fly ash and weathered drilled ash core S1 [number of determinations for fresh ash and S1 are 3 and 30 respectively]

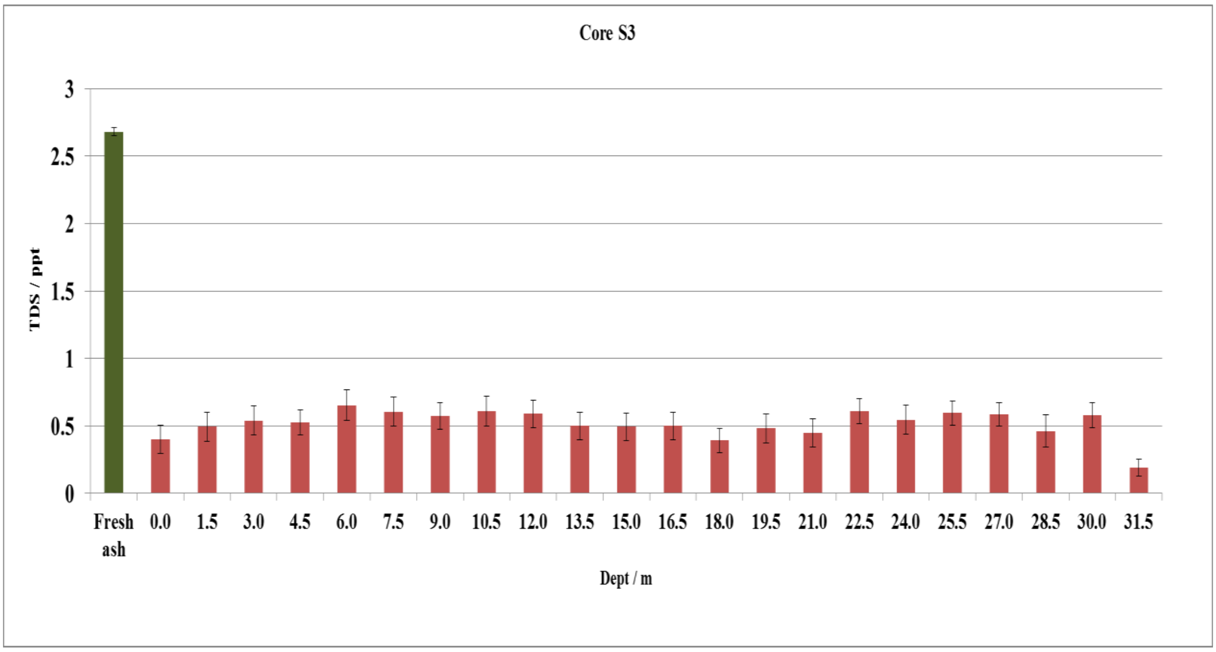


Figure 4.2.6: TDS profile of Secunda fresh fly ash and weathered drilled ash core **S3** [number of determinations for fresh ash and S3 are 3and 44 respectively]

A TDS (total dissolved solid) value (Figure 4.2.5 and 4.2.6) of 2.68 g/L i.e. parts per thousand (ppt) was observed for the fresh Secunda fly ash sample. The drilled Secunda ash core S1 had TDS values ranging from 0.49 ppt at 22.5 m to 0.76 ppt at 7.5 m (Figure 4.2.5) and for drilled Secunda ash core S3 the TDS values were between 0.19–0.68 parts per thousand (ppt) with the minimum at 31.5 depth and the maximum TDS at depth of 6 m (Figure 4.2.6). These values were indicative of the relative release and entrapment of various elements during weathering. The TDS values essentially follow the same trend as that observed for the EC. The EC and TDS of the drilled Secunda ash cores show a large decrease in value when compared to the values of the Secunda fresh fly ash. This indicates the extent of leaching and poor salt sink capacity of the fly ash dam because the EC and TDS values would have been considerably higher in the drilled cores if the fly ash dam was holding salts. Usually ionic species from salts are responsible for high EC and TDS readings.

4.2.4 MC (Moisture content)

Figures 4.2.3 to 4.2.4 present The MC of the extracted pore water of the fresh fly ash and two drilled ash cores (S1 and S3) as a function of depth.

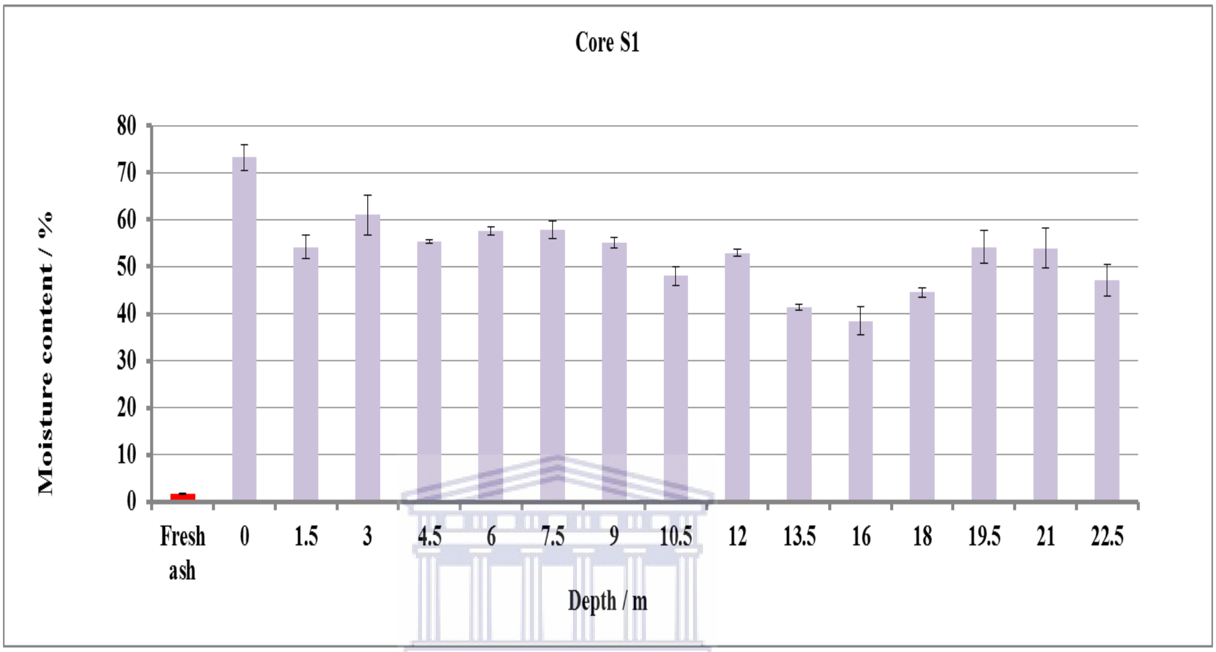


Figure 4.2.7: Moisture content profile of Secunda fresh fly ash and drilled ash core S1 [number of determinations for fresh ash and S1 are 3 and 30 respectively]

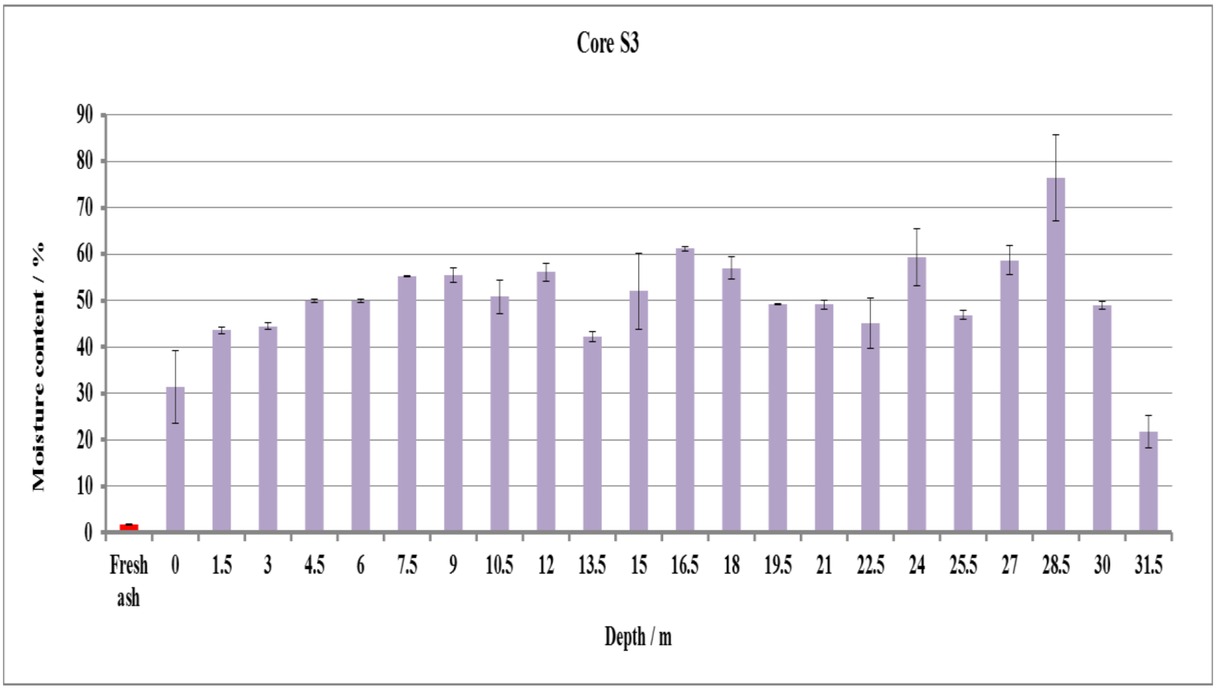


Figure 4.2.8: Moisture content profile of Secunda fresh fly ash and drilled ash core S3 [number of determinations for fresh ash and S3 are 3and 44 respectively]

While the moisture content (MC) of the fresh Secunda fly ash (Figure 4.2.7 and 4.2.8) was 1.8%, the drilled Secunda ash core samples had MC of 41.4-73.2% for S1 and 21.7-76.2% for S3. The high moisture content of the weathered Secunda core results from the wet disposal method used in Sasol, Secunda plant. Though the surface of the ash dam has dried out, the drilled ash cores show that on the interior of the dump the ash is still in a paste, with higher moisture values at lower depth due to hydraulic seepage of water from rain water or the slurry water used to place the ash and gravitational forces or during the drilling process before the samples were collected. Like the pH and EC values the trend in the moisture content values of the weathered drilled Secunda core at different depths were also different and can be attributed to uneven flow paths due to inconsistent placement conditions or variations in ambient weather conditions during placement.

4.3 Morphological analysis

The scanning electron micrographs (SEM) showing the surface morphology of the fresh and weathered fly ashes from Secunda power stations are shown in Figure 4.3.1. and 4.3.2

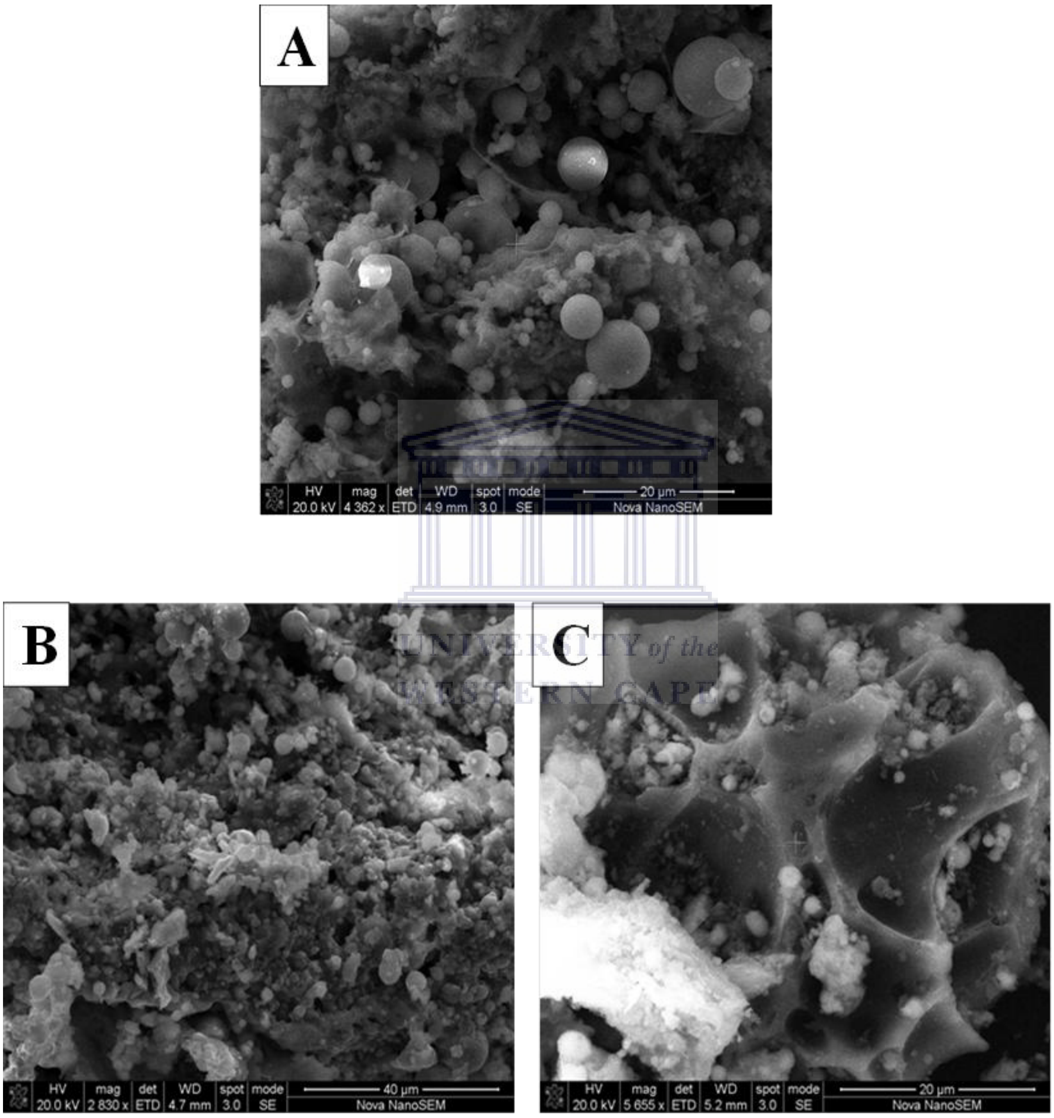


Figure 4.3.1: SEM micrographs of Secunda ash. A= Fresh ash, B = S1 (Surface), C = S3 (Surface)

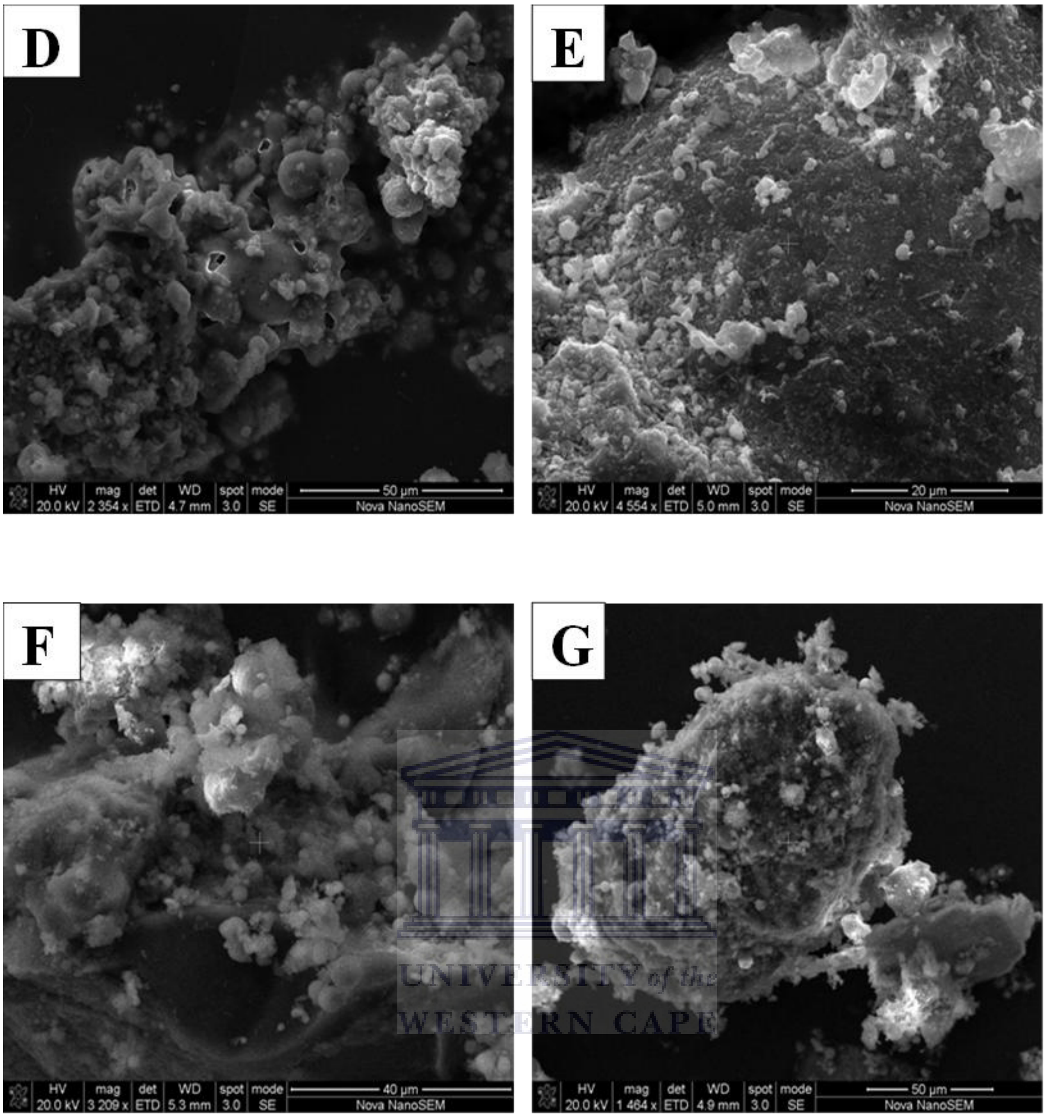


Figure 4.3.2: SEM micrographs of Secunda weathered ash. D = S1 (7.5 m), E = S3 (7.5 m), F = S1 (22.5 m) and G = S3 (31.5 m)

SEM micrographs of the fresh Secunda fly ash (Figure 4.3.1 A) and the drilled Secunda ash core samples (Figure 4.3.1 B and C and Figure 4.3.2 D to G) show that the fly ashes consist of irregular and spherically shaped particles. Many agglomerated particles were observed in both the fresh ash sample and drilled Secunda core samples, (Fig 4.3.1 (A and B)). The outer surfaces of the fresh Secunda ash particles (Fig. 4.3.1 A) are smooth while the surfaces of the particles from the drilled core samples (Fig. 4.3.1 B to G) appear to be etched and corroded (Fig. 4.3.1 E and G), encrusted (Fig. 4.3.1 D). Figure 4.3.1 C shows a fractured fly ash sphere showing vesicular interior. According to Seames (2003), these smooth outer surfaces of the fresh ash particles are assumed to be mainly aluminosilicate structures. The change (encrustations, etchings and corrosion) of the surface morphology of ash spheres of samples from the drilled Secunda ash cores could be as a result of leaching (Praharaj et al., 2002), or the formation of secondary mineral phases in the fly ash (Yeheyis et al., 2009). The spherical shapes and the agglomeration observed in the fresh fly ash sample could be attributed to high temperature and the conditions during the coal combustion process (Kutchko and Kim, 2006). The spherical shape of fresh ash is an indication that the particles were formed under un-crowded free fall conditions and a relatively sudden cooling, which helps to maintain the spherical shape; while the agglomerated nature of some particles is an indication that the particles were produced due to high temperature sintering reactions (Saikia et al., 2006). The occurrence of irregular shapes in the fly ash samples could be the consequence of fragmentation mechanisms relating to particle inflation, cracking, and cenosphere fracture within the coal particles or through the formation and shedding of partially melted attachment or mineral inclusions during char combustion (Seames, 2003).

The elemental composition of the samples, based on EDS analysis (wt. %) of the fresh Secunda fly ash and drilled Secunda ash core samples are presented in Table 4.4 and 4.5. The methodology is specified in section 3.36. The major advantage of EDS analysis is for the qualitative verification of the elements that are present and their relative abundance in the fresh ash and drilled core samples. EDS analysis is not an appropriate technique for the quantitative determination of the chemical compositions of the fresh fly ash and drilled cores samples due to the large variations in the elemental compositions of the analysed spots (Fatoba, 2008). Thus XRF was performed to confirm the quantitative composition and results are presented in section 4.4.

Table 4.3.1: SEM-EDS elemental analysis (wt. %) of the fresh Secunda ash and drilled Secunda ash core (S1) samples [number of determinations for fresh ash and S1 are 2 and 12 respectively]

Element	Fresh Ash	S1 - 0 m	S1 - 7.5 m	S1 - 22.5 m
Na	ND	0.48	0.31	0.32
Mg	0.57	0.61	0.49	0.26
Al	8.3	6.1	6.56	6.95
Si	11.01	8.49	9.72	7.02
S	0.32	0.38	0.34	0.3
K	0.39	0.26	0.43	0.24
Ca	2.1	1.43	2.64	1.37
Ti	0.53	0.6	0.39	ND
Fe	ND	0.67	ND	0.47

Table 4.3.2: SEM-EDS elemental analysis (wt. %) of the fresh Secunda ash and drilled Secunda ash cores (S3) samples [number of determinations for fresh ash and S1 are 2 and 12 respectively]

Element	Fresh Ash	S3 - 0 m	S3 - 7.5 m	S3 - 31.5 m
Na	ND	ND	2.55	0.61
Mg	0.57	0.36	0.56	0.68
Al	8.3	3	8.51	6.71
Si	11.01	3.22	16.87	9.21
S	0.32	0.2	0.4	1.21
K	0.39	ND	1.77	0.78
Ca	2.1	1	2.27	0.62
Ti	0.53	0.44	ND	15.04
Fe	ND	ND	0.45	1.21

Generally the predominant elements are Si, Al and Ca in all the samples, while Mg and S were also detected in all the samples but in lower quantities, the accumulation of S, in drilled Secunda core S3 at depth of 31.5 m may be as a result of the formation of secondary mineral phases. Na and Fe were not detected in the fresh Secunda ash sample but Na was detected in all Secunda ash core S1 and S3 samples at 7.5 m and

31.5 m, while Fe was only detected in samples S1 at 0 m and 22.5 m and in samples S3 at 7.5 m and 31.5 m. The content of Al was observed to be associated with Si, i.e. where Si was detected in low quantity, Al also followed the trend. From the variations in the composition of Si in the fresh fly ash and weathered drilled cores it can be easily observed that this technique is merely qualitative.

4.4 Chemical composition and classification of Secunda fresh fly ash and drilled cores samples (S1and S3) from XRF analysis

XRF analysis was used to quantitatively determine the chemical composition of the Secunda fresh fly ash and drilled core. The methodology is specified in section 3.3.4. All analysis was done in triplicate. The results of the chemical composition (XRF data) of the fresh Secunda fly ash and the Secunda core S1 and S3 samples are presented in this section.

4.4.1 Chemical composition (XRF analysis)

Figures 4.4.1 to 4.4.4 present the chemical compositions of the Secunda fresh fly ash and the two drilled ash core (S1 and S3) samples based on XRF analysis. The compositions of the major and minor elements are reported as weight percentage (wt. %) while the trace elements are reported in parts per million (ppm). The concentrations of the major, minor and trace elements in the fresh Secunda ash samples are compared to the mean value [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] of their concentrations in the two drilled Secunda ash cores S1 and S3.

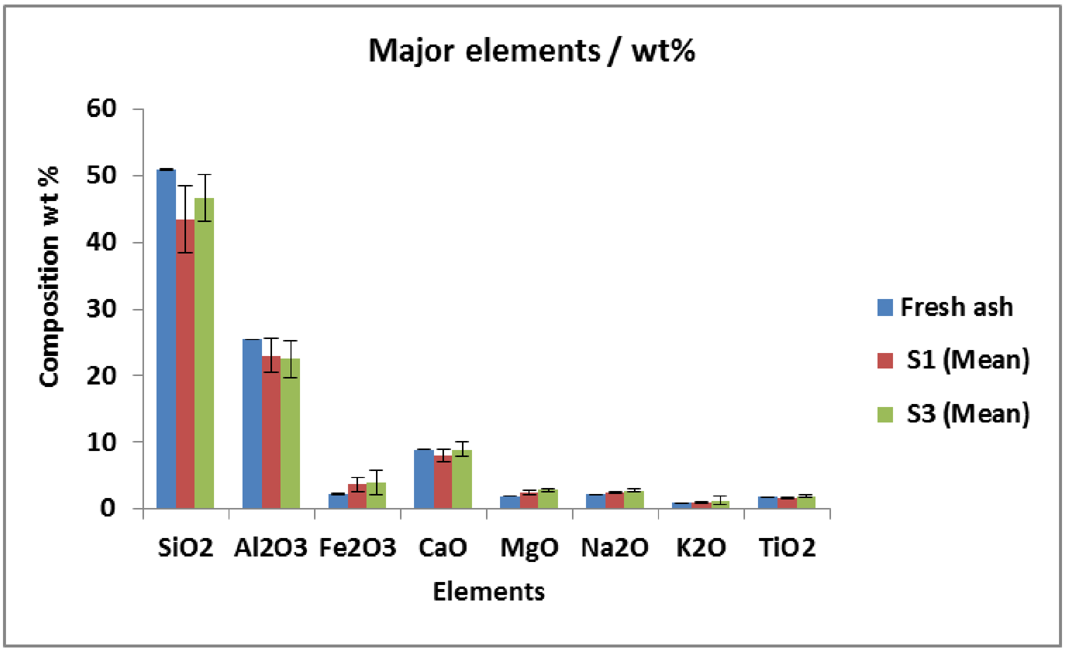


Figure 4.4.1: Chemical composition of the major elements in the fresh Secunda fly ash and drilled ash cores (S1and S3) samples [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]

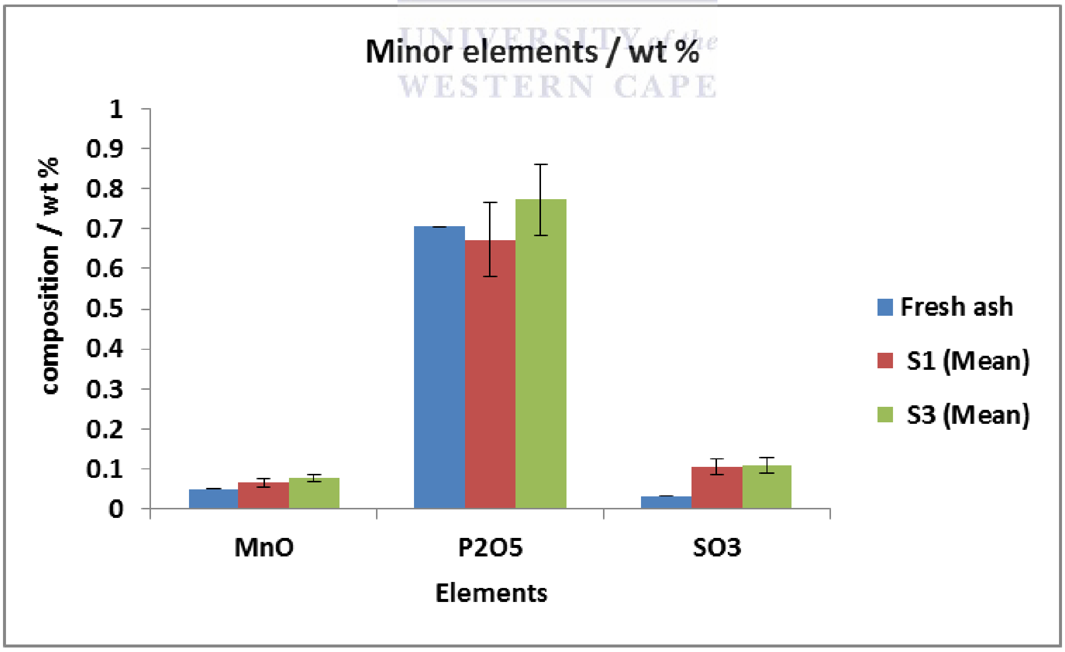


Figure 4.4.2 : Chemical composition (wt. %) of the minor elements in the fresh Secunda fly ash and drilled cores (S1and S3) samples [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]

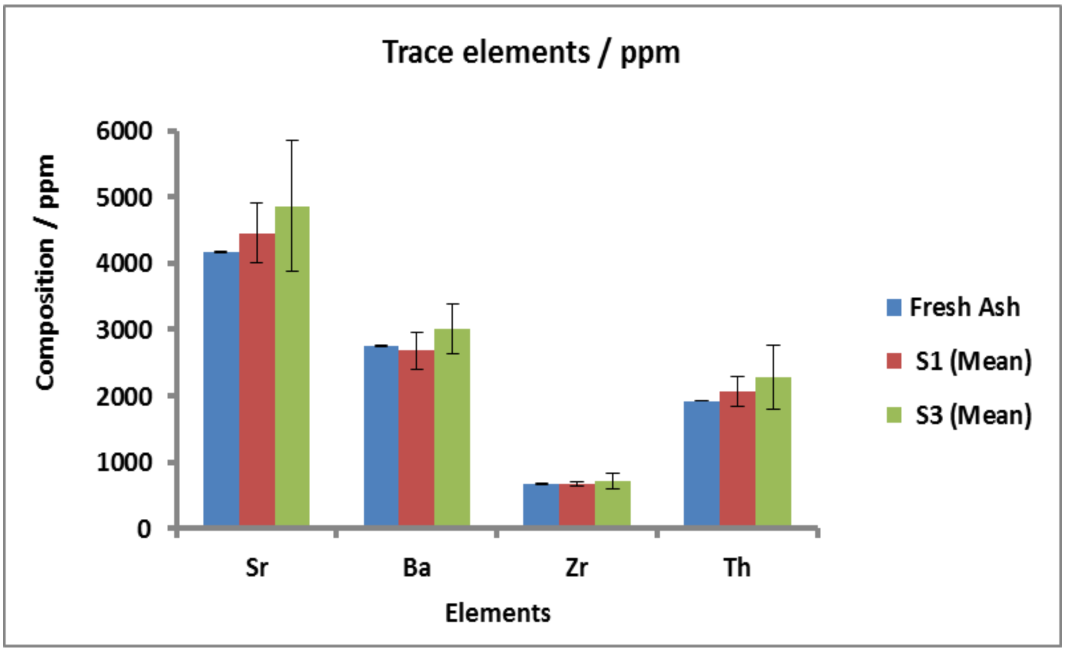


Figure 4.4.3: Chemical composition (ppm) of Sr, Ba, Zr and Th in the fresh Secunda fly ash and drilled ash cores (S1and S3) samples [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]

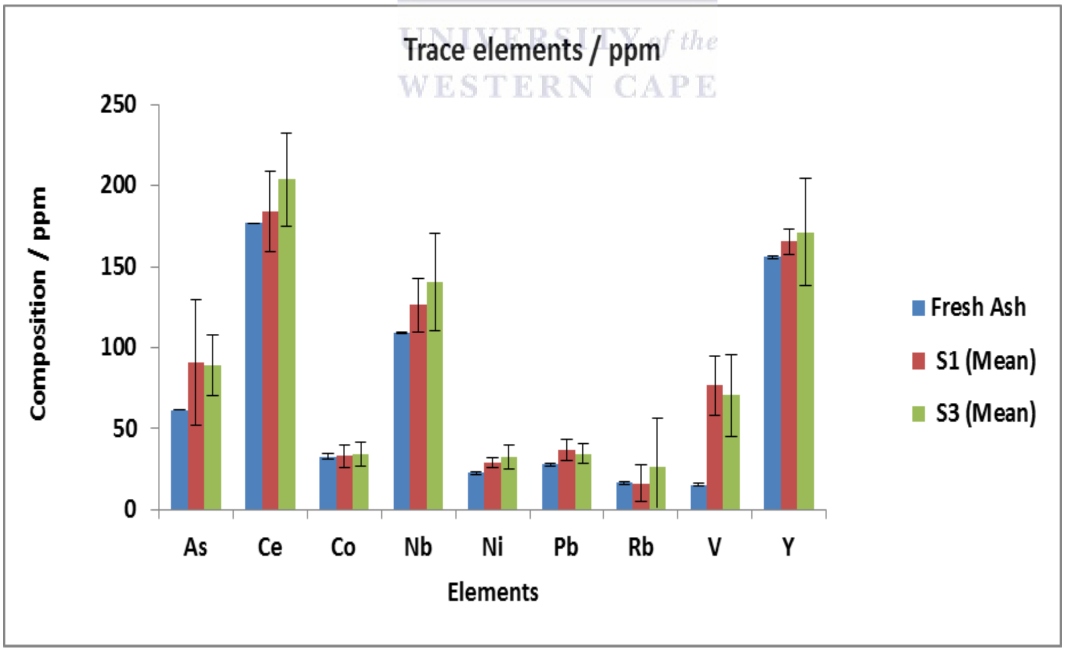


Figure 4.4.4: Chemical composition (ppm) of As, Ce, Co, Nb, Pb, Rb, V and Y in the fresh Secunda fly ash and drilled ash cores (S1and S3) samples [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]

The chemical composition (Figures 4.4.1.1 to 4.4.1.4) shows that the fresh Secunda fly ash sample contains some major oxides such as SiO_2 (50.91 %), Al_2O_3 (25.49 %), CaO (8.95 %), Fe_2O_3 (2.27%), MgO (1.87 %), Na_2O (2.21 %), TiO_2 (1.87 %), K_2O (0.95 %), P_2O_5 (0.71 %), SO_3 (0.03 %) and MnO (0.05 %). The concentration of the trace elements in the fresh Secunda ash sample were found to be (Sr (4160 ppm), Ba (2749 ppm), Th (1922 ppm), Zr (664 ppm), Y (156 ppm), Ce (117 ppm), Nb (109 ppm), As (61 ppm), Co (32 ppm), Ni (23 ppm), Pb (28 ppm), Rb (16 ppm) and V (15 ppm.

For the drilled Secunda ash core sample, S1 the concentrations of the major oxides are; SiO_2 (43.46 %), Al_2O_3 (23.05 %), CaO (8.01 %), Fe_2O_3 (3.67 %), MgO (2.44 %), Na_2O (2.47 %), TiO_2 (1.70 %), K_2O (0.97 %), P_2O_5 (0.67%), SO_3 (0.11 %) and MnO (0.07 %) while the concentrations of the trace elements were found to be Sr (4456 ppm), Ba (2682 ppm), Th (2075 ppm), Zr (667 ppm), Y (166 ppm), Ce (184 ppm), Nb (126 ppm), As 91 ppm), Co (33 ppm), Ni (29 ppm), Pb, (37 ppm), V (77 ppm) and Rb (16 ppm). The chemical composition of the drilled Secunda ash core S3 showed that the concentrations of the major oxides were; SiO_2 (46.61%), Al_2O_3 (22.43%), CaO (8.94%), Fe_2O_3 (3.90%), MgO (2.83 %), Na_2O (2.76%), TiO_2 (1.90%), K_2O (1.29%), P_2O_5 (0.77%), SO_3 (0.09%) and MnO (0.08%). The concentrations of the trace elements in core S3 were found to be; Sr (4864 ppm), Ba (3014 ppm), Th (2283 ppm), Zr (720 ppm), Y (171 ppm), Ce (202 ppm), Nb (141 ppm), As (89 ppm), Co (34 ppm), Ni (32 ppm), Pb (34 ppm),V (71 ppm) and Rb (25 ppm).

In comparison, the concentrations of Si and Al (reported as oxides) in the fresh Secunda fly ash were observed to be higher than their concentrations in the drilled Secunda ash cores (S1 and S3) (Fig 4.4.1). The decrease (7.45 % and 4.30 % in core S1 and S3 respectively) in the concentrations of Si in the core samples could be attributed to the weathering process which may have led to dissolution of the ash matrix and the release of Si from the core samples over time. According to Zevenbergen et al., (1999), leaching of Si and Al increases with weathering. The case was different for elements such as Mn, Fe, Na, Mg and S where the concentrations of these elements in the Secunda core samples were slightly higher than in the fresh Secunda fly ash (Figures 4.4.1.1 and 4.4.1.2). The slight overall increase in the concentrations of Na (0.26 % in core S1 and 0.55 % in core S3); Mg (0.37 % in core S1 and 0.96 % in core S3) and S (0.08 % in core S1 and 0.06 % in core S3) in the drilled Secunda ash core sample compared to the fresh Secunda fly ash could be as a result of its contact with brine, while the increase in the concentration of Fe (1.40 % in core S1 and 1.63 % in core S3) could be attributed to the disposal of the spent Fe-catalyst on the ash dump where the drilled core samples were collected (Pretorius, 2010). According to the study carried out by Nyamhingura, (2009) on the characterization and speciation of brine from Secunda power stations, elements such as Na, Cl, Ca, K and Mg were found in the brine in high concentrations. Therefore, the slight overall increase in the concentrations of these species in the drilled core samples could be attributed to the fly ash and brine interaction at the dump. Although considering the high volumes of brine disposed over 20 years of operation one would have expected higher salt content than what was found.

The loss on ignition (LOI) which is an indication of unburned carbon or organic content was 4.78 %, 13.45 % and 8.32 % for the fresh ash, drilled ash cores S1 and S3 respectively. The high LOI values for the drilled ash cores could indicate high hydrocarbon content in the ash dump because of co-disposal practises where hydrocarbon waste included in the brine stream for disposal on the ash.

Figure 4.4.1.3 shows increase in the amount of Sr (296 ppm and 704 ppm in core S1 and S3 respectively), Ba (263 ppm in core S3), Zr (56 ppm in core S3) and Th (153 ppm and 361 ppm in core S1 and S3 respectively) in both the Secunda fresh and weathered drilled core S1 and S3 when compared to the other trace elements such as As, Ce, Co, Nb, Ni, Pb, Rb, V, and Y. The higher concentrations of these elements may be due to their composition in the source coal that was combusted. Also these elements could have being enriched due to the dissolving away of the soluble components leaving these elements behind as a result of the decrease in pH of the ash. In the case of the trace elements such as As, Ce, Co, Cu, Nb, Ni, Pb, Rb, V and Y their concentrations in the drilled core samples were observed to be higher than in the fresh fly ash sample (Figures 4.4.3 and 4.4.4). Dudas, (1981) reported a decrease in the concentrations of trace elements in weathered fly ash (not brine impacted) when compared with the fresh fly ash. Thus the increase in the concentrations of As, Ce, Nb, Ni, Pb, Rb, V, and Y in the drilled core samples could be attributed to the contact of the ash with brine because these trace elements are also present in brine being used for ash transport (Nyamhingura, 2009).

4.4.2 Enrichment and depletion of major and trace elements

The results showing the enrichment/depletion factors of the major and trace elements in the fresh ash and drilled core samples are presented and discussed in this sub-section. The enrichment/depletion factors were determined in order to understand the changes in the chemical compositions of the drilled core samples as a function of the depth at the dump.

To calculate the enrichment/depletion factors, the XRF analysis data of the drilled cores (S1 and S3) samples was normalized with that of the fresh fly ash. The enrichment/depletion factor was calculated using equation 4.1 and the values below 1.0 represent relative depletion and values above 1.0 represent relative enrichment (Table 4.4.1 and 4.4.2). The actual concentration of each fly ash sample's elemental makeup is given in Appendix 1 and 2, and should be kept in mind when reading Table 4.4.1 and 4.4.2

$$\text{Enrichment/Depletion} = \frac{\text{wt \% of element in drlled core samples at specific depth}}{\text{wt \% of the element in fresh fly ash sample}} \ldots\ldots 4.1$$

Table 4.4.1: The enrichment/depletion of the major and trace elements in Secunda core S1 based on XRF analysis

	Fresh Ash	0m	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	16.5m	18m	19m	21m	22.5m
Major																
Si	1.00	0.92	0.98	0.94	0.94	0.92	0.91	0.91	0.84	0.88	0.85	0.86	0.68	0.81	0.73	0.65
Al	1.00	0.95	0.99	1.00	1.00	0.98	0.97	0.98	0.88	0.92	0.89	0.92	0.74	0.86	0.79	0.69
Fe	1.00	1.98	1.64	1.02	1.27	1.31	1.74	1.42	1.30	1.89	2.90	1.89	1.59	1.33	1.49	1.44
Mn	1.00	1.21	0.99	1.06	1.31	1.28	1.42	1.42	1.29	1.46	1.59	1.43	1.21	1.16	1.14	1.09
Mg	1.00	1.41	1.24	0.25	1.42	1.54	1.41	1.41	1.28	1.42	1.38	1.36	0.98	1.22	1.14	0.95
Ca	1.00	0.69	0.76	0.86	0.92	0.96	0.98	0.96	0.95	0.97	1.10	1.02	0.81	0.84	0.82	0.77
K	1.00	0.95	0.79	1.12	1.01	1.05	0.99	1.03	1.02	1.00	1.04	1.11	1.01	1.14	1.01	0.96
Na	1.00	1.09	1.05	1.14	1.15	1.22	1.16	1.20	1.12	1.18	1.14	1.12	1.06	1.11	1.04	0.99
Ti	1.00	0.98	0.87	1.02	1.02	1.05	0.98	1.00	0.98	1.00	0.56	1.00	0.86	0.95	0.86	0.81
P	1.00	0.76	0.73	1.15	1.07	1.09	1.03	1.04	0.96	0.97	0.93	1.01	0.80	0.97	0.89	0.77
S	1.00	1.84	3.24	4.42	4.43	4.95	4.85	4.27	4.41	4.79	4.65	4.40	4.42	3.99	4.30	4.32
LOI	1.00	1.06	0.76	0.84	0.71	0.79	0.85	0.90	1.65	1.08	0.97	1.12	3.16	2.01	2.72	3.66
Trace																
As	1.00	1.21	0.80	1.08	0.98	1.16	1.06	1.18	1.50	1.24	1.23	1.34	2.60	1.73	2.16	3.03
Ba	1.00	0.76	0.77	1.11	1.04	1.09	0.94	0.97	1.01	0.98	0.93	0.99	0.98	1.05	1.02	1.00
Ce	1.00	0.97	0.89	0.99	0.89	1.09	0.83	0.90	1.12	1.10	1.01	1.13	1.37	1.07	1.07	1.19
Co	1.00	0.82	1.10	0.98	1.10	1.18	0.63	1.23	0.92	0.88	1.13	0.96	1.08	0.82	1.01	1.56
Nb	1.00	0.95	0.96	1.36	1.10	1.28	0.98	1.07	1.31	1.23	0.97	1.04	1.22	1.32	1.26	1.31
Ni	1.00	1.03	1.18	1.10	1.22	1.27	1.27	1.20	1.22	1.54	1.43	1.28	1.35	1.36	1.34	1.24
Pb	1.00	1.04	1.52	1.35	1.62	1.72	1.46	1.54	1.35	1.38	1.10	1.18	1.04	1.24	1.23	0.95
Rb	1.00	1.93	2.02	0.29	0.81	0.32	1.91	0.96	0.29	0.53	2.26	1.30	0.77	0.81	0.27	0.77
Sr	1.00	0.81	0.85	1.14	1.09	1.10	1.04	1.07	1.12	1.07	1.02	1.12	1.14	1.17	1.13	1.19
V	1.00	6.22	6.90	6.06	5.53	4.38	4.58	5.40	4.93	4.60	2.66	3.59	4.65	7.37	4.99	4.65
Y	1.00	0.97	0.98	1.11	1.08	1.11	1.05	1.06	1.11	1.08	0.96	1.06	1.07	1.11	1.08	1.08
Zr	1.00	0.90	0.88	1.02	1.03	1.01	1.01	1.01	1.07	1.04	0.97	1.03	1.02	1.03	1.03	1.00
Th	1.00	0.79	0.85	1.16	1.10	1.11	1.04	1.07	1.13	1.08	1.02	1.13	1.16	1.20	1.15	1.20

Table 4.4.2: The enrichment/depletion of the major and trace elements in Secunda core S3 based on XRF analysis

	Fresh Ash	0m	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5m	27m	28.5m	30m	31.5m
Major																							
Si	1.00	0.91	0.93	0.93	0.93	0.89	0.89	0.90	0.94	0.98	0.81	0.90	0.90	0.94	0.94	0.95	0.80	0.92	0.92	0.88	0.88	0.86	1.16
Al	1.00	0.92	1.01	0.97	1.00	0.96	0.93	0.81	0.87	0.83	0.84	0.93	0.84	0.88	0.90	0.88	0.91	0.83	1.00	0.84	0.79	0.96	0.47
Fe	1.00	1.40	1.20	1.37	1.26	1.54	2.19	1.89	1.39	1.49	4.58	2.24	1.85	1.46	1.40	1.29	2.42	1.09	0.96	1.28	1.28	1.16	3.00
Mn	1.00	1.36	1.16	1.36	1.16	1.16	1.16	1.55	1.16	1.16	1.94	1.16	1.55	1.16	1.55	1.55	1.74	1.55	1.16	1.55	1.74	1.55	2.32
Mg	1.00	1.77	1.48	1.36	1.39	1.38	1.37	1.48	1.56	1.60	1.37	1.30	1.47	1.55	1.50	1.55	1.46	1.66	1.46	1.70	1.77	1.51	1.55
Ca	1.00	0.94	0.90	0.91	0.83	0.99	0.96	1.11	1.00	0.95	1.03	0.87	0.98	0.97	1.04	1.07	1.16	1.11	0.96	1.10	1.26	1.09	0.75
K	1.00	1.20	1.15	1.28	1.31	1.30	1.21	1.36	1.41	1.46	1.03	1.21	1.30	1.33	1.32	1.27	0.95	1.16	1.03	1.05	0.92	1.00	4.63
Na	1.00	1.07	1.11	1.16	1.16	1.26	1.18	1.36	1.29	1.31	1.14	1.08	1.20	1.30	1.23	1.27	1.27	1.37	1.16	1.41	1.43	1.24	1.44
Ti	1.00	1.07	1.03	1.07	0.98	1.07	0.98	1.18	1.15	1.17	0.95	0.98	1.06	1.11	1.11	1.17	1.01	1.19	1.04	1.15	1.19	1.04	0.85
P	1.00	1.17	1.06	1.00	1.04	1.10	1.01	1.14	1.15	1.17	0.94	1.00	1.06	1.18	1.07	1.14	1.13	1.18	1.13	1.25	1.34	1.20	0.51
S	1.00	1.67	4.00	3.00	3.00	3.33	4.00	3.67	3.33	3.33	3.00	2.67	3.00	3.00	3.00	3.00	3.33	3.33	2.67	3.67	3.00	3.33	1.33
LOI	1.00	1.89	1.44	1.53	1.62	1.72	1.83	1.89	1.61	1.41	1.83	1.90	2.16	1.63	1.48	1.42	1.59	2.28	1.94	2.16	2.15	2.12	0.67
Trace																							
As	1.00	1.56	1.32	1.25	0.99	1.51	1.18	1.70	1.50	1.30	1.82	1.31	1.29	1.37	1.28	1.34	1.26	1.77	1.41	1.41	1.50	1.27	2.49
Ba	1.00	1.14	1.13	1.02	1.12	1.15	1.02	1.16	1.17	1.13	0.97	0.98	1.09	1.18	1.06	1.13	1.11	1.13	1.21	1.21	1.26	1.14	0.61
Ce	1.00	1.07	0.90	1.06	0.92	0.99	0.95	1.40	1.19	1.28	1.40	1.23	1.13	1.15	1.12	1.26	0.94	1.27	1.21	1.31	1.23	1.28	0.80
Co	1.00	1.15	0.74	1.01	1.16	1.02	0.73	1.19	0.85	1.27	0.82	1.60	1.18	1.07	0.99	0.82	0.57	0.97	1.08	1.32	1.13	0.87	1.53
Nb	1.00	1.34	1.32	1.29	1.27	1.32	1.03	1.45	1.47	1.35	1.04	1.20	1.23	1.44	1.21	1.36	1.44	1.46	1.55	1.51	1.49	1.40	0.25
Ni	1.00	1.21	1.06	1.26	1.30	1.24	1.29	1.33	1.40	1.47	1.33	1.01	1.26	1.37	1.27	1.32	1.33	1.71	1.44	1.57	1.59	1.40	2.63
Pb	1.00	1.17	0.85	1.21	1.49	1.49	1.22	1.60	1.21	1.23	0.86	1.29	1.32	1.23	0.90	1.26	1.17	1.15	1.10	1.48	1.09	1.14	1.68
Rb	1.00	0.73	ND	1.43	1.48	0.83	1.13	1.07	1.18	1.85	2.06	0.58	1.59	1.36	1.84	0.70	0.14	ND	0.11	ND	ND	ND	8.41
Sr	1.00	1.15	1.15	1.10	1.08	1.21	1.05	1.31	1.26	1.15	1.17	1.13	1.21	1.25	1.17	1.16	1.20	1.38	1.34	1.35	1.34	1.31	0.22
V	1.00	3.18	4.79	7.49	4.92	7.73	3.82	5.98	4.63	5.39	3.56	4.07	3.98	8.10	4.20	2.75	5.67	3.90	6.75	4.64	3.58	3.20	1.97
Y	1.00	1.11	1.11	1.05	1.01	1.10	1.04	1.19	1.17	1.12	0.96	1.08	1.13	1.18	1.13	1.14	1.12	1.21	1.24	1.31	1.30	1.19	0.25
Zr	1.00	1.09	1.07	1.06	0.97	1.06	1.04	1.17	1.12	1.10	1.08	1.04	1.13	1.14	1.13	1.16	1.11	1.12	1.21	1.23	1.25	1.16	0.40
Th	1.00	1.16	1.17	1.11	1.09	1.23	1.06	1.35	1.29	1.17	1.17	1.13	1.22	1.28	1.19	1.18	1.23	1.41	1.38	1.39	1.38	1.35	0.18

The enrichment/depletion factors are expected to show the patterns of mobility or retardation of the species as a result of dissolution of the ash matrix and soluble salts contained in the ash. The discussion is presented for the weathered drilled cores S1 and S3.

In the drilled cores samples S1 and S3, the concentrations of elements such as Si and Al, were depleted relative to fresh Secunda fly ash. The trends of Si and Al are similar in both drilled cores. Although the concentration of Al remained unchanged at depths of 3 m and 4.5 m in core S1 and 1.5 m, 4.5 m and 25.5 m for core S3. Al and Si were consistently depleted down the core. This depletion in Si and Al indicates that these species are continuously leached from the ash as a result of weathering. As stated in section 4.4.1 the leaching of Si and Al from fly ash increased with weathering. Since Al and Si form the major matrix of the ash, the weathering will release other components locked in the ash matrix.

The concentration of Fe, Mn, Na, K, Mg and SO_4 were observed to be somewhat enriched consistently in both drilled ash cores. The enrichment of Fe (1.40 % in core S1 and 1.63 % in core S3) may be a result of the spent Fe catalysts that were also disposed in the fly ash dump (Pretorius, 2010), while the slight enrichment in concentrations of S may be as a result of the fly ash interactions with the co-disposed brine that has a substantial concentration of SO_4^{2-} (Mooketsi et al., 2007), According to Gitari et al. (2009) usually Na, K and Mg are highly leached from fresh fly ash. Hence the slight enrichment or accumulation of these species noted in the weathered drilled core samples may have resulted from the co-disposed brine that contained substantial concentrations of these elements (Mooketsi et al., 2007; Nyamhingura 2009). Though a high enrichment value of Na would be expected due to the large amount of salt laden brine disposed on the dump over 20 years it is noteworthy that Na_2O levels never increased above an enrichment factor of 1.22 – 1.43 showing that the dump is not holding or encapsulating Na to any significant extent. This shows that the salt holding capacity of the ash dump is very low which has a major implication for using it as a salt sink.

The trend of Ca concentration in drilled Secunda core S1 was observed to be different from the trend in drilled core S3. In drilled core S1, Ca was depleted at most of the depths but enriched only at depths of 13.5 m and 16, 5 m. The depletions in the concentrations of CaO could be due to the leaching and weathering as a result of interaction with infiltrating pore-waters due to co-disposal of brine with the fly ash (Lee and Spears, 1997). In drilled core S3, depletion in the concentration of Ca was observed to be consistent from surface to 7.5 m, 12 m to 18 m, 22.5 m and 31.5 m while the concentration of CaO was enriched at other depths. The geophysics (Figure 3.1.1) also indicated a fault line (crack) in the dump at the position of core S3hence the enrichment in concentrations of Ca may have resulted due to the accumulation of brine in preferential leaching pathways or the formation of secondary mineral phases in the fault. These results highlight the inhomogeneity of the ash dump.

The concentrations of the trace elements in the drilled core sample from Secunda ash core S1 were observed to have similar trends to the samples taken from drilled core S3. In both drilled Secunda ash core samples, the concentrations of Pb, V, Zn, Cr, Ni and Co were observed to be enriched somewhat within the entire cores. These trace elements are also present in Sasol brine (Mooketsi et al., 2007; Nyamhingura 2009). Hence this enrichment of the trace elements in the drilled core samples could be due to the capturing of these species form the co-disposed brine.

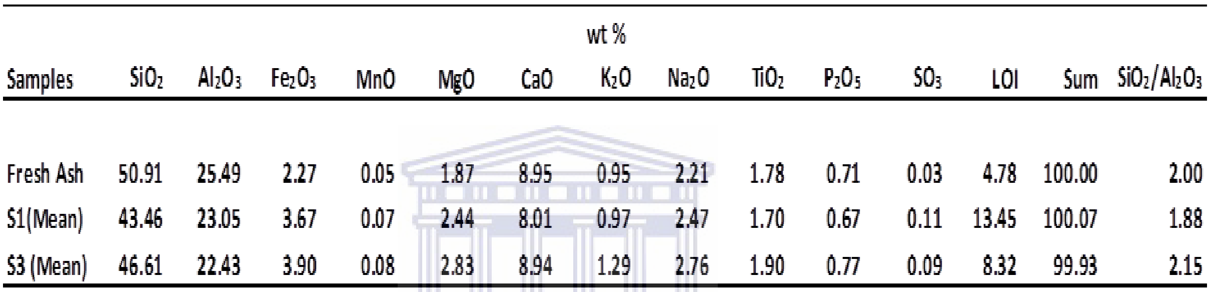
The LOI of the two drilled cores samples (S1and S3) was observed to be enriched in the weathered ash when compared to the LOI of the fresh ash. The enrichment in LOI could probably be due to changes in burner conditions over time resulting in more or less carbon or to the structural incorporation of H2O into secondary mineral phases formed in the disposal of the fly ash (Yeheyis et al., 2009).

The inhomogeneous enrichment and depletion observed along the entire length of the two drilled cores could be explained by the processes occurring in the dam which involves the dissolution, precipitation and flushing of the soluble salts bearing these elements as a result of rain water infiltration and brine percolation that was co-disposed with the coal fly ashes. From the enrichment and depletion tables (Tables 4.6 and 4.7), no significant enrichment or accumulation of any particular element was observed down the two drilled Secunda core S1and S3 compared to the fresh Secunda ash.

4.4.3 Fly ash classification

Table 4.8 presents the mean chemical composition (XRF data of the major and minor elements) of the fresh fly ash sample and the drilled cores (S1 and S3) samples at different depths, which was used for the classification of the fly ash used in this study.

Table 4.4.3: Mean chemical composition (wt. %) of the drilled core (S1 and S3) at different depths and the fresh fly ash samples



							wt %							
Samples	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	K_2O	Na_2O	TiO_2	P_2O_5	SO_3	LOI	Sum	SiO_2/Al_2O_3
Fresh Ash	50.91	25.49	2.27	0.05	1.87	8.95	0.95	2.21	1.78	0.71	0.03	4.78	100.00	2.00
S1(Mean)	43.46	23.05	3.67	0.07	2.44	8.01	0.97	2.47	1.70	0.67	0.11	13.45	100.07	1.88
S3 (Mean)	46.61	22.43	3.90	0.08	2.83	8.94	1.29	2.76	1.90	0.77	0.09	8.32	99.93	2.15

The sum of the mean values of SiO_2, Al_2O_3 and Fe_2O_3 was 78.67 %, 70.19 % and 72.94 % for the fresh fly ash, core S1 and S3 respectively (Table 4.3). Thus the fresh fly ash and drilled cores (S1 and S3) can be classified as Class F. According to the American Society for Testing and Materials (ASTM C 618-92a), fly ash can be classified as class F or C based on the sum of the oxides of aluminium, silicon and iron in the fly ash. Class F fly ash are characterised by (i) the sum of SiO_2, Al_2O_3, Fe_2O_3 >70 %, (ii) SO_3<5 %, (iii) moisture content <3% and (iv) loss on ignition (LOI) <6 %. (v) CaO<20 %. The fresh fly ash contained 8.95 % CaO while cores S1 and S3 contained 8.01 % and 8.95 % CaO respectively. These values of CaO are in the mid-range among Class F fly ashes that usually have low calcium content (Vassilev and Vassileva, 2007).

Apart from the ASTM classification which showed that the fly ash is class F, the fresh fly ash and drilled cores can be classified as silico-aluminate ash based on the SiO_2/Al_2O_3 ratio. The fresh fly ash and drilled cores (S1 and S3) samples have

SiO_2/Al_2O_3 ratios of 2.0, 1.88 and 2.5 respectively (Table 4.3). According to the United Nations subcommittee of Fly Ash Utilization, fly ash is classified as silico-aluminate fly ash when the SiO_2/Al_2O_3 ratio is ≥ 2 and CaO content is < 15 % (Vassilev and Vassileva, 2007).

Roy and Griffin (1982), proposed a taxonomic system for classifying fly ash into seven chemical categories based on the sialic ($SiO_2 + Al_2O_3 + TiO_2$), ferric (Fe_2O_3 + MnO + SO_3 + P_2O_5) and calcic (CaO + MgO + Na_2O + K_2O) contents of the fly ash. The ternary plot of the Secunda drilled core (S1 and S3) samples based on XRF data are presented in Figures 4.4.5 and 4.4.6. This plot also shows the classification of drilled core samples (S1 and S3) based on the contents of sialic, ferric and calcic contents from the XRF data.

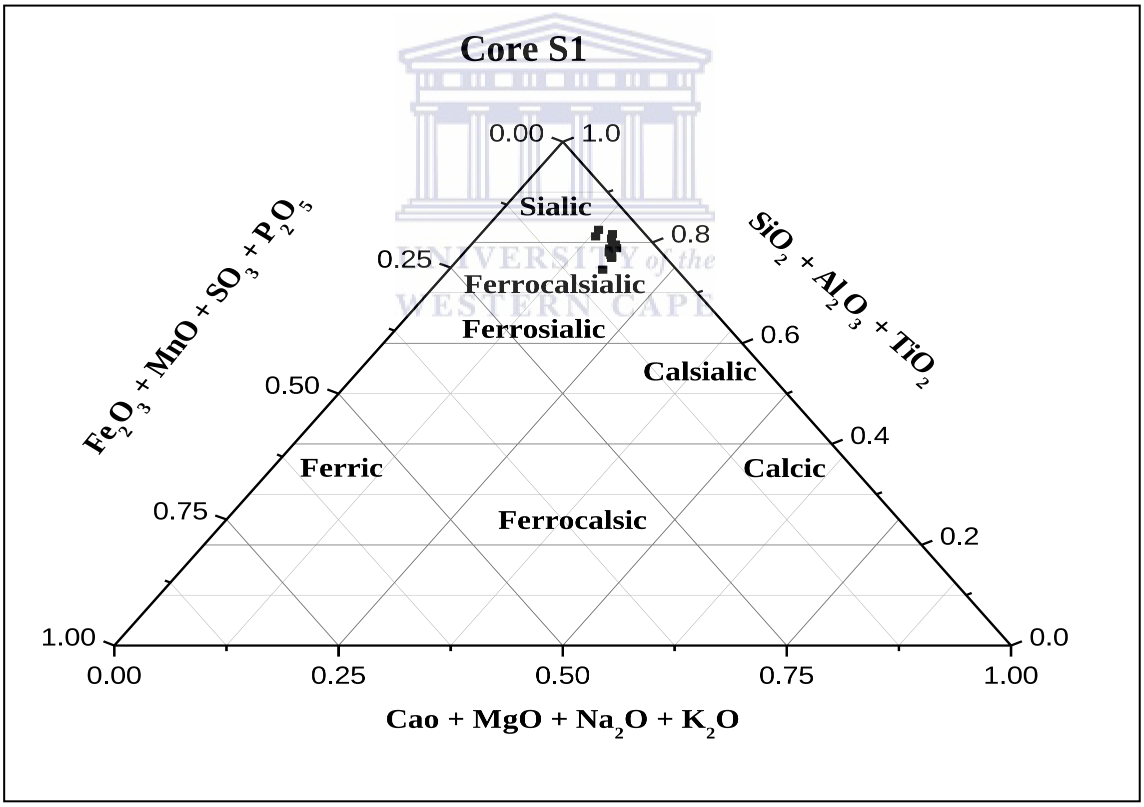


Figure 4.4.5: Ternary plot of Secunda core S1 samples based on the XRF analysis

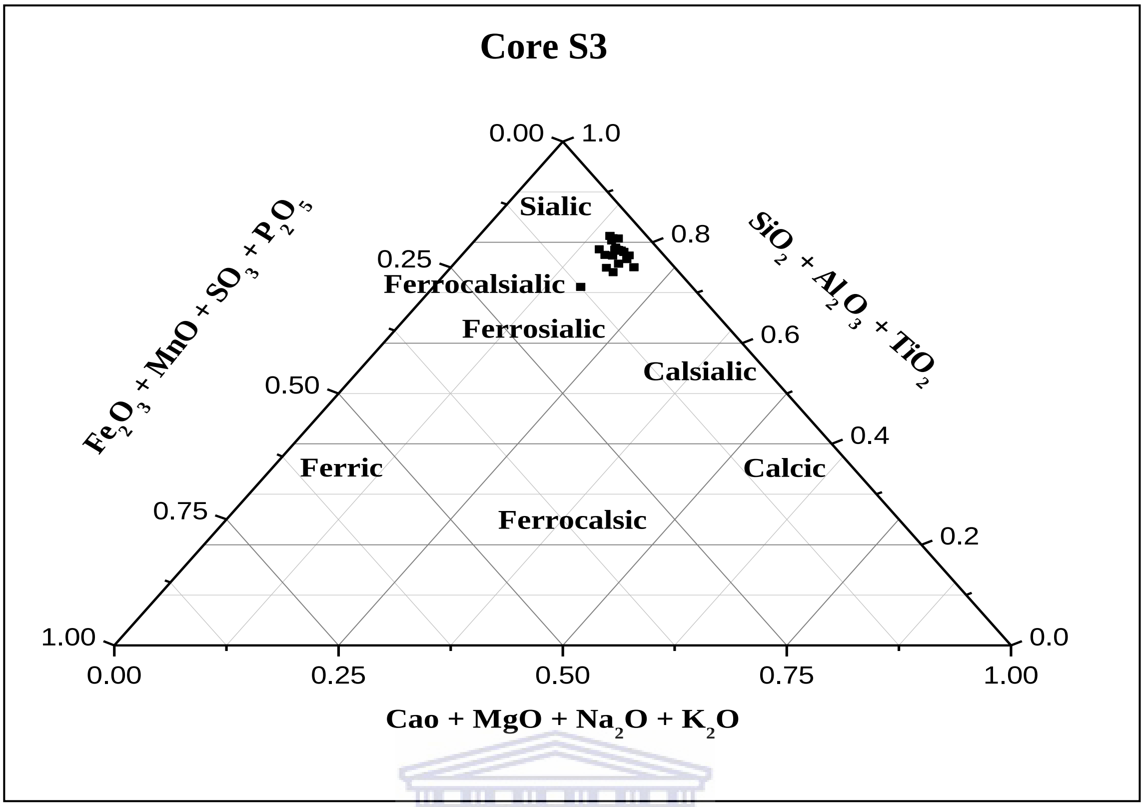


Figure 4.4.6: Ternary plot of Secunda core S3 samples based on the XRF analysis

It was observed from the ternary plot that some samples extracted from the drilled core S1 and S3 (Figure 4.4.5 and 4.4.6) show some sialic nature but most samples fell into the ferrocalsialic category. The ferrocalsialic fly ash type has the sialic (SiO_2 + Al_2O_3 + TiO_2) component >48-88%; Calcic (CaO + MgO + Na_2O + K_2O) component between 0-29%; and ferric (Fe_2O_3 + MnO + SO_3 + P_2O_5) component between 0 - <23% (Roy and Griffin, 1982). Modic fly ashes may generally correlate with class F fly ashes as they meet the requirement of this group of fly ash according to the ASTM classification. This classification system could be used to help determine which utilization and recycling method might be best suited for a particular type of fly ash.

Based on the XRF analysis (Fig 4.4.1) it is postulated that the ferrocalsialic category in the drilled cores samples S1 and S3 could be due to disposal of spent Fe containing catalysts upon this region of the Secunda dump. This result again shows the inhomogeneity of the Secunda dump, which may be exacerbated by co-disposal practices, where metal containing spent catalyst waste, may be mixed with ash during dumping, which is reported by Secunda site personnel.

4.5 Mineralogical analysis

Figures 4.5.1 and 4.5.2 show the XRD patterns of the fresh ash and drilled core samples S1 and S3 respectively. XRD was applied to identify the mineralogical phases present in the fresh Secunda fly ash and any changes taking place over time in the drilled Secunda core samples at different depths.

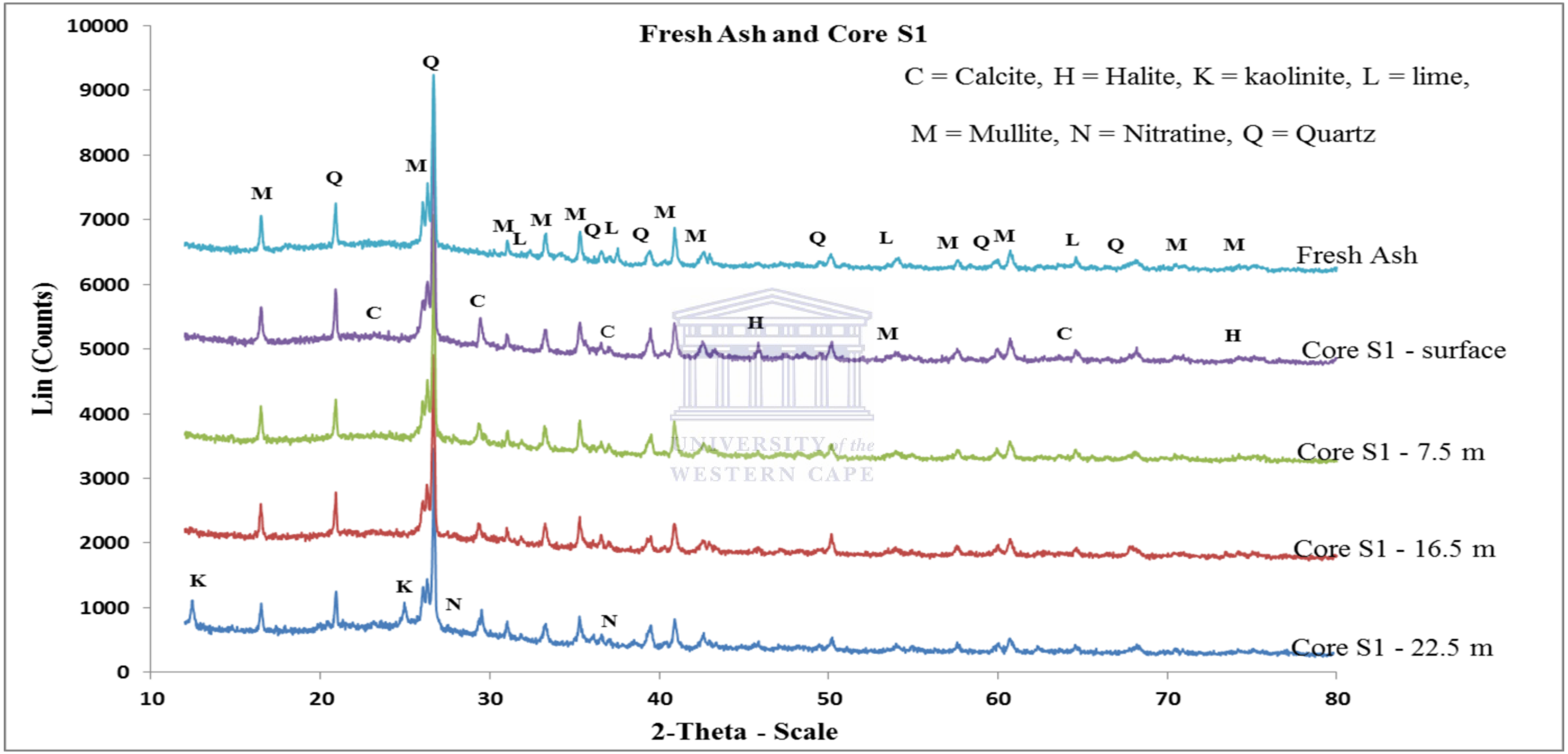


Figure 4.5.1: XRD patterns of Secunda fresh and weathered fine coal ash core S1 at different depths: surface, 7.5 m, 16.5 m and 22.5 m

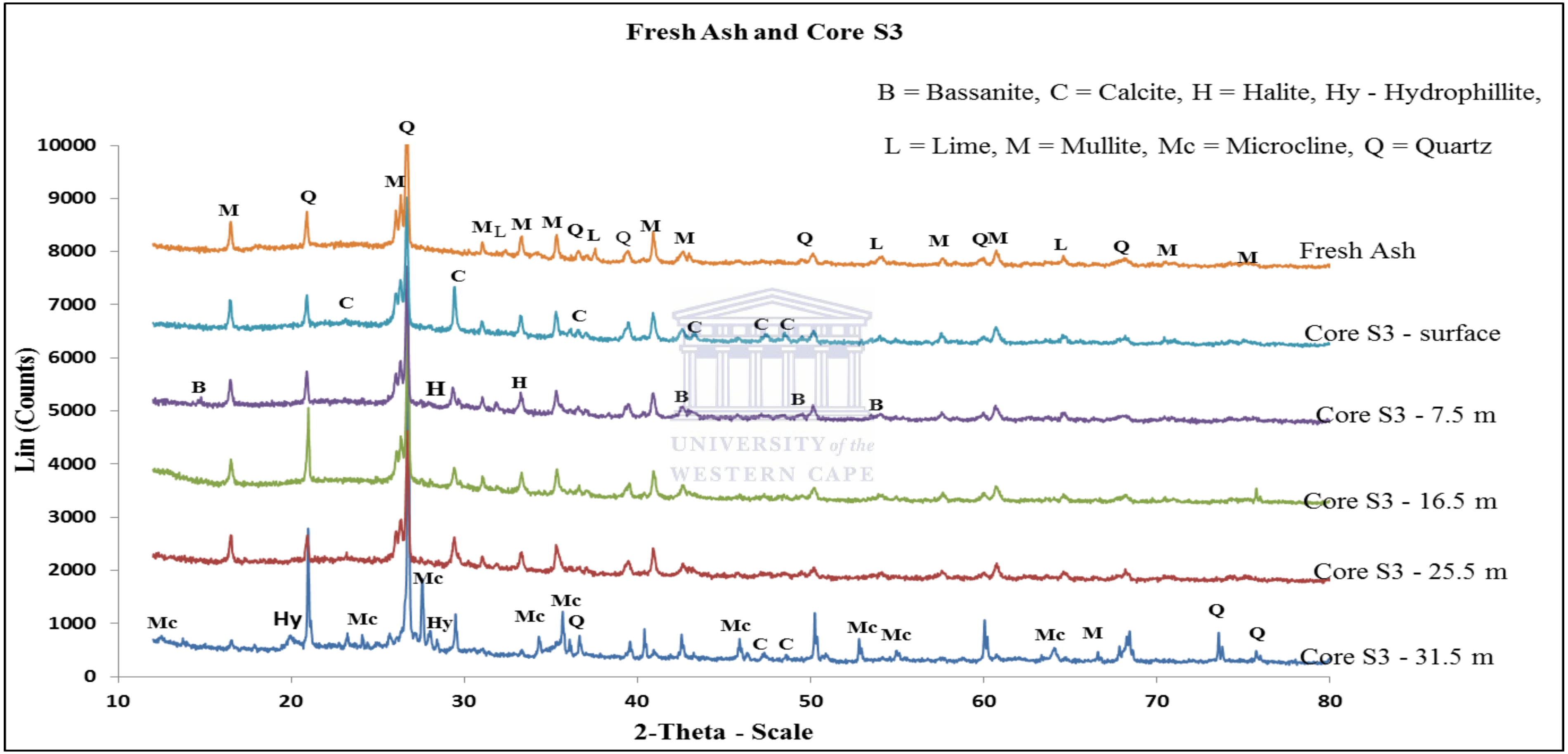


Figure 4.5.2: XRD patterns of Secunda fresh and weathered fine coal ash core S3 at different depths: surface, 7.5 m, 16.5 m, 22.5 m and 31.5 m

The XRD results (Fig4.5.1 and 4.5.2) revealed that the major crystalline mineral phases for the Secunda fresh fly ash samples were quartz (SiO_2) and mullite ($Al_6Si_2O_{13}$). Lime (CaO) was also identified but was present in low amounts as can be seen from the relatively minor peaks when compared to those of quartz and mullite. According to Singh and Kolay (2002) quartz and mullite are the major crystalline constituents of class F fly ashes. Quartz is a hard mineral commonly found as cell and pore infillings in the organic matter of coal and is regarded as a primary mineral. It is basically considered as non-reactive in combustion processes due to its high fusion temperature (Ward, 2002). Mullite is a secondary mineral that is assumed to be formed during the thermal decomposition of kaolinite, an aluminosilicate mineral in the coal (Koukouzas et al., 2009, White and Case, 1990). Lime, which is also a secondary mineral may have resulted from the decomposition of calcite or dolomite, which are the most important and common calcium-bearing minerals in coal.

For the two drilled Secunda cores (S1and S3), core S1 showed quartz and mullite as the major crystalline mineral phases from the surface down to the depth of 16.5 m. Lime and calcite ($CaCO_3$) were also identified but as minor peaks, calcite is a secondary mineral formed by contact of lime (CaO) contained in the ash with ingressed CO_2 (Vassilev and Vasssileva, 1996). At a depth of 22.5 m, apart from quartz and mullite, minor phases of kaolinite ($Al_2(Si_2O_5)(OH)_4$) and nitratine ($NaNO_3$) were also identified. Nitratine is a tertiary mineral that may have resulted from the interaction of brine with the fly ash or may be due to the drying process in the sample preparation prior to analysis. The kaolinite in the weathered ash sample (core S1) at the bottom of the dump (depth 22.5m) may have been derived from the erosion of the rock and soil surrounding the ash dam. It could also have resulted from the alteration of the glass phase or weathering of the ash in the dump (Ward et al., 2009).

Core S3 had quartz and mullite as the major crystalline mineral phases and calcite as the minor phase at the surface (0 m) of the ash dump. Core S3 presents a unique transformation in mineralogy down the depth of the Secunda dump. At depths of 7.5 m, 16.5 m and 25.5 m, the major crystalline mineral phases were quartz and mullite with calcite, halite (NaCl) and bassanite ($CaSO_4.2H_2O$) showing up as minor phases. At depth 31.5 m, quartz was the major phase. Other minerals also tentatively identified at this depth in minor quantities were calcite, microline ($KAlSi_3O_8$) and hydrophitte ($CaCl_2$).

Halite, bassanite, nitratine, hydrophitte, microline and albite low are considered as transient mineral that may also have formed from the interaction of brine with the fly ash. This is based on the chemical composition of these mineral phases which can be associated with the chemical compositions of the co-disposed brine. Also these transient mineral could have formed at the point of analysis due to the drying process used prior to XRD analysis. Pore-water analysis (EC and TDS) in section 4.2 revealed the high presence of ionic species from salts in the pore-water of Secunda fly ash samples. Alai et al., (2004) in their study of brine containing Na, Cl, NO_3, K, SO_4, Ca, Mg, CO_2(aq), F, and Si predicted that halite, bassanite and nitratine may form during brine evolution in complex aqueous systems at elevated temperatures.

The XRD spectra of the Secunda fly ash samples extracted at different depths of the two drilled cores (S1 and S3) were inconsistent in terms of secondary mineral phases although the major mineral components in all cases were quartz, calcite and mullite regardless of the sampling depth. The quartz peaks of the drilled core samples are quite prominent and have a tendency to obscure other less abundant or less crystalline mineral phases. This as well as the fact that samples cannot be analysed in situ was the major limitation of XRD analysis. The XRD patterns agree with the results of the XRF showing high percentages of the oxides of Si, Al and Ca which were the major components of the mineral phases observed in the XRD. The three phases detected namely: quartz, mullite and calcite correspond to the significant levels of Si, Al and Ca respectively in the ash (Figure 4.4.1) while lower levels of Fe and Mg (Figure 4.4.2) could account for the non-detection of any mineral phases such as hematite (Fe_2O_3) and enstatite ($Mg_2Si_2O_6$) that are typically associated with these species (Nathan et al., 1999). The geophysics profile of the profile ash dam (Figure 4.1.1) similarly provides clues to explaining the observed mineralogy. Contact with rocks prevented coring to deeper depths in cores S1 and S3. Furthermore, the geophysics of core S3 also showed indication of a fault (crack) at a depth of 16.5 m which coincided with the point where the new mineral phases were found. This may indicate a preferred flow pathway for the brine, resulting in a region with highly salt saturated conditions promoting the precipitation of the salts detected either in situ in the dump or during sampling handling.

4.6 Summary of comparative bulk chemistry and mineralogy of weathered fine coal ash cores S1 and S3 from Sasol Synfuels-Secunda ash dam

The investigation provided significant insight into the mineralogy, morphology, chemical composition and pore water chemistry of the fly ash co-disposed with brine in Secunda. Based on the concentrations of the elements determined by the XRF analysis for the fresh fly ash and drilled core samples, the major oxides identified were SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, Na_2O and TiO_2, minor elements were K, P, S and Mn and trace elements in the samples were As, Ba, Ce, Co, Cu, Nb, Ni, Pb, Rb, Sr, U, V, Y, Zr and Th. Sr (4465 ppm and 4864 ppm in core S1 and S3 respectively), Ba (2682 ppm and 3014 ppm in core S1 and S3 respectively) and Th (2075 ppm and 2283 ppm in core S1 and S3 respectively) recorded the highest levels among the trace elements in the ash dump cores while Rb and Ni recorded the lowest levels.

The fresh Secunda fly ash and drilled core samples from Secunda were further shown to be class F and silico-aluminate fly ash showing sialic and modic or ferrocalsialic chemical properties. The XRF analysis further indicated how the species were enriched and (or) depleted along the depths of the drilled core samples when compared to the fresh ash samples showing considerable mobility and inconsistency/ inhomogeneity of the ash dump.

The bulk mineral analysis by XRF also agreed with the XRD result which shows that the prominent mineral phases corresponded to the elements of oxides (Si and Al) with highest percentages in the samples. While quartz and mullite mineral phases were very prominent in the weathered Secunda drilled core samples, transient minerals such as lime, calcite, halite, bassanite, and kaolinite were much less abundant. The morphological changes (encrustations, etchings and corrosion) observed in the morphologies (by SEM) of the weathered ash particles from the drilled Secunda cores may thus be attributed to the formation of small amounts of transient secondary mineral phases due to leaching/reprecipitation processes that may have occurred as a result of weathering.

The pH profile of the drilled cores showed that the Secunda dump had become considerably less alkaline over time than the fresh Secunda ash indicating that acidification processes accompany the weathering of the ash in the Secunda wet disposed ash dams over time. The pH analysis showed a significant decrease in pH from 12.38 in fresh ash to a range of 9 – 11 in the wet disposed ash. The trend of acidification in the weathered ash is attributable to the chemical interactions of the ash and brine used to transport the ash as well as with the atmospheric CO_2 and percolating rain water. Also the variations in the pH values along the depth indicate that there are different weathering zones within the dump. This is attributed to varying placement conditions during disposal and preferential flow pathways causing different rates and zones of weathering in the ash dump, which has as result a change of pH; which in turn impacts on the mobility of the chemical species in the fly ash. The very high moisture content of the cores obtained from the ash dams formed by the wet ash handling system is of concern due to the dissolution and potential leaching of toxic species from the ash dump.

The shortcoming of the bulk chemical analysis is that the behaviour of various elements in the environment (toxicity, distribution and bioavailability) cannot be dependably predicted on the basis of their total concentration. However, it is necessary to stress that the assessment of the bulk concentration still provided vital information. It should be the first step in the evaluation of the environmental and biological risk associated with this material; on the basis of this information it can be decided if more information on the species availability should be acquired during the sequential fractionation studies, which results and discussions are to follow in the next chapter.

The most noteworthy aspect of the Secunda drilled core mineralogical and chemical sample analysis thus far is that Na containing secondary mineral phases in the Secunda ash drilled cores were not very evident and such as were observed, were of low abundance. Moreover, Na_2O content in Secunda ash drilled cores was low and ranged between only 2.2 and 3 mass % throughout the profiles of the various cores examined compared to the fresh ash that had 2.21 wt. % Na_2O thus no accumulation of Na is evident which should be the case if the ash acted as a salt sink. Thus it is not evident from the mineralogy or chemistry of the ash cores sampled that Secunda ash could act as a long term sustainable salt sink especially considering the volume of salts conveyed in the brine slurry.

Chapter Five

Mobility and Partitioning Patterns of Elements

5 Introduction

This chapter presents and discusses the results obtained from the total acid digestion test, the analysis of the anions obtained from the pore water chemistry and sequential extraction tests performed on the fresh Secunda fly ash samples and weathered drilled ash core samples, S1 and S3. These experiments were carried out in order to understand the mobility and partitioning patterns of the major, minor and trace elements in the Secunda ash samples resulting from the brine-ash interaction and weathering. In section 5.1 the results of the total metal content obtained from the total acid digestion test is presented and discussed. In section 5.2 the anionic species (SO_4^{2-} and Cl^-) are presented and discussed. Section 5.3 presents and discusses the partitioning patterns of the major and trace elements in the water soluble fraction, exchangeable fraction, carbonate fraction, Fe/Mn fraction and residual fraction. Section 5.4 presents and discusses the assessment of data quality for total metal concentration for the major and trace elements (mass balance). This chapter ends with a summary of the mobility and partitioning patterns of the major and trace elements in the Secunda fresh fly ash and weathered drilled core S1 and S3.

5.1 Total metal content

The total acid digestion experiment was carried out as reported in section 3.2.3 to determine the total metal content of the unleached fresh Secunda fly ash and drilled ash cores S1 and S3. The total elemental composition of the Secunda fly ashes was determined for comparative study. The digestates obtained were analysed using the ICP-OES (see section 3.3.8). The results of the total metal content analysis of the Secunda fresh fly ash and drilled Secunda core (S1 and S3) samples are shown in Figure 5.1.1 to 5.1.4 and Appendix 3and 4. Due to inhomogeneity of the ash dump, the mean value [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] of the concentration of the elements along the depth of the drilled Secunda ash core S1 and S3 are compared to the concentration of the Secunda fresh fly ash. The discussion of the trends observed for major (Si, Al, Ca, Fe, Na, Mg, and K), minor (Sr, Ba and Mn) and trace (As, Pb, Cr, Mo, Cu, Ni, and Zn) elements follows after the presentation of the figures.

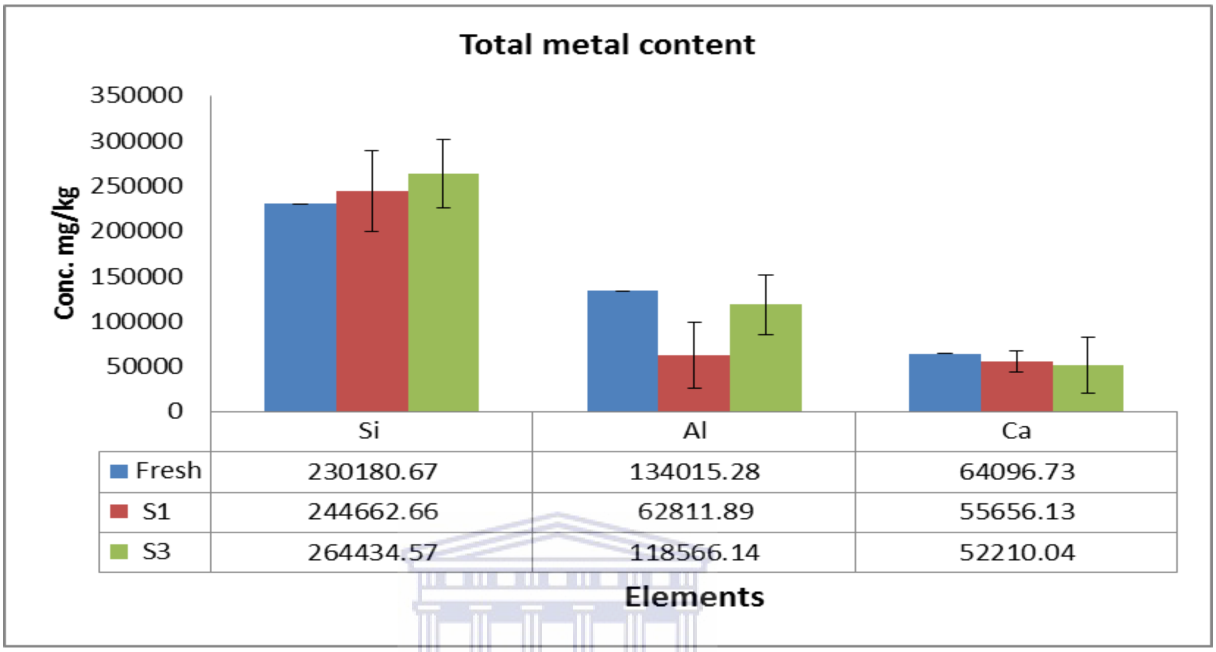


Figure 5.1.1: Total concentrations (ICP) of major elements (mg/kg) in Secunda fresh fly ash [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]

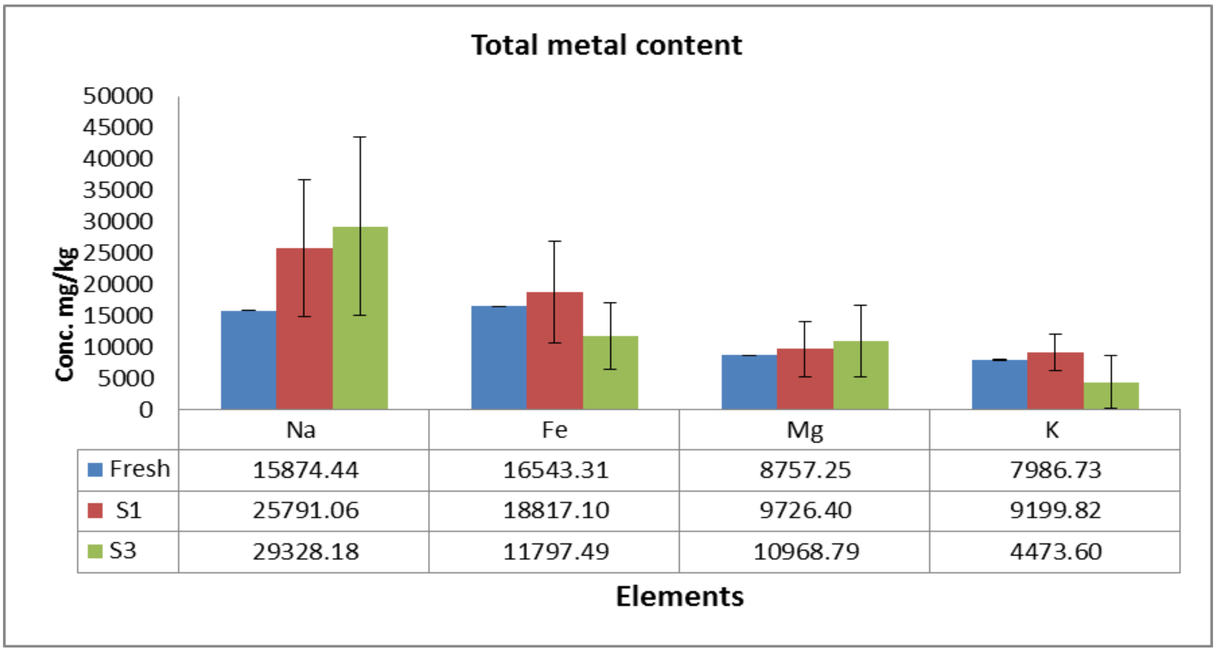


Figure 5.1.2: Total concentrations (ICP) of major elements (mg/kg) in Secunda weathered drilled core S1 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]

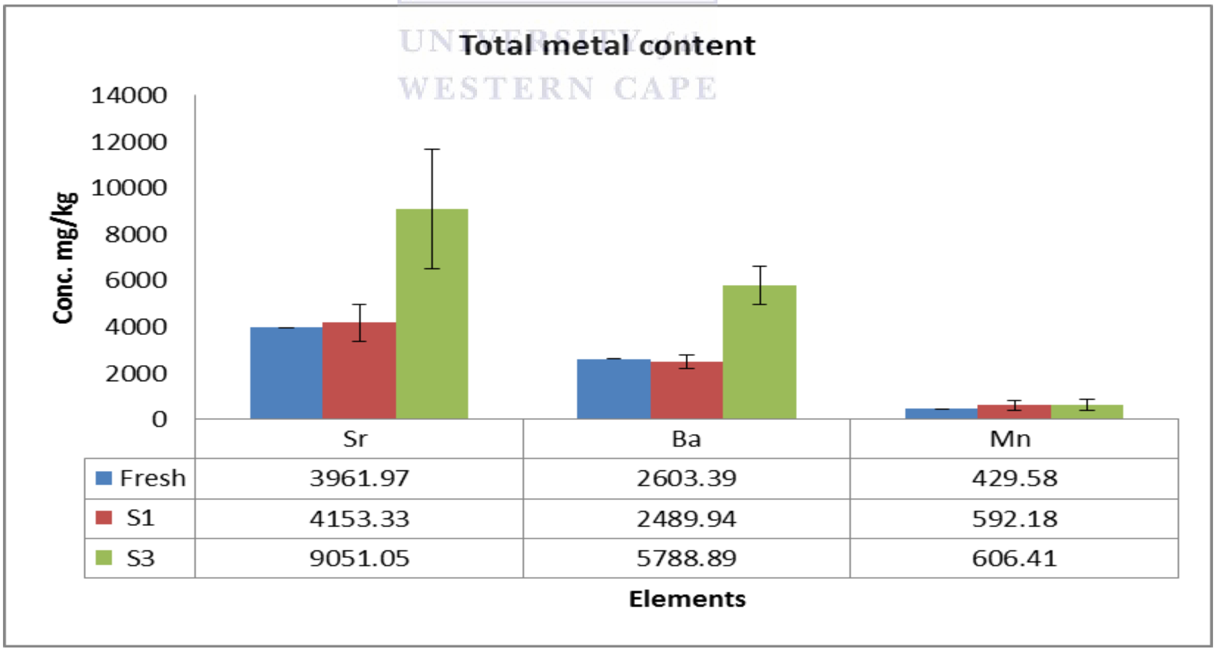
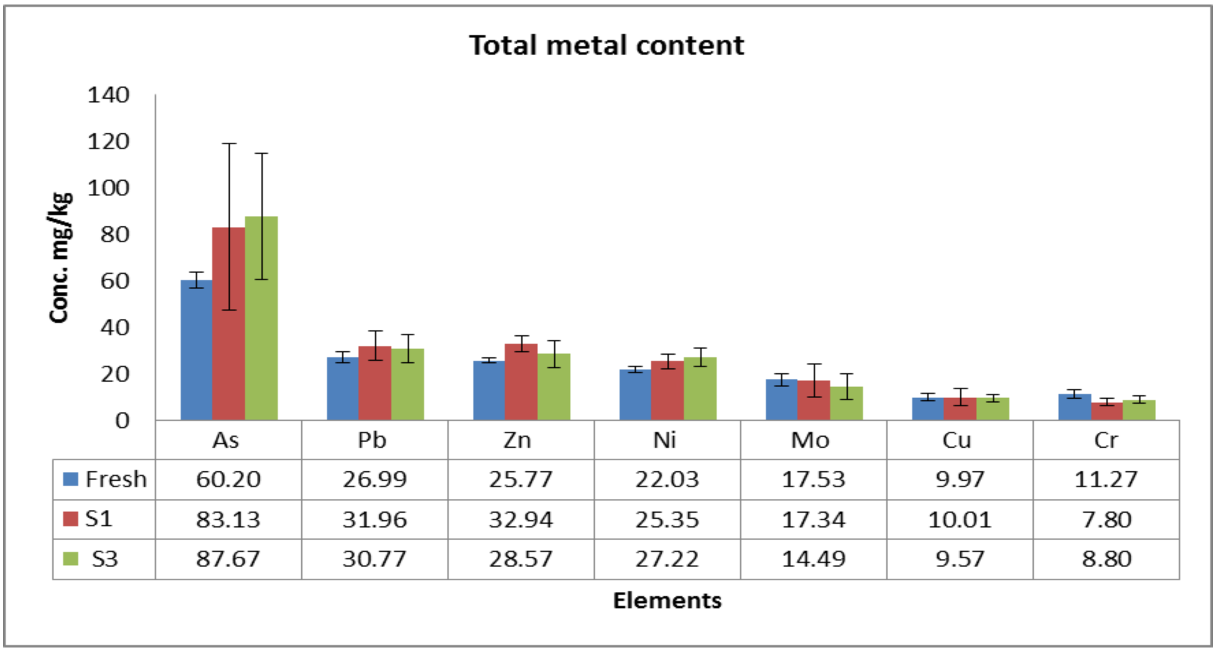


Figure 5.1.3: Total concentrations (ICP) of minor elements (mg/kg) in Secunda weathered drilled core S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]



	As	Pb	Zn	Ni	Mo	Cu	Cr
🟦 Fresh	60.20	26.99	25.77	22.03	17.53	9.97	11.27
🟥 S1	83.13	31.96	32.94	25.35	17.34	10.01	7.80
🟩 S3	87.67	30.77	28.57	27.22	14.49	9.57	8.80

Figure 5.1.4: Total concentrations (ICP) of trace elements (mg/kg) in Secunda weathered drilled core S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]

Figure 5.1.1 to 5.1.4 presents the mean values of the total concentrations of major, minor and trace elements in the Secunda fresh fly ash and drilled core samples for cores S1 and S3 determined by the total acid digestion test. The results reveal that the concentrations of the major and minor elements in the Secunda fresh fly ash were Si 230180.67 mg/kg, Al 134015.28 mg/kg, Ca 64096.73 mg/kg, Fe 15874.44 mg/kg (, Na 16543.31 mg/kg, Mg 8757.25 mg/kg, K 7986.73 mg/kg, Sr 3961.97 mg/kg, Ba 2603.39 mg/kg and Mn 429.58 mg/kg (Refer to figures 5.1.1 to 5.1.4). The total concentrations of the trace elements (As, Pb, Zn, Ni, Mo, Cu and Cr) were found to be 60.20 mg/kg, 26.99 mg/kg, and 25.77 mg/kg, 22.03 mg/kg 17.53 mg/kg, 9.97 mg/kg, and 11.27 mg/kg respectively (Figure 5.1.4).

For the drilled Secunda core sample, S1 the mean total concentrations as a function of depth for the major and minor elements were; Si 244662.66 mg/kg, Al 62811.89 mg/kg, Ca 75656.13 mg/kg, Fe 25791.06 mg/kg, Na 18817.10 mg/kg, Mg 9199.83 mg/kg, K 9726.40 mg/kg, Sr 4153.33, Ba 2489.94 mg/kg and Mn 592.18 mg/kg(figures 5.1.1 to 5.1.3), while the concentrations of the trace elements were found to be As 83.13 mg/kg, Pb 31.96 mg/kg, Zn 32.57 mg/kg, Ni 25.35 mg/kg, Mo 17.34 mg/kg, Cu 10.01 mg/kg, and Cr 7.80 mg/kg, (Figure

5.1.4). The chemical composition of the drilled core S3 showed that the concentrations of the major oxides were; Si 264434.57 mg/kg, Al 118566.14 mg/kg, Ca 52210.04 mg/kg, Fe 29328.18 mg/kg, Na 11797.49 mg/kg, Mg 10968.79 mg/kg. Minor elements were K 4473.60 mg/kg, Sr 9051.05 mg/kg, Ba 5788.89 mg/kg and Mn 606.41 mg/kg. The concentrations of the trace elements in core S3 were found to be; As 87.67 mg/kg, Pb 30.77 mg/kg, Zn 28.57 mg/kg, Ni 27.22 mg/kg , Mo 14.49 mg/kg, Cu 9.57 mg/kg, and Cr 8.80 mg/kg .

The total concentrations of the major and trace elements in the Secunda fresh fly ash and weathered drilled cores S1 and S3 as determined by ICP show that the concentrations of the major elements (Si, Al and Ca) and minor elements (Fe, Na, Mg, Sr, Ba and Mn) were high in all the Secunda fly ash samples. The concentrations of these elements accounted for 99.96 % of the total elemental components analysed in the fresh Secunda fly ash; 99.95 % and 99.96 % in drilled Secunda ash cores S1 and S3 respectively. The concentrations of the trace elements (As, Pb, Zn, Ni, Mo, Cu and), accounted for 0.04 % of the total elemental components analysed in the fresh Secunda fly ash and drilled ash core S3 and 0.05 % of drilled Secunda ash core S1. The variations in the total elemental compositions of Sr and Br in the two drilled cores S1 and S3 shows the inhomogeneity between different sections of the Secunda ash dump (Figure 5.1.3). The concentrations recorded in the total acid digestion analysis of the fly ashes were found to be similar to what was observed in the XRF analysis given in section 4.4.1. The observed significant depletion in the total concentrations of Al and Ca is similar to the trend observed in the XRF analysis. The high concentrations recorded for Si and Al indicates the aluminosilicate property of the fly ashes. Even though the results of the chemical compositions of the fresh fly ashes and the core ash samples revealed that Si and Al were leached out during the disposal at the ash dumps (section 4.4.1), the comparison of Si and Al concentration in the total metal content analysis showed that proportionally more Si and Al is present in the core ash samples than in the fresh fly ash. Due to the loss of other leachable elements such as Ca, Mg, Na, K, and S. The higher concentrations of Ca, Na, and Mg in the drilled ash cores than in the fresh fly ash may have resulted from the interaction of the fly ash and the co-disposed brine which has been reported to be rich in these species (Nyamhingura, 2009). Also the increase in concentration of the trace elements such as As, Pb, Zn, Ni, Mo, Cu and Cr in the drilled Secunda ash core samples compared to the Secunda fresh fly ash may also be attributed to brine interaction or weathering.

5.2 Anionic Species (sulphate and chloride)

The pore water chemistry experiment was carried out as reported in section 3.2.2 to determine the anion content (SO_4^{2-} and Cl^-) of the Secunda fresh fly ash and weathered drilled cores S1 and S3. The supernatants obtained after leaching the Secunda ash core S1 and S3 samples were analysed using the using a Dionex ICS-16000 ion chromatograph (IC) (see section 3.3.7). Figures 5.2.1 and appendix 3 and 4 show the distribution of readily soluble anionic species down the ash cores as revealed by ion chromatography (IC) analysis in samples from drilled Secunda ash cores S1 (0-22.5 m) and S3 (0-31.5 m) in comparison with fresh fly ash collected from Secunda power station. A detailed discussion is given after presentation of the figure.

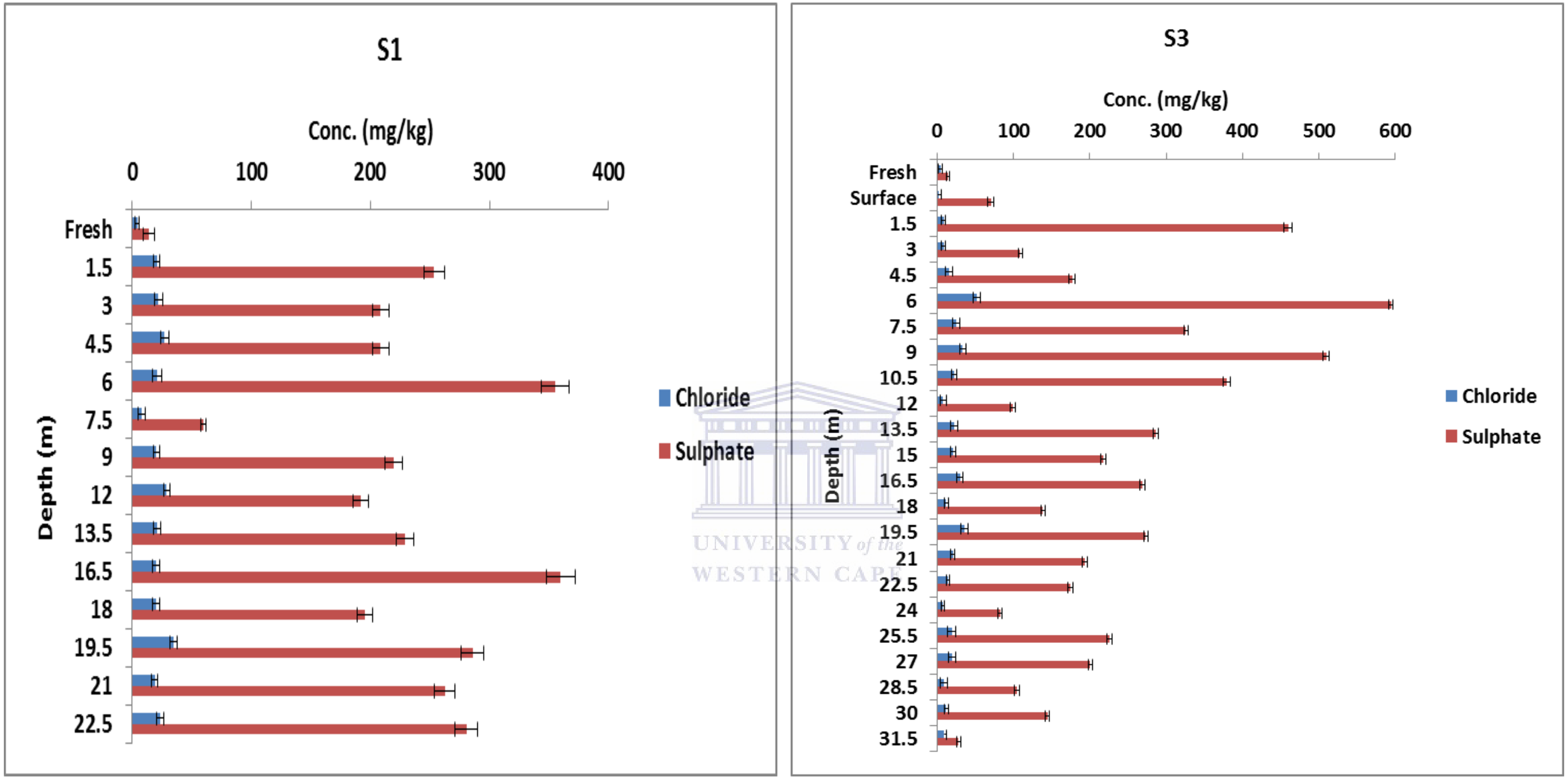


Figure 5.2.1 Distribution of sulphate and chloride ions in the Secunda fresh fly ash and drilled cores S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively]

Figures 5.2.1: The concentration of sulphate in the fresh fly ash was 13.64 mg/kg, while the drilled core samples showed high accumulation of sulphate in the range of 59.40 - 359.87 mg/kg and 27.98 - 594.13 mg/kg in core S1 and S3 respectively. There was a significant enrichment in the concentration of sulphate ions in the weathered drilled cores S1 and S3 when compared to the fresh fly ash. Also the sulphate concentrations were significantly increased at some depths and lower at other depths showing significant inhomogeneity. The concentration of chloride in the Secunda fresh fly ash was 4.05 mg /kg while drilled core samples had chloride concentration in the range of 7.62 - 34.34 mg/kg and 2.56 - 51.32 mg/kg in core S1 and S3 respectively. There was slight enrichment in the concentration of the chloride ions in the weathered ash compared to the fresh fly ash. In the two weathered drilled ash cores S1 and S3 there was no significant change in the concentration trend of the chloride ions along the depth of the dam which shows that there was little retention or accumulation of chloride ions in the ash dam showing this anion's conservative nature. The enrichment of sulphate anions in the weathered drilled core samples compared to the Secunda fresh fly ash may have resulted from the interaction of Secunda brine that is rich in sulphates and chlorides (Mooketsi et al., 2007; Nyamhingura, 2009) with the co-disposed fly ash.

The anion analysis of the Secunda fresh ash and weathered drilled core samples show that although the co-disposal of the fly ash with brine leads to the enrichment of sulphate ions in the weathered fly ash. The pore water analysis also showed that although higher amounts of sulphate was present in samples from the drilled Secunda ash cores (S1 and S3) than in the fresh Secunda fly ash, the sulphate was very soluble, leaching out rapidly when the pore water was extracted. The lack of consistent enrichment of chloride ions along the depth of the dump and rapid dissolution of the sulphate upon contact with water indicates the unsustainability of the Secunda fly ash dam as a sustainable salt sink.

5.3 Phase association and distribution patterns of the major and trace elements

This section presents and discusses the results obtained from the sequential extraction tests performed on the Secunda fresh fly ash sample and the weathered fly ash drilled core samples S1 (0 - 22.5 m) and S3 (0 - 31.5 m) and fresh fly. The sequential extraction tests were carried out as reported in section 3.2.4.in order to determine the distribution patterns of the elements in the five geochemical phases of the Secunda fresh fly ash and weathered fly ash co-disposed with brine from drilled Secunda ash cores S1 and S3. The leachates obtained were analysed using the ICP-OES (see section 3.3.8). As in the case of the total metal content, the mean value [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] of the concentration of the elements along the depth of the drilled Secunda ash core S1 and S3 are compared to the concentration of the Secunda fresh fly ash due to the inhomogeneity of the ash dump. Due to possible sample loss during the sequential extraction experiments the calculated amount of each element extracted (%) is based on the total sum of the concentrations of the element in the water soluble fraction, the exchangeable fraction, the carbonate fraction, the Fe and Mn fraction and the residual fraction.

5.3.1 Silicon

The proportions of the total Si extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions are presented in Figure 5.3.1 and appendix 7 to 16.

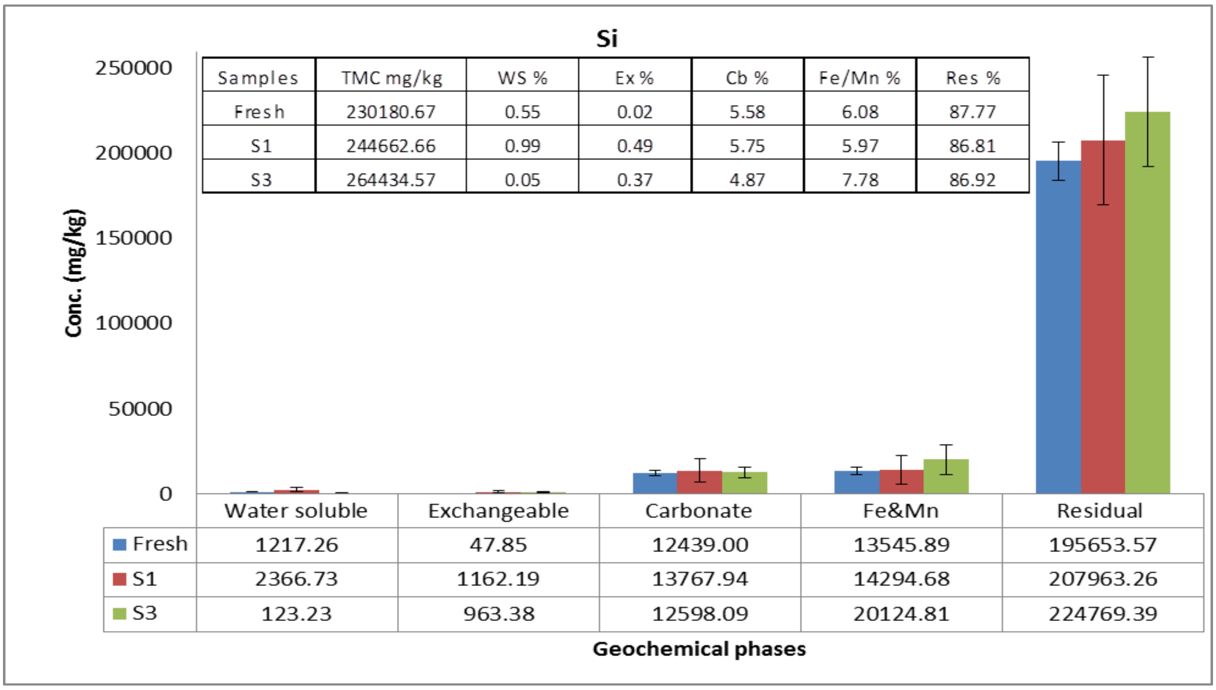


Figure 5.3.1: Distribution patterns of Si in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

From Figure 5.3.1, it is observed that the residual fraction, Fe and Mn fraction and the carbonate fraction had the largest proportion of Si extracted from the fresh Secunda fly ash and weathered drilled core S1 and S3. In the residual fraction, the concentration of Si released from the fresh fly ash was 206815.56 mg/kg (87.77 %); 207963.26 mg/kg (86.81 %) from core S1 and 224769.39 mg/kg (86.92 %) from core S3. The residual fraction which involved total acid digestion dissolved the ash matrix completely leading to the high concentrations of Si observed. The species in the residual fraction are contained in the insoluble matrix of the fly ash which cannot be easily released except in extreme conditions (Warren and Dudas 1984; Gitari et al., 2009).

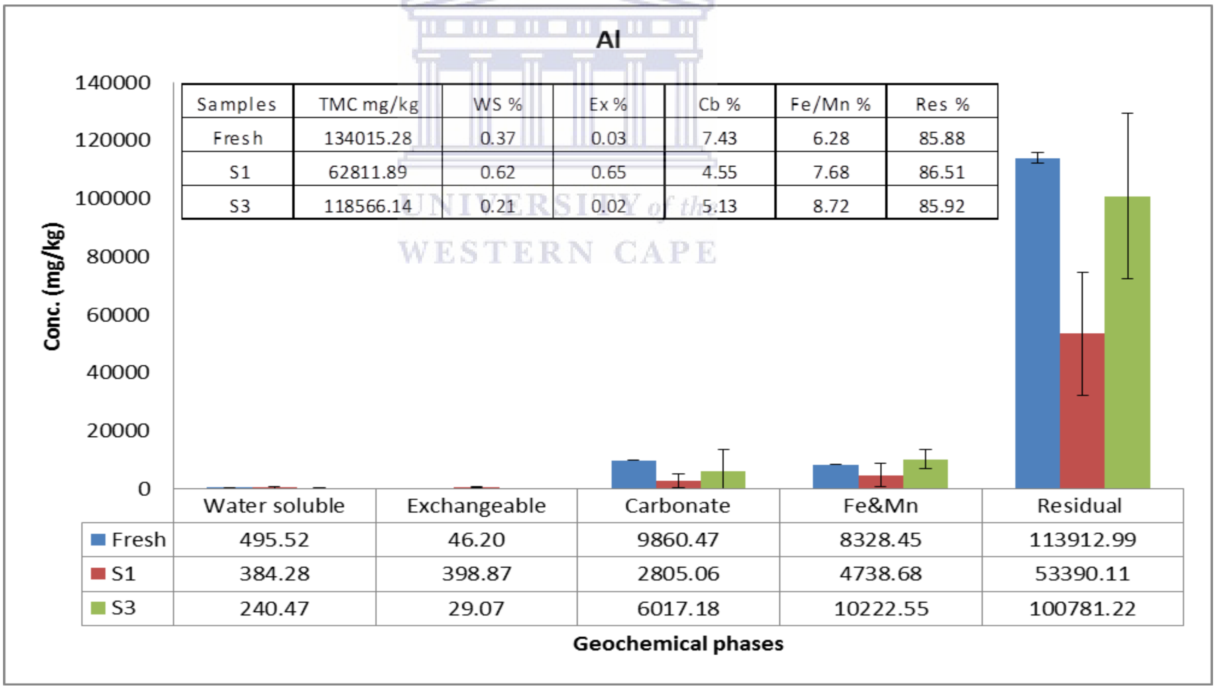
Apart from the bulk Si content extracted from the residual fraction, the Fe and Mn fraction and the carbonate fraction also contained significant amounts of Si. In the Fe and Mn fraction the concentration of Si in the fresh fly ash was 13545.9 mg/kg (6.08 %) while the mean concentrations of Si extracted in the two drilled cores were 14294.68 mg/kg (5.97 %) for S1 and 20124.81 mg/kg (7.78 %) for S3. For the carbonate fraction the concentration of Si extracted in the fresh fly ash was 12439.00 mg/kg (5.58 %,) and the extracted mean concentrations in the two drilled cores were 13767.95 mg/kg (5.75 %) for core S1 and 12598.09 mg/kg (4.87 %) for core S3. The observed high concentration of Si extracted from the Fe and Mn fraction and the carbonate fraction may be attributed to the dissolution of the aluminosilicate matrix of fly ash due to the low pH of the leachant used in the extractions of these fractions (pH 2 and 5 for the Fe and Mn fraction and carbonate fraction respectively). This indicates that Si is pH sensitive and can be mobilised as pH decreases over time in the ash dump. Since very large amount of fly ash are dumped, the ± 5 % of Si released pose a significant problem since this is a major component of the fly ash matrix and its release would cause the release of other, more toxic components in the Si matrix.

The water soluble and exchangeable fraction of the fresh Secunda fly ash and drilled ash core S1 and S3 reported low concentration of Si released. In the exchangeable fraction the concentration of Si released was 47.85 mg/kg (0.02 %,) and the mean concentrations of Si extracted from the weathered drilled cores were 1162.19 mg/kg (0.49 %) for core S1 and 963.38 mg/kg (0.37 %) for core S3. In the water soluble fraction the concentration of Si released was 1217.26 mg/kg (0.55 %) in the fresh fly ash while the mean of the total concentrations of Si extracted in the water soluble fraction from the weathered drilled cores S1 and S3 were 2366.73 mg/kg (0.99 %) and 123.23 mg/kg (0.99 %) respectively. These low concentrations of Si in exchangeable fraction and the water soluble fraction show that Si is not very mobile in these fractions and may not be quickly leached from the fly ash.

The differences in the concentrations of the Si released from the two drilled cores sample in the five fractions highlights the inhomogeneity of the ash dam. Si in fly ash are contained in the aluminosilicates and silicates minerals which also contain other elements such as Al, Ca, Mg, Na, K and other trace elements (Tiruta-Barna et al., 2006). The concentration of Si 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 and Griffin, 1984; Zevenbergen et al., 1999). This extraction study indicate that most of the Si content is locked up in the fly ash in the residual fraction (aluminosilicate) and Fe and Mn fraction which cannot be easily dissolved except at extreme conditions such as very low pH, a situation that is unlikely to occur naturally in the ash dam. Although in the drilled ash cores, S1 and S3, it was evident that residual and iron and manganese had the bulk concentration of Si, a proportion of Si was also released from the carbonate, exchangeable and water soluble fractions which could indicate the dissolution of the aluminosilicate ash matrix over time due to changes in pH. About 5-6 % of the fly ash matrix is thus soluble. The release of Si at lower pH as a result of the dissolution of the aluminosilicate matrix will also result in the release of other toxic elements that are locked in the matrix.

5.3.2 Aluminium

Figure 5.3.2 and appendix 7 to 16 presents the proportions of the total Al extracted from the fresh Secunda fly ash and drilled Secunda ash core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	134015.28	0.37	0.03	7.43	6.28	85.88
S1	62811.89	0.62	0.65	4.55	7.68	86.51
S3	118566.14	0.21	0.02	5.13	8.72	85.92

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
■ Fresh	495.52	46.20	9860.47	8328.45	113912.99
■ S1	384.28	398.87	2805.06	4738.68	53390.11
■ S3	240.47	29.07	6017.18	10222.55	100781.22

Figure 5.3.2: Distribution patterns of Al in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

Al, as in the case of Si had the major proportion associated with the residual fraction, Fe and Mn fraction and the carbonate fraction of the fresh Secunda fly ash and drilled ash cores S1 and S3. From Figure 5.3.2, in the residual fraction the concentration of Al extracted in the fresh fly ash was 107158.44 mg/kg (85.88 %) while the mean concentration of Al extracted in the two drilled cores was 53390.11 mg/kg (86.51 %) for S1 and 100781.22 mg/kg (85.92 %) for S3 The residual fraction which involved total acid digestion seemed to dissolve the ash matrix completely leading to the high concentrations of Al observed.

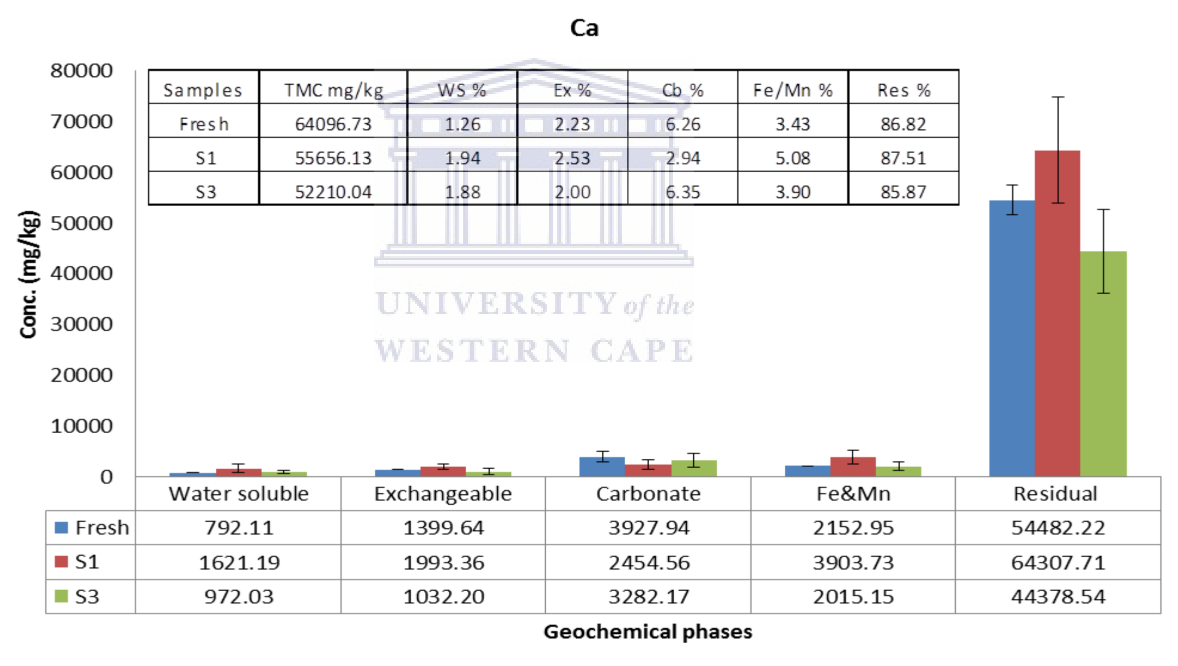
In the Fe and Mn fraction the concentration of Al released in the fresh fly ash was 8328.45 mg/kg (6.28 %,). The mean concentrations of Al extracted for the two drilled cores were 4738.68 mg/kg (7.68 %) for S1 and 10222.55 mg/kg (8.72 %) for S3. The carbonate fraction had 9860.47 mg/kg (7.43 %) of Al released from the fresh fly ash while the mean concentrations of Al extracted for the two cores were 2805.06 mg/kg (4.55 %) in core S1 and 6017.18 mg/kg (5.13 %) in core S3. As explained in the case of Si in section 5.3.1, the observed high concentration of Al extracted from these fractions may due to the low pH of the leachant used in the extractions of these fractions. Extraction of the carbonate fraction was carried out at a pH of 5 while the extraction of the Fe/Mn fraction was carried out at pH 2.

Again as in Si the the proportion of Al extracted in the exchangeable fraction and water soluble fractions of the fresh fly ash and weathered drilled cores S1 and S3 are low. The exchangeable fraction had 46.20 mg/kg (0.03 %); 398.87 mg/kg (0.65 %) and 240.5 mg/kg (0.02 %) of Al released from the fresh fly ash, core S1 and core S3 respectively. In the water soluble fraction the concentration of Al extracted from the fresh fly ash was 495.52 mg/kg (0.37 %) while the mean values of the total concentration of Al extracted from the weathered drilled cores S1 and S3 were 384.28 mg/kg (0.62 %) and 240.47 mg/kg (0.21 %) respectively (Figure 5.3.2).

The differences in the concentrations of the Al released from the two drilled cores sample also highlights the inhomogeneity of the ash dam. The fly ash pH value influenced the leaching pattern of Al in fly ash where it exists in both amorphous and crystalline form. Several studies have reported that the release of Al is controlled by amorphous $Al(OH)_3$ for pH ranging between 6 and 9, and by gibbsite ($Al(OH)_3$) for pH greater than 9 (Fruchter et al., 1990; Roy and Griffin, 1984; and Garavaglia and Caramuscio, 1994). This extraction study show that Al, like Si, is locked up in the fly ash matrix as a phase (aluminosilicate) which cannot be easily dissolved except at extreme conditions such as very low pH. However since Al is a major component of the ash matrix and 4-5 % can be released from the carbonate fraction, pH decrease could cause simultaneous release of other more toxic components from the ash matrix.

5.3.3 Calcium

Figure 5.3.3 and appendix 7 to 16 presents the proportions of the total Ca extracted in the five geochemical phases from the Secunda fresh fly ash and drilled core samples (cores S1 and S3).



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	64096.73	1.26	2.23	6.26	3.43	86.82
S1	55656.13	1.94	2.53	2.94	5.08	87.51
S3	52210.04	1.88	2.00	6.35	3.90	85.87

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
Fresh	792.11	1399.64	3927.94	2152.95	54482.22
S1	1621.19	1993.36	2454.56	3903.73	64307.71
S3	972.03	1032.20	3282.17	2015.15	44378.54

Figure 5.3.3: Distribution patterns of Ca in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

From figure 5.3.3, it can be seen that the proportion of the total Ca released in the Secunda fresh fly ash and drilled ash core S1 and S3 were predominant in the residual fraction, the carbonate fraction and the Fe and Mn fraction. In the residual fraction the fresh fly ash had a

Ca concentration of 54324.33 mg/kg (86.82 %) and the mean concentrations of Ca contained in residual fraction of the two drilled cores were 64307.71 mg/kg (87.51 %) for S1 and 44378.54 mg/kg (85.87 %) for S3. The residual fraction had the highest proportion of the total Ca associated with it.

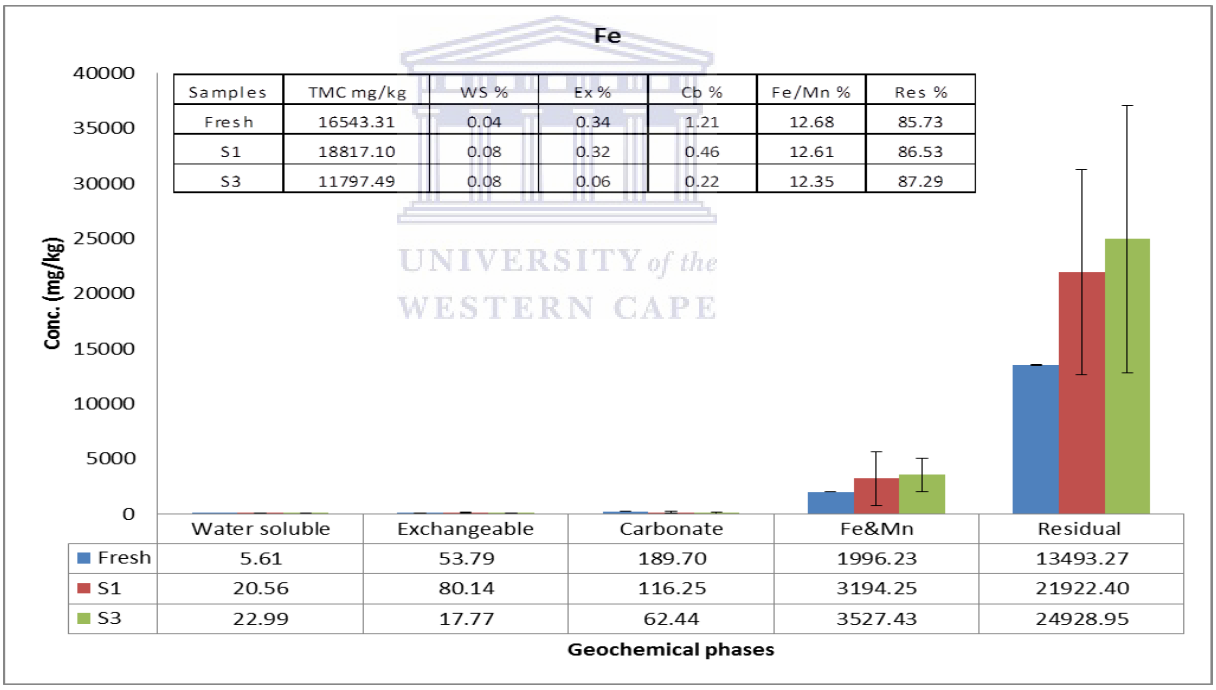
Figure 5.3.3 also shows that the concentration of Ca extracted in the carbonate fraction was 3927.94 mg/kg (6.26 %) for the fresh fly ash and the mean concentrations of Ca extracted in the two drilled cores were 2454.56 mg/kg (2.94 %) and 3282.17 mg/kg (6.35 %) for Core S1 and S3 respectively. In the Fe and Mn fraction the concentration of Ca released in the fresh fly ash was 2152.95 mg/kg (3.43 %) and the mean concentrations of Ca extracted from the two drilled cores were 3903.73.19 mg/kg (5.08 %) for S1 and 2015.15 mg/kg (3.90 %) for S3. The observed high percentage of Ca associated with carbonate fraction can be attributed to the presence of the calcite mineral in the stored fly ash (Johnson et al., 1995; Iwashita et al., 2005). The fresh fly ash and the weathered fly ash from the two drilled cores S1 and S3 showed the presence of this mineral in the XRD analysis (figure 4.5.1 and 4.5.2 in section 4.5).

The exchangeable fraction and water soluble fraction also had significant proportions of Ca released from the fresh Secunda fly ash and drilled ash core S1 and S3. In the water soluble fraction, the total mean concentrations of Ca extracted from the drilled core S1 and S3 were 1621.19 mg/kg (1.94 %) and 972.03 mg/kg (1.88 %) respectively. The concentration of Ca released in the fresh fly ash was 792.11 mg/kg (1.26 %). In the exchangeable fraction the concentration of Ca released in the fresh fly ash was 1399.64 mg/kg |(2.23 %) while the extracted mean concentration in the two drilled cores were 1993.36 mg/kg (2.53 %) in core S1 and 1032.20 mg/kg (2.00 %) in core S3. Again there is a significant difference in the mean concentration values of the two drilled ash cores due to the inhomogeneity of the ash dump. A larger amount of the exchangeable fraction of Ca in the fresh fly ash and both drilled cores (S1 and S3) was released into the solution than that observed in the water soluble fraction. The slightly higher amounts of Ca extracted in the water soluble fraction from the weathered drilled cores (0.68 % in core S1 and 0.62 % in core S3) than the fresh Secunda fly ash show some enrichment of Ca in the weathered ash cores possibly due to remineralisation processes as a result of CO2 interaction, infiltrating water, co-disposed brine and air.

This extraction study showed that the slightly higher concentration of Ca in the Secunda weathered drilled core samples may have resulted from secondary mineralisation due to weathering or the interaction with the co-disposed brine that is rich in calcium (Mooketsi et al., 2007; Nyamhingura, 2009). The high proportion of the total Ca released in the water soluble, exchangeable and carbonate fraction indicate that Ca is however highly mobile in these phases and is likely to leach out of the ash dump.

5.3.4 Iron

The proportions of the total Fe extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions are presented in Figure 5.3.4 and appendix 7 to 16.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	16543.31	0.04	0.34	1.21	12.68	85.73
S1	18817.10	0.08	0.32	0.46	12.61	86.53
S3	11797.49	0.08	0.06	0.22	12.35	87.29

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	5.61	53.79	189.70	1996.23	13493.27
🟥 S1	20.56	80.14	116.25	3194.25	21922.40
🟩 S3	22.99	17.77	62.44	3527.43	24928.95

Figure 5.3.4: Distribution patterns of Fe in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

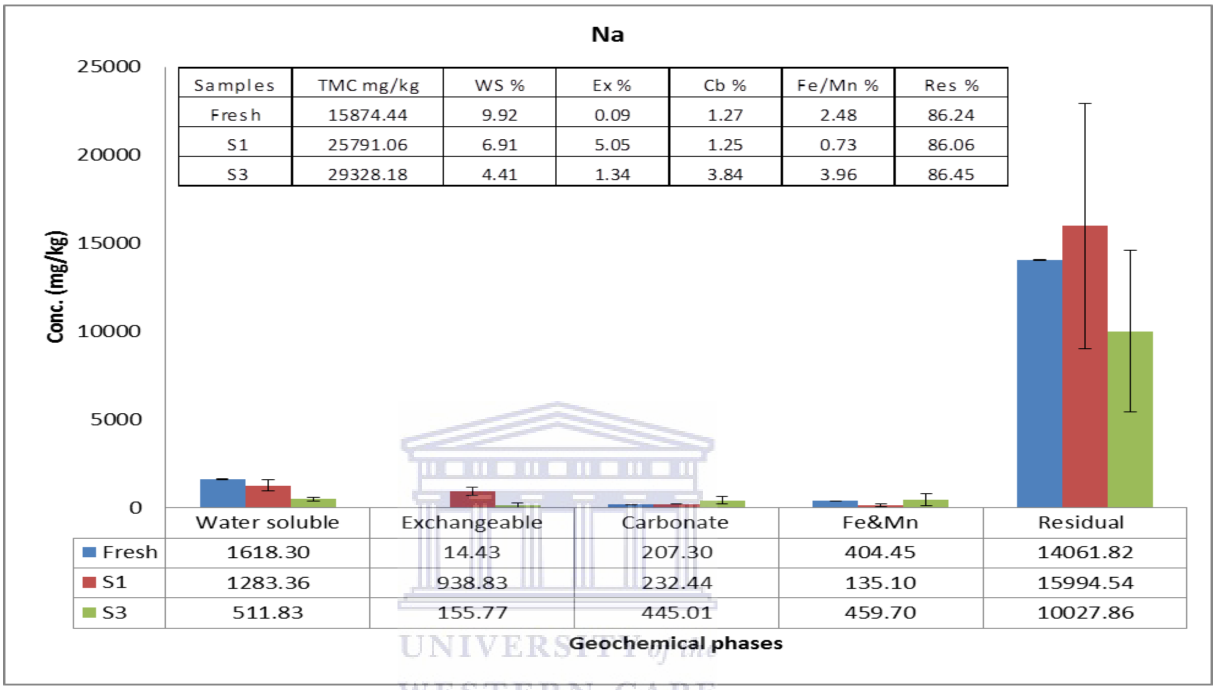
Figure 5.3.4, shows that the proportion of the total Fe is predominant in the residual fraction and the Fe and Mn fraction of the fresh Secunda fly ash and drilled ash core S1 and S3. In the residual fraction the concentrations of Fe extracted were 13493.27 mg/kg (85.73 %); 21922.40 mg/kg (86.53 %) and 24928.95 mg/kg (87.29 %) for the fresh fly ash, drilled ash cores S1 and S3 respectively. The concentrations of Fe extracted from the Fe and Mn fraction was 1996.23 mg/kg (12.68 %) in the fresh ash while the mean concentrations of Fe extracted from the two drilled cores were 3194.25 mg/kg (12.61 %) for drilled ash core S1 and 3527.43 mg/kg (12.35 %) for S3. The large amount of Fe released in the residual fraction and the Fe and Mn fraction may be attributed to dissolution of the iron bearing mineral phases in the fly ash or could have also resulted from the dissolution of the aluminosilicate matrix due to the low pH of the leachant used in the extractions of these fractions.

The proportions of total Fe extracted in the water soluble fraction, exchangeable fraction and carbonate fraction of the fresh Secunda fly ash and drilled ash core S1 and S3 were observed to be low. In water soluble fraction, Fe concentration in the fresh fly ash was 5.61 mg/kg (0.04 %) while in the drilled ash cores S1 and S3 the mean values of the concentration of Fe extracted were 20.56 mg/kg (0.08 %) and 22.99 mg/kg (0.08 %) respectively. The concentration of Fe extracted in the exchangeable fraction of the fresh fly ash was 53.79 mg/kg (0.34 %) and the extracted mean concentration in the two drilled cores S1 and S3 were 80.14 mg/kg (0.32 %) and 17.77 mg/kg (0.06 %) respectively. In the carbonate fraction the concentration of Fe in the fresh fly ash was 189.70 mg/kg (1.21 %) while the mean concentration of Fe extracted from the two drilled cores were 116.25 mg/kg (0.46 %) for S1 and 62.44 mg/kg (0.22 %) for S3.

The small proportion of Fe extracted from the water soluble, exchangeable and carbonate fraction may be due to the occurrence of Fe in fly ash as an insoluble oxide, either hematite or magnetite (Kim et al,. 2003). The amount of Fe released from the fresh fly ash and weathered drilled core samples in the water soluble, exchangeable and carbonate fractions is very low (0.04-1.21%) when compared to the very high amount in the relatively immobile Fe and Mn fraction (12.35-12.68 %). This shows that Fe in the Secunda fresh fly ash and weathered drilled cores are locked up in mineral phases that are not easily dissolved under natural conditions and are therefore not likely to leach out of the ash dump.

5.3.5 Sodium

Figure 5.3.5 and appendix 7 to 16 presents the proportions of the total Na extracted in the five geochemical phases from the Secunda fresh fly ash and drilled core samples (cores S1 and S3).



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	15874.44	9.92	0.09	1.27	2.48	86.24
S1	25791.06	6.91	5.05	1.25	0.73	86.06
S3	29328.18	4.41	1.34	3.84	3.96	86.45

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	1618.30	14.43	207.30	404.45	14061.82
🟥 S1	1283.36	938.83	232.44	135.10	15994.54
🟩 S3	511.83	155.77	445.01	459.70	10027.86

Figure 5.3.5: Distribution patterns of Na in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

Figure 5.3.5: The mineral phase association of Na in the Secunda fresh fly ash and weathered drilled Secunda ash core samples showed its predominance in the water soluble and residual fractions. In the residual fraction, the concentration of Na was 13569.38 mg/kg while the mean concentration of Na contained in the two drilled cores was 15994.54 mg/kg for S1 and 10027.86 mg/kg for S3. The amount of Na extracted from residual fraction accounts for 86.24 %; 86.06 % and 86.45 % of the mean value of the amount of Na extracted from the fresh ash and weathered drilled cores S1 and S3 respectively. As stated earlier the species in the residual

fraction are contained in the matrix of the fly ash which cannot be easily released except in extreme conditions (Warren and Dudas 1984; Gitari et al., 2009).

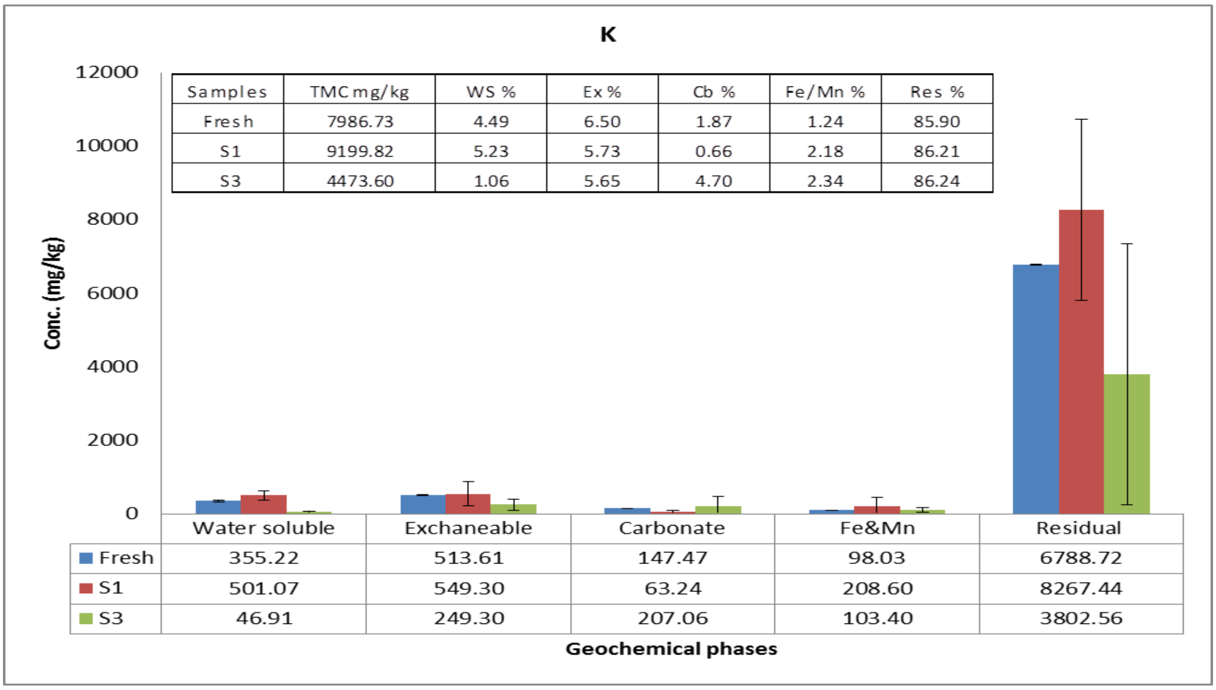
The concentration of Na released in the water soluble fraction of the fresh Secunda fly ash and weathered drilled ash core S1 and S3 were 1618.30 mg/kg in the fresh fly ash; 1283.36 mg/kg in core S1 and 511.83 mg/kg core S3. This concentration values represents 9.92 %, of the total Na content in the fresh fly ash and 6.91 % and 4.41 % of in the weathered drilled core S1 and S3 respectively. Na is usually associated with the highly soluble phase of the fly ash particles (Choi et al., 2002). Thus the release of Na from samples collected at various depths in the two drilled ash core probably resulted from the dissolution of the soluble salts such as halite. XRD results (Section 4.5) showed the presence of halite in some of the weathered ash samples. This high proportion of the total Na found in the water soluble fraction shows that Na is mobile in this fraction and may be easily leached out of the fly ash. Therefore, the proportion of Na released in the water soluble fraction is of importance in order to study its mobility in the brine co-disposed fly ash over time. The species that exist in association with the water soluble fraction and exchangeable fraction are the most labile species as they can be easily leached and readily reach the environment when fly ash is infiltrated by rain water (Yuan, 2009). The release of Na in the water soluble fraction showed that any Na captured from the brine during the interaction of brine with fly ash could be rapidly leached out of the dump when in contact with infiltrating water. Thus it is highly unlikely that the ash dump is a sustainable salt sink irrespective of the co-disposal method used.

A significant proportion of the total Na was also found in the exchangeable fraction while the carbonate fraction and the Fe and Mn fraction had negligible difference in the concentration of Na released from both fractions. In the exchangeable fraction the concentration of Na released was 14.43 mg/kg in the fresh fly ash while the concentration of Na released in the drilled ash core S1 and S3 were 938.83 mg/kg and 155.77 mg/kg were respectively. The amount of Na extracted from the exchangeable fraction accounts for 0.09 %; 5.05 % and 1.34 % of the total amount of Na in the fresh fly ash, drilled core S1 and S3 respectively. Thus only about 4.96 % (core S1) and 1.25 % (core S3) of Na was captured in the Secunda drilled ash cores compared to the fresh Secunda fly ash in the exchangeable fraction. The concentration of Na released in the carbonate fraction was 207.30 mg/kg in the fresh fly ash and the mean concentrations of Na extracted from the two drilled cores were 232.44 mg/kg in core S1and 445.01 mg/kg in core S3. The amount of Na extracted from the carbonate fraction accounts for 1.27 %, of the total amount of Na in the fresh fly ash and 1.25 % and 3.48 % of the mean value of the total amount of Na extracted from the weathered drilled cores S1 and S3 respectively. The proportions of the captured Na in the carbonate fraction of the drilled ash cores S1 and S3, compared to the fresh Secunda fly ash are also negligible (±0.02 % in core S1 and ±2.57 % in core S3). In the Fe and Mn fraction the concentration of Na extracted in the fresh fly ash was 404.45 mg/kg while the mean concentrations of Na extracted from the two drilled cores were 135.10 mg/kg for S1 and 495.70 mg/kg for S3. The amount of Na extracted from Fe and Mn fraction accounts for 2.48 %, of the amount of Na in the fresh fly ash and 0.73 % and 3.96 % of the mean value of the total amount extracted weathered drilled cores S1 and S3 respectively. The lesser amount of Na extracted in the carbonate fraction and Fe and Mn fraction when compared with the water soluble fraction and exchangeable fraction shows that Na release is not pH dependant (Warren and Dudas, 1984; Tiruta-Barna et al., 2004). Hence Na poses a great risk at the ash dam due to its leaching potential at natural pH.

This extraction study shows that Na was slightly retained by the fly ash but was never the less released in the water soluble, exchangeable and carbonate fractions. Hence overall there was no retention of Na in the Secunda fly ash dump as can be seen from the XRF analysis (section 4.4) which shows only a slight enrichment in the total Na content in the drilled Secunda ash core samples S1 (0.26 %) and S3 (0.55 %). This poor retention of Na a major component of Secunda brine ((Nyamhingura, 2009 and Mooketsi et al., 2007), in the drilled ash cores S1 and S3 clearly shows the unsustainability of the Secunda fly ash dump as a salt sink

5.3.6 Potassium

The proportions of the total K extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions are presented in Figure 5.3.6 and appendix 7 to 16.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	7986.73	4.49	6.50	1.87	1.24	85.90
S1	9199.82	5.23	5.73	0.66	2.18	86.21
S3	4473.60	1.06	5.65	4.70	2.34	86.24

	Water soluble	Exchaneable	Carbonate	Fe&Mn	Residual
🟦 Fresh	355.22	513.61	147.47	98.03	6788.72
🟥 S1	501.07	549.30	63.24	208.60	8267.44
🟩 S3	46.91	249.30	207.06	103.40	3802.56

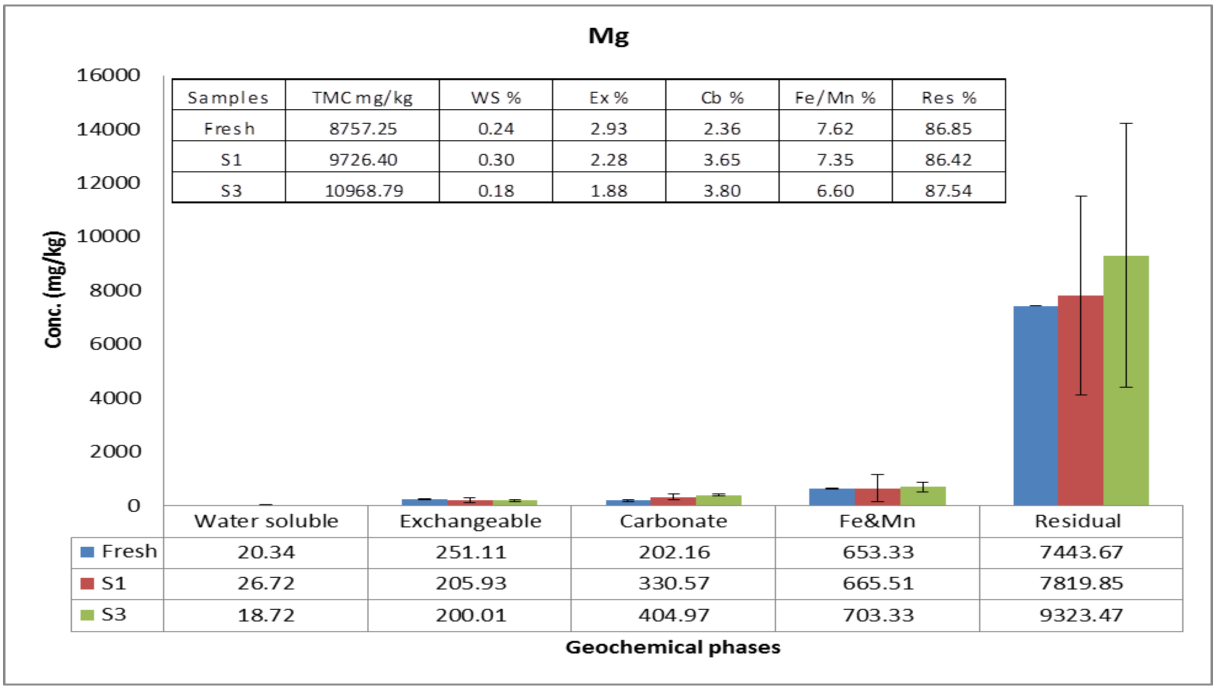
Figure 5.3.6: Distribution patterns of K in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

From Figure 5.3.6, shows that the proportion of the total K was dominant in the water soluble, exchangeable and residual fraction in the fresh Secunda fly ash and drilled ash cores S1 and S3. In the residual fraction the concentration of K in the fresh fly ash was 6762.07 mg/kg (85.90 %) and the mean concentrations of K contained in the two drilled cores were 8267.44 mg/kg (86.21 %) for core S1 and 3802.56 mg/kg (86.24 %) for core S3. Again the residual fraction contained the largest amount of the K released from the fresh Secunda fly ash and drilled ash core S1 and S3. The concentrations of K released in the water soluble fraction were 355.22mg/kg (4.49 %); 501.07 mg/kg (5.23 %) and 46.91 mg/kg (1.06 %) in the fresh fly ash, drilled ash core S1 and S3 respectively. In the exchangeable fraction the concentration of K extracted from the fresh fly ash was 513.61 mg/kg (6.50 %) while the extracted mean concentration extracted from the two drilled cores was 549.30 mg/kg (5.73 %) for core S1 and 249.30 mg/kg (5.65 %) for core S3. The carbonate fraction and the Fe and Mn fraction also contained significant amounts of K. In the carbonate fraction the concentration of K in the fresh fly ash was 147.47 mg/kg (1.87 %) while the mean concentration of K extracted for the two drilled cores were 207.06 mg/kg (4.70 %) for core S3 and 63.24 mg/kg (0.66 %) for core S1. The concentration of K extracted in the Fe and Mn fraction from the fresh fly ash was 98.03 mg/kg (1.24 %) and the mean concentrations of K extracted for the three cores were 208.60 mg/kg (2.18 %) in S1 and 158.40 mg/kg (2.34 %) in S3. Na and K exist as soluble salts on the surface of fly ash particles and their leaching behaviour is not pH dependent. K had significant presence in the water soluble fraction, exchangeable fraction for the two drilled cores S1 and S3. Also as in the case of Na, potassium poses a great risk at the ash dam due to its leaching potential at natural pH.

From this extraction it is observed that K as in the case of Na was also captured in the fly ash but was quickly released in the water soluble, exchangeable and carbonate fractions. Thus K was retained in the Secunda fly ash dump. The XRF analysis (section 4.4) shows that only a slight enrichment in the total K content in the drilled Secunda ash core samples S1 (0.02 %) and S3 (0.34 %). This poor retention of K as in the case of Na in the drilled ash cores S1 and S3 also highlights the unsustainability of the Secunda fly ash dump as a salt sink

5.3.7 Magnesium

Figure 5.3.7 appendix 7 to 16 presents the proportions of the total Mg extracted in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions from the Secunda fresh fly ash and drilled core samples (cores S1 and S3).



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	8757.25	0.24	2.93	2.36	7.62	86.85
S1	9726.40	0.30	2.28	3.65	7.35	86.42
S3	10968.79	0.18	1.88	3.80	6.60	87.54

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	20.34	251.11	202.16	653.33	7443.67
🟥 S1	26.72	205.93	330.57	665.51	7819.85
🟩 S3	18.72	200.01	404.97	703.33	9323.47

Figure 5.3.7 Distribution patterns of Mg in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

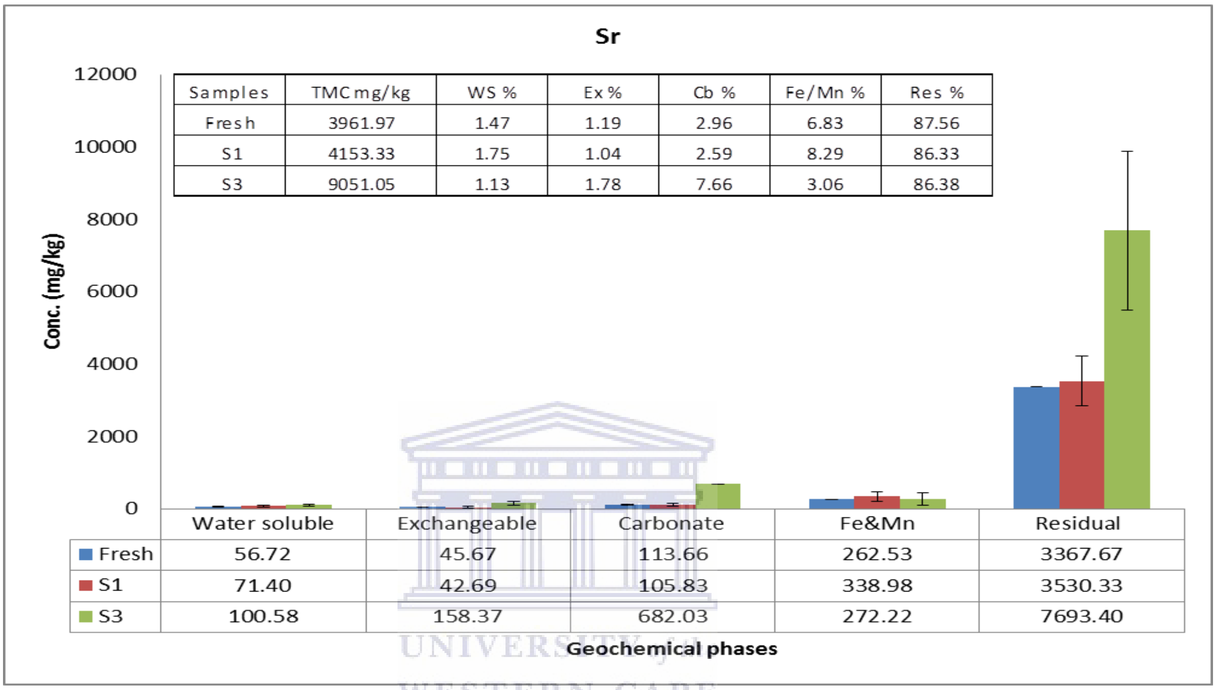
The largest proportion of Mg released was observed in the residual fraction and in the iron and manganese fraction of the fresh Secunda fly ash and weathered drilled cores S1 and S3. In the residual fraction the concentration of Mg extracted were 7423.53 mg/kg in the fresh fly ash; 7819.85 mg/kg for core S1 and 9323.47 mg/kg for core S3 which accounts for 86.85 %, 86.42 % and 87.54 % of the Mg content in the fresh fly ash and weathered drilled core S1 and S3 respectively. The concentration of Mg in the Fe and Mn fraction of the fresh Secunda fly ash was 653.33 mg/kg while the mean concentrations of Mg extracted for the two drilled cores were 665.51 mg/kg for S1 and 719.23 mg/kg for S3. These concentration values accounts for 7.26 %, 7.35 % and 6.60 % of the Mg content extracted from the fresh Secunda fly ash and drilled core S1 and S3 respectively. The large proportion of Mg extracted from the residual fraction and Fe and Mn fraction supports the suggestion that Mg is incorporated in the glass phases of the fly ash (Ugurlu, 2004). This large Mg content in the residual fraction and Fe and Mn fraction shows that Mg is not mobile in this fraction and may not be easily leached out of the fly ash.

A significant amount of the total Mg was also extracted from the carbonate fraction and exchangeable fraction of the fresh Secunda fly ash and drilled ash cores S1 and S3. The concentration of Mg released in the exchangeable fraction was 351.11 mg/kg in the fresh ash and for the two drilled core S1 and S3, 205.93 mg/kg and 200.01 mg/kg respectively. The Mg content extracted in the exchangeable fraction accounts for 2.93 %, of the Mg content in the fresh fly ash while 2.28 % and 1.88 % were the mean values of the Mg content extracted from the drilled ash cores S1 and S3 respectively. In the carbonate fraction the concentration of Mg released from the fresh Secunda fly ash was 202.16 mg/kg and the mean concentrations of Mg released from the two drilled cores were 330.57 mg/kg for S1 and 404.97 mg/kg for S3. The Mg content released from the carbonate fraction accounts for 2.36 %, of the Mg content in the fresh fly ash while 3.65 % and 3.80 % were the mean values of the Mg content extracted from the weathered drilled cores S1 and S3 respectively. The significant proportion of Mg in the carbonate fraction may be due to the presence of dolomite ($CaMg(CO_3)_2$) in the fly ash (Garavaglia and Caramuscio, 1994). Though dolomite was not detected in the XRD results for the two drilled cores as it may have been obscured by the more dominant quartz and mullite peaks (a major shortcoming of XRD analysis), however the XRF results showed significant quantities of Mg in the fly ash.

The mean values of the total concentrations of Mg extracted in the water soluble fraction from the fresh ash and weathered drilled cores were 20.34 mg/kg in the fresh ash; 26.72 mg/kg in core S1 and 18.72 mg/kg in core S3. The Mg content extracted from the water soluble fraction accounts for 0.24 %, of the Mg content in the fresh fly ash while 0.30 % and 0.18 % were the mean value of the Mg content extracted from the weathered drilled cores S1 and S3 respectively. The water soluble fraction compared to the other fractions has the lowest amount of Mg extracted. This low proportion of Mg im the water soluble fraction coupled with the predominance of Mg in the Fe and Mn fraction and residual fraction is an indication that the Mg in fly ash exist in mineral phases that are not easily soluble under normal environmental condition.

5.3.8 Strontium

The proportions of the total Sr extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions are presented in Figure 5.3.7 appendix 7 to 16.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	3961.97	1.47	1.19	2.96	6.83	87.56
S1	4153.33	1.75	1.04	2.59	8.29	86.33
S3	9051.05	1.13	1.78	7.66	3.06	86.38

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	56.72	45.67	113.66	262.53	3367.67
🟥 S1	71.40	42.69	105.83	338.98	3530.33
🟩 S3	100.58	158.37	682.03	272.22	7693.40

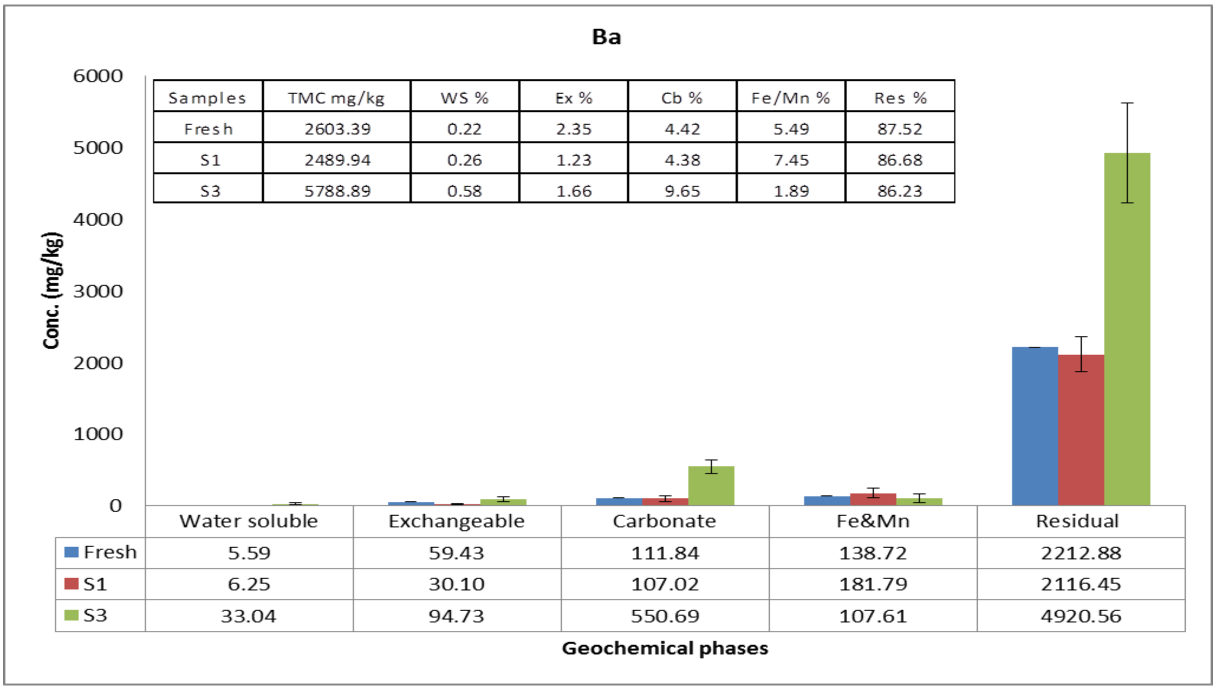
Figure 5.3.8: Distribution patterns of Sr in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

Figures 5.3.8 show that the proportion of the total Sr released is predominant in the residual fraction carbonate fraction, Fe and Mn fractions and the residual fraction of the fresh Secunda fly ash and drilled ash cores S1 and S3. The concentrations of Sr released in the residual fractions were 3523.42 mg/kg (87.56 %); 3530.33 mg/kg (86.33 %); and 7693.40 mg/kg (86.38 %) for the fresh fly ash and drilled ash core S1 and S3 respectively. In the carbonate fraction the concentration of Sr extracted was 113.66 mg/kg (2.96 %) in the fresh fly ash and the mean concentration of Sr extracted for the two drilled cores were 105.83 mg/kg (2.59 %) for S1 and 682.03 mg/kg (7.66 %) for S3. The concentration of Sr extracted in the Fe and Mn fraction from the fresh fly ash was 262.53 mg/kg (6.83 %) and the mean concentrations of Sr extracted for the two drilled cores were 338.98 mg/kg (8.29 %) for S1 and 272.22 mg/kg (3.06 %) for S3. The large amounts of Sr extracted amount in the carbonate fraction, Fe and Mn fraction and residual fraction may be due to Sr existing as SrO2 in fly ash or as Sr(OH)2 in solution and these compounds are dissolved in fly ash at low pH (Wang et al.,1999). This indicates that Sr release depend on the pH of the leachant. This release of Sr as a function of pH could also be due to its incorporation in the aluminosilicate matrixes of the fly ashes, which could only be released into solution as the aluminosilicate phases dissolve.

In the water soluble fraction the concentration of Sr released was 56.72 mg/kg; 71.40 mg/kg and 100.58 mg/kg in the fresh fly ash, core S1 and cores S3 respectively. This concentration represents 1.47 %; 1.75 % and 1.13 % of the mean amount of Sr in the fresh fly ash and drilled cores S1 and S3 respectively. The concentration of Sr released in the exchangeable fraction of the fresh Secunda fly ash and drilled ash core S1 and S3 were 45.67 mg/kg; 42.69 mg/kg and158.37 mg/kg respectively, which represents 1.19 %; 1.04 % and 1.78 % of the amount of Sr in the fresh fly ash and drilled cores S1 and S3 respectively. The concentrations of Sr extracted from the water soluble fraction and exchangeable fraction of the fresh Secunda fly ash and drilled ash core S1 and S3 are low when compared to the carbonate fraction, Fe and Mn fractions and the residual fraction. This also corroborates with the existence of Sr in mineral phases the can only be dissolved at low pH or locked up in the aluminosilicate matrix.

5.3.9 Barium

Figure 5.3.9 appendix 7 to 16 presents the proportions of the total Ba extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	2603.39	0.22	2.35	4.42	5.49	87.52
S1	2489.94	0.26	1.23	4.38	7.45	86.68
S3	5788.89	0.58	1.66	9.65	1.89	86.23

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	5.59	59.43	111.84	138.72	2212.88
🟥 S1	6.25	30.10	107.02	181.79	2116.45
🟩 S3	33.04	94.73	550.69	107.61	4920.56

Figure 5.3.9: Distribution patterns of Ba in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

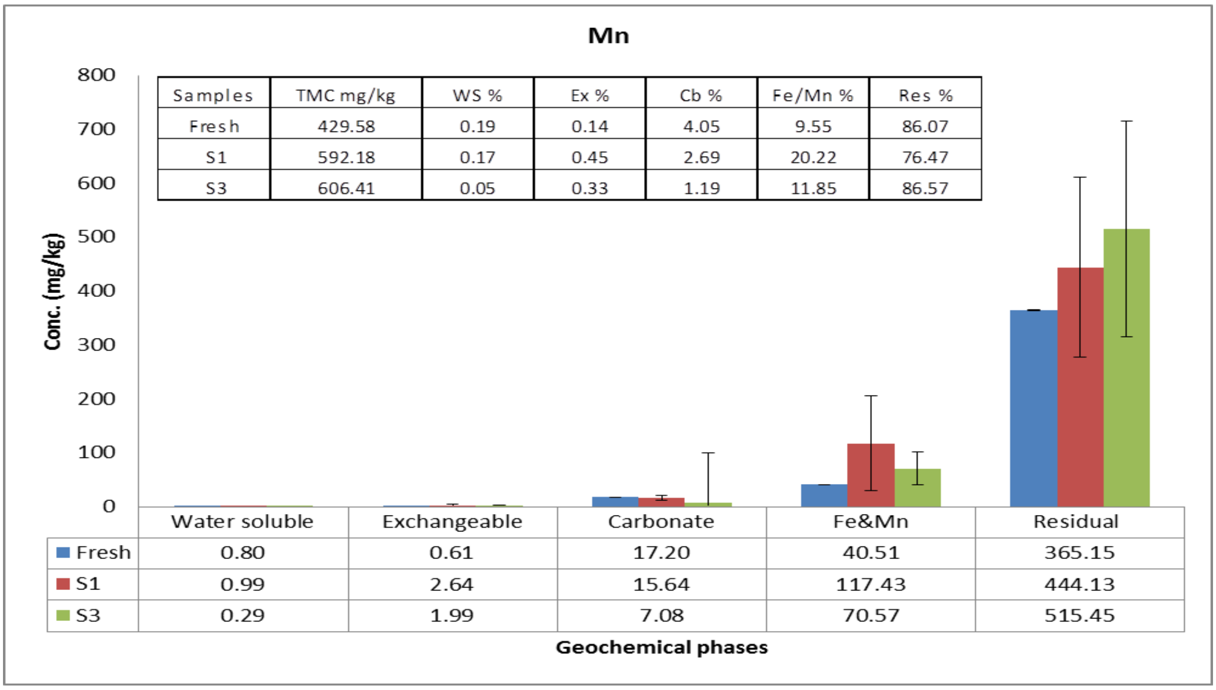
In Figure 5.3.9 the trend of the extracted amounts of Ba in the five geochemical phases are similar to the trend observed in the release of Sr in Figure 5.3.8. The carbonate fraction, exchangeable fraction and the residual fraction had the largest proportion of the total Ba extracted. The concentration of Ba released in the carbonate fraction was 111.84 mg/kg in the fresh fly ash while 107.02 mg/kg and 550.69mg/kg were the concentrations released from drilled ash core S1 and S3 respectively. This concentration values accounts for 4.42 %; 4.38 % and 9.65 % of the Ba content in the fresh fly ash, drilled ash core S1 and S3 respectively. In the Fe and Mn fraction the concentration of Ba released were 138.72 mg/kg; 181.79 mg/kg and 107.61 mg/kg for the fresh fly ash, core S1 and core S3 respectively, which represents 5.49 %, of the Ba content in the fresh fly ash while 7.45 % and 1.89 % represents the Ba content in the drilled ash core S1 and S3 respectively. The largest amount of Ba released in the Secunda fresh fly ash and drilled ash cores S1 and S3 were in the residual fraction. The fresh fly ash had Ba concentration of 2305.13 mg/kg while the mean concentrations of Ba contained in the two drilled cores were 2116.45 mg/kg for S1 and 4920.56 mg/kg for S3 and represents

87.52 %; 86.68 % and 86.23 % of the amount of Ba in the fresh fly ash, core S1 and core S3 respectively. The large amounts of Ba that were released may have resulted from the low pH of the solvents that were used in the carbonate fraction, exchangeable fraction and the residual fraction. Andac and Glasser, (1999) reported the strong leaching of Ba in acidic environment which also indicate the pH dependence of the release of Ba in fly ash. Thus Ba as in the case of Sr exists in mineral phases the can only be dissolved at low pH or locked up in the aluminosilicate matrix.

In the exchangeable fraction and water soluble fraction the concentrations of Ba released were observed to be low compared to the carbonate fraction, exchangeable fraction and the residual fraction. The exchangeable fraction had released Ba concentration of 59.43 mg/kg; 30.10 mg/kg and 94.73 mg/kg for the fresh fly ash, core S1 and S3 respectively, which represents 2.35 %, of the total concentrations of Ba in the fresh fly ash while 1.23 % and 1.66 % are for core S1 and S3 respectively. The low amounts of Ba extracted in the exchangeable fraction and water soluble fraction also support the existence of Ba in fly ash in phases that are not easily dissolved.

5.3.10 Manganese

The proportions of the total Mn extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions are presented in Figure 5.3.10 appendix 7 to 16.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	429.58	0.19	0.14	4.05	9.55	86.07
S1	592.18	0.17	0.45	2.69	20.22	76.47
S3	606.41	0.05	0.33	1.19	11.85	86.57

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	0.80	0.61	17.20	40.51	365.15
🟥 S1	0.99	2.64	15.64	117.43	444.13
🟩 S3	0.29	1.99	7.08	70.57	515.45

Figure 5.3.10: Distribution patterns of Mn in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

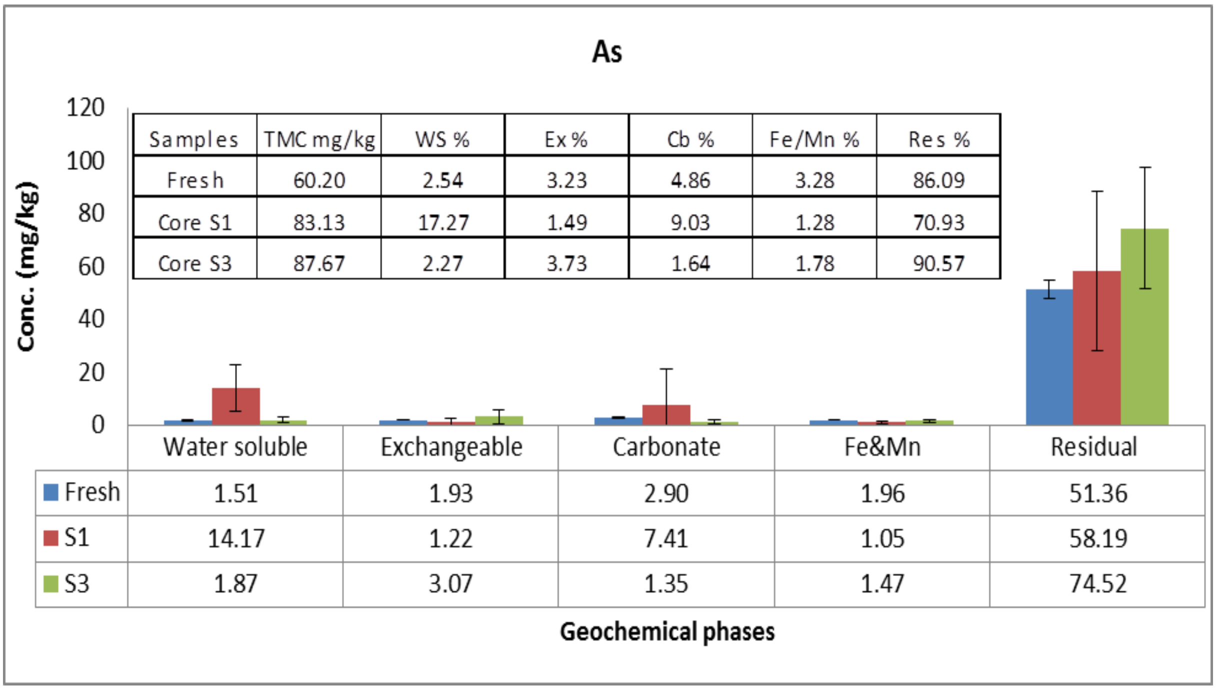
The pattern of release of Mn observed in five fractions show the predominance of the released proportion of the total Mn in the residual fraction, the Fe and Mn fraction and the carbonate fraction and is similar to the trend observed for Fe in section 5.3.5. In the residual fraction the concentration of Mn in the fresh fly ash was 348.89 mg/kg (86.07 %) while the mean mean concentrations of Mn contained in the two drilled cores were 444.13 mg/kg (76.47%) for core S1 and 515.45 mg/kg (86.57 %) for core S3. The concentration of Mn released in the Fe and Mn fraction was in the fresh fly ash was 40.51 mg/kg (9.55 %) and the mean concentrations of Mn released in the two drilled cores were 117.43 mg/kg (20.22%) for S1 and 70.57 mg/kg (11.85 %) for S3. In the carbonate fraction the concentration of Mn in the fresh fly ash was 17.20 mg/kg (4.05 %,) and the mean concentrations of Mn released in the two drilled cores were 15.64 mg/kg (2.69 %) for S1 and 7.08 mg/kg (1.19 %) for S3. The large amount of Mn extracted from the residual fraction, the Fe and Mn fraction and the carbonate fraction as in the case of Fe may also be attributed to dissolution of the Mn bearing mineral phases in the fly ash or could have resulted from the dissolution of the aluminnosilicate matrix.

The concentrations of Mn released in the exchangeable fraction and water soluble fraction of the fresh Secunda fly ash and drilled ash core S1 and S3 were observed to be low In the exchangeable fraction the concentration of Mn released in the fresh fly ash was 0.61 mg/kg (0.14 %) while the extracted mean concentrations in the two weathered drilled cores was 2.64 mg/kg (0.45 %) in S1 and 1.99 mg/kg in (0.33 %) S3. The concentration of Mn released in the water soluble fraction were 0.80 mg/kg (0.19 %,); 0.99 mg/kg (0.17 %) and 0.29 mg/kg (0.05 %) in the fresh fly, core S1 and S3 respectively. Generally the two drilled ash cores S1 and S3 had low concentration of Mn in the water soluble fraction. In the exchangeable Fraction the mean concentrations of Mn in the fresh ash and weathered drilled core S1 and S3 were much higher than that observed in the water soluble fraction. The fresh fly ash has a lower concentration of Mn than that observed in the water soluble extraction fraction. The low concentration of Mn in the water soluble and exchangeable fractions may be due to the precipitation of its metal hydroxide. According to Gitari et al., (2009), Mn in alkaline solution forms hydrous manganese.

This extraction study showed that the release pattern of Mn observed in five fractions could be as a result of formation and dissolution of oxides of these elements at different pH levels. Since the highest concentration of Mn extracted were in the residual fraction, Fe and Mn and carbonate fractions respectively, it implies that Mn may only be leached out of the ash dump at extreme conditions such as low pH.

5.3.11 Arsenic

Figure 5.3.11 and appendix 7 to 16 presents the proportions of the total As extracted from the from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	60.20	2.54	3.23	4.86	3.28	86.09
Core S1	83.13	17.27	1.49	9.03	1.28	70.93
Core S3	87.67	2.27	3.73	1.64	1.78	90.57

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
■ Fresh	1.51	1.93	2.90	1.96	51.36
■ S1	14.17	1.22	7.41	1.05	58.19
■ S3	1.87	3.07	1.35	1.47	74.52

Figure 5.3.11: Distribution patterns of As in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

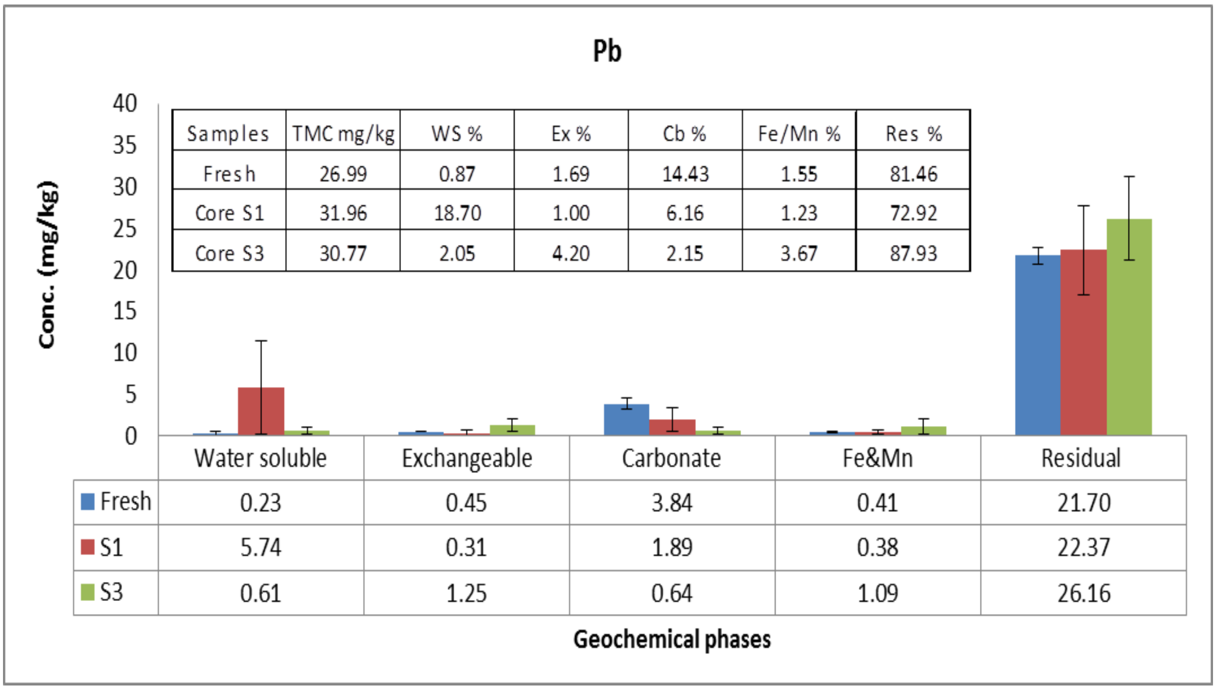
From figure 5.3.11 it can be seen that significant proportion of the total As was released in all the five geochemical fraction of the fresh Secunda fly ash and drilled ash core S1 and S3. The residual fraction had the largest amount of As released with concentration values of 51.36 mg/kg (86.09 %,) in the fresh fly ash and the mean concentrations of As contained in the two drilled cores were 58.19 mg/kg (70.93 %) for core S1 and 74.52 mg/kg (90.57 %) for core S3. In the water soluble fraction Core S1 had the highest mean concentration of As extracted from the drilled cores with a value of 14.17 mg/kg (17.27 %) while cores S3 had 1.87 mg/kg (2.27 %). The concentration of As in the fresh fly ash was 1.51 mg/kg (2.54 %,). The difference in the mean values of the total concentrations of As extracted from the two drilled cores S1 and S3 also highlights the inhomogeneity of the ash dump. The large amount of As released from core S1in the water soluble fraction may resulted from the dissolution of aluminosilicate matrix of the fly ash due to weathering. The concentrations of As extracted in the exchangeable fraction from the fresh fly ash was 1.93 mg/kg (3.23 %) and for the two weathered drilled cores S1 and S3 the extracted mean concentrations in the two drilled cores were 1.22 mg/kg (1.49 %) and 3.67 mg/kg (3.73 %) respectively. In the carbonate fraction the concentration of As extracted in the fresh fly ash was 2.90 mg/kg (4.86 %) and the mean concentration of As extracted from the two drilled cores were 7.41 mg/kg (9.02 %) for S1 and 1.35 mg/kg (1.63 %) for S3. The relatively high amount of As in the carbonate fraction could be attributed to the formation of calcite in fly ash. Galbreath and Zygarlicke, (2004) reported that a high proportion of calcium oxide in coal fly ash can acts as a reactive capture of arsenic in fly ash.

The Fe and Mn fraction had the lowest concentration of As released compared to the other fractions with 1.96 mg/kg (3.28 %) released in the fresh fly ash. The mean concentrations of As extracted from the two drilled cores were 1.05 mg/kg (1.28 %) for S1 and 1.47 mg/kg (1.78 %) for S3. The percentage of As in the iron and manganese fraction is relatively low compared with the other fractions.

The fairly high concentration of As in the water soluble, exchangeable and carbonate fractions indicates its association with readily soluble mineral phases which implies that As is mobile in these fractions and can be easily leached and readily reach the environment when fly ash is infiltrated by rain water (Yuan, 2009).

5.3.12 Lead

Figure 5.3.12 and appendix 7 to 16 presents the proportions of the total Pb extracted in the five geochemical phases from the Secunda fresh fly ash and drilled core samples (cores S1 and S3).



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	26.99	0.87	1.69	14.43	1.55	81.46
Core S1	31.96	18.70	1.00	6.16	1.23	72.92
Core S3	30.77	2.05	4.20	2.15	3.67	87.93

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	0.23	0.45	3.84	0.41	21.70
🟥 S1	5.74	0.31	1.89	0.38	22.37
🟩 S3	0.61	1.25	0.64	1.09	26.16

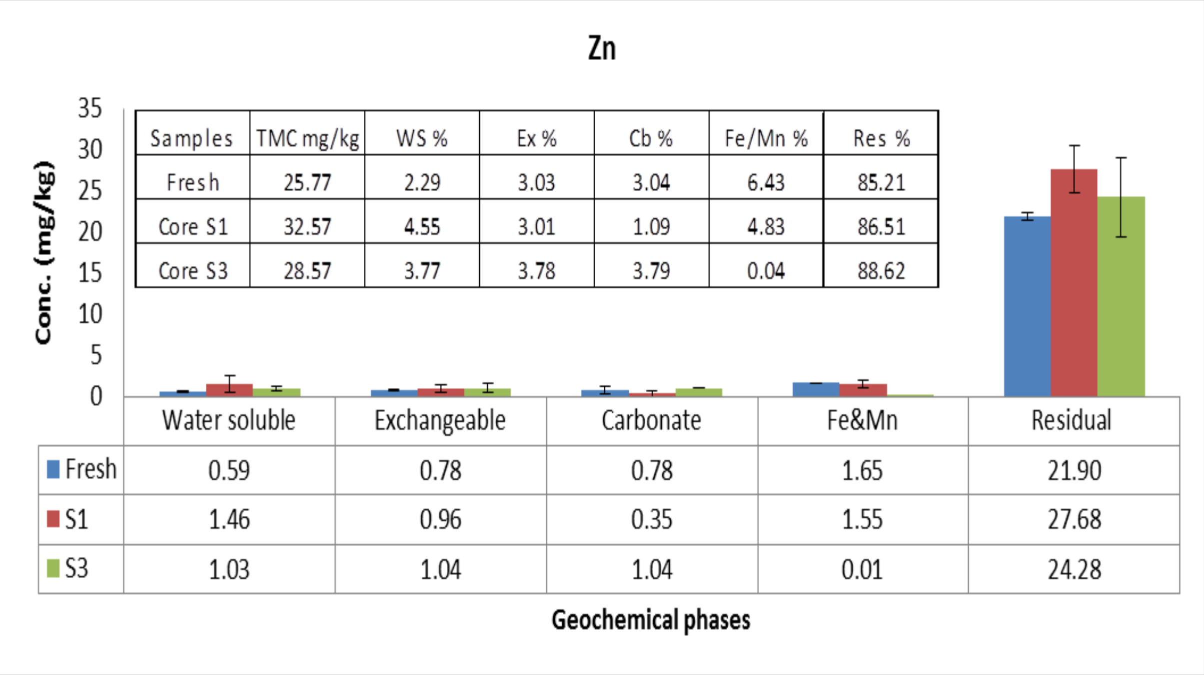
Figure 5.3.12: Distribution patterns of Pb in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

Figure 5.3.12 shows that the residual fraction had the largest proportion of the total Pb extracted from the fresh Secunda fly ash and weathered drilled core S1 and S3 followed by the water soluble and carbonate fraction. Also significant amounts were also extracted from the exchangeable fraction and the Fe and Mn fraction. The concentrations of Pb extracted in the residual fraction were 21.70 mg/kg (81.46 %); 22.37 mg/kg (72.92 %) and 26.16 mg/kg (97.93 %) for the fresh fly ash, core S1 and S3 respectively. In the water soluble fraction core S1 had the highest mean value of the Pb extracted with a value of 5.74 mg/kg (18.70 %) while cores S3 had 0.61 mg/kg (2.05 %). Pb had a concentration of 0.23 mg/kg (0.87 %) in the fresh fly ash. . The large amount of Pb released from core S1in the water soluble fraction may resulted from the dissolution of aluminosilicate matrix of the fly ash due to weathering. The carbonate fraction had 3.84 mg/kg (14.43 %) in the fresh fly ash, while the mean concentration of Pb extracted from the two drilled ash cores were 1.89 mg/kg (6.16 %) for S1and 0.64 mg/kg (2.15 %) for S3. The exchangeable fraction and the Fe and Mn fraction had lower amounts of Pb extracted compared to the other fractions. In the exchangeable fraction the concentration of Pb extracted from the fresh fly ash was 0.45 mg/kg (1.69 %) while the extracted mean concentrations in the two weathered drilled cores was 0.30 mg/kg (1.00 %) in S1 and 1.25 mg/kg (4.20 %) in S3. For the Fe and Mn fraction the concentration of Pb released in the fresh fly ash was 0.41 mg/kg (1.55 %) while the mean concentrations of Pb extracted for the two drilled cores were 0.38 mg/kg (1.23 %) for S1 and 1.09 mg/kg (3.67 %) for S3.

The fairly high concentration of Pb released in the and carbonate fraction may be associated with the gradual dissolution of the glass fractions phase present in fly ash due to weathering. According to Hulett et al., (1980) substantial portions of Pb are incorporated into the glass matrix of the fly ash with lesser portions existing as surface precipitates. Thus Pb will be easily leached from the fly ash. It has been reported that Pb leaching in coal fly ash can be controlled by acidity and alkalinity of the ash pore water (Vitkova et al., 2009).

5.3.13 Zinc

The proportions of the total Zn extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions are presented in Figure 5.3.13 and appendix 7 to 16.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	25.77	2.29	3.03	3.04	6.43	85.21
Core S1	32.57	4.55	3.01	1.09	4.83	86.51
Core S3	28.57	3.77	3.78	3.79	0.04	88.62

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	0.59	0.78	0.78	1.65	21.90
🟥 S1	1.46	0.96	0.35	1.55	27.68
🟩 S3	1.03	1.04	1.04	0.01	24.28

Figure 5.3.13: Distribution patterns of Zn in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

The proportions of the total of Zn extracted from the fresh Secunda fly ash and drilled as cores S1 and S3 in the water soluble fraction, exchangeable fraction, carbonate fraction and Fe and Mn fraction had similar values, while the bulk amount was extracted from the residual fraction. The concentrations of Zn extracted in the residual fraction were 21.90 mg/kg (85.21 %) in the fresh fly ash; 27.68 mg/kg (86.51 %) and 24.28 mg/kg (88.62 %) in the drilled ash cores S1 and S3 respectively. In the Fe and Mn fraction the concentration of Zn released in the fresh fly ash was 1.65 mg/kg (6.43 %,). The mean concentrations of Zn extracted from the two drilled cores were 1.55 mg/kg (4.83 %) for S1 and 0.11 mg/kg (0.04 %) for S3. The bulk of Zn was contained in the residual fraction indicating that the significant concentrations of Zn cannot be leached out of the Secunda fly ash under normal environmental conditions. Metals in the residual fraction are suggested to be safer for the environment due to their lower mobility and bioavailability (Yuan, 2009).

The difference in the amounts of Zn extracted from the water soluble fraction, exchangeable fraction and carbonate fraction were negligible. In the water soluble fraction the concentrations of Zn extracted from the fresh Secunda fly ash and the drilled ash cores were 0.59 mg/kg (2.29 %) in the fresh ash; 1.46 mg/kg (4.55 %) in core S1 and 1.03 mg/kg (3.77 %) in cores S3. The concentrations of Zn extracted in the exchangeable fraction were 0.78 mg/kg (3.03 %); 0.96 mg/kg (3.01 %) and 1.04 mg/kg (3.78 %) in in the fresh ash and drilled ash cores S1 and S3 respectively. The carbonate fraction had 0.78 mg/kg (3.04 %,) of Zn released in the fresh fly ash while the mean concentrations of Zn extracted from the two drilled cores were 0.35 mg/kg (1.09 %) for S1 and 1.04 mg/kg (3.79 %) for S3.

This extraction studies has shown that the bulk of Zn was contained in the residual fraction but the amount released in the water soluble fraction, exchangeable fraction and carbonate fraction were significant indicating the association of Zn in the Secunda ash samples with mineral phases that may be readily leached out of fly ash under normal environmental conditions.

5.3.14 Nickel

Figure 5.3.14 and appendix 7 to 16 presents the proportions of the total Ni extracted from the from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions.

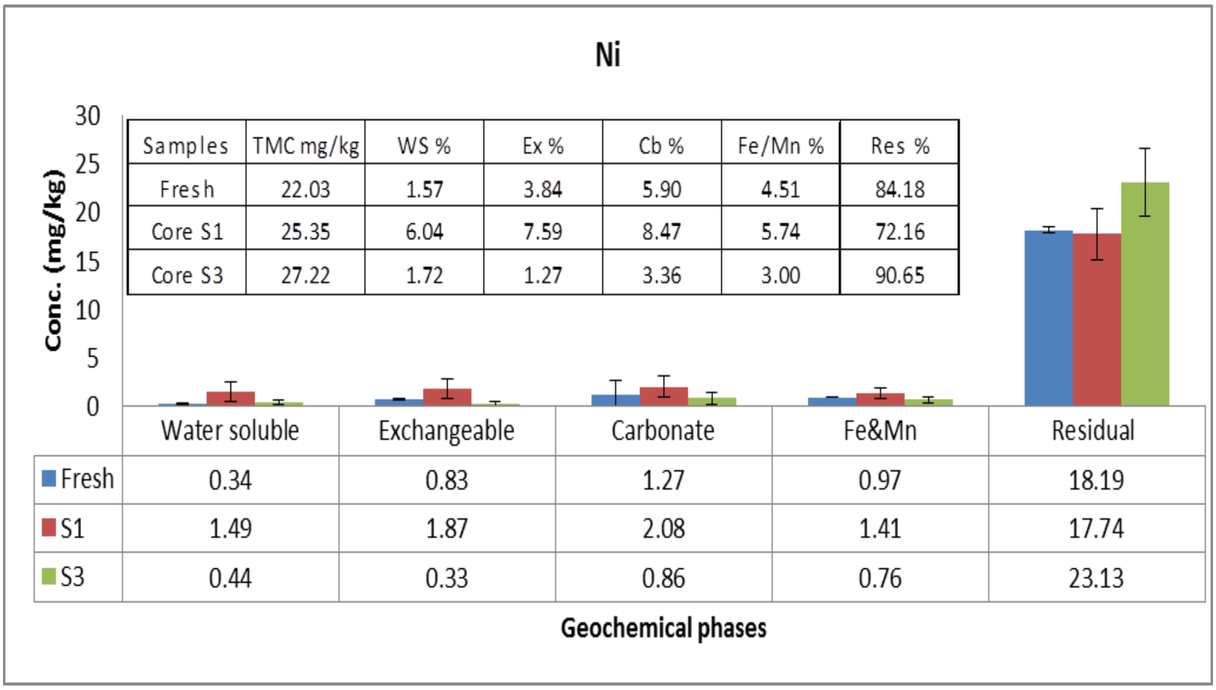


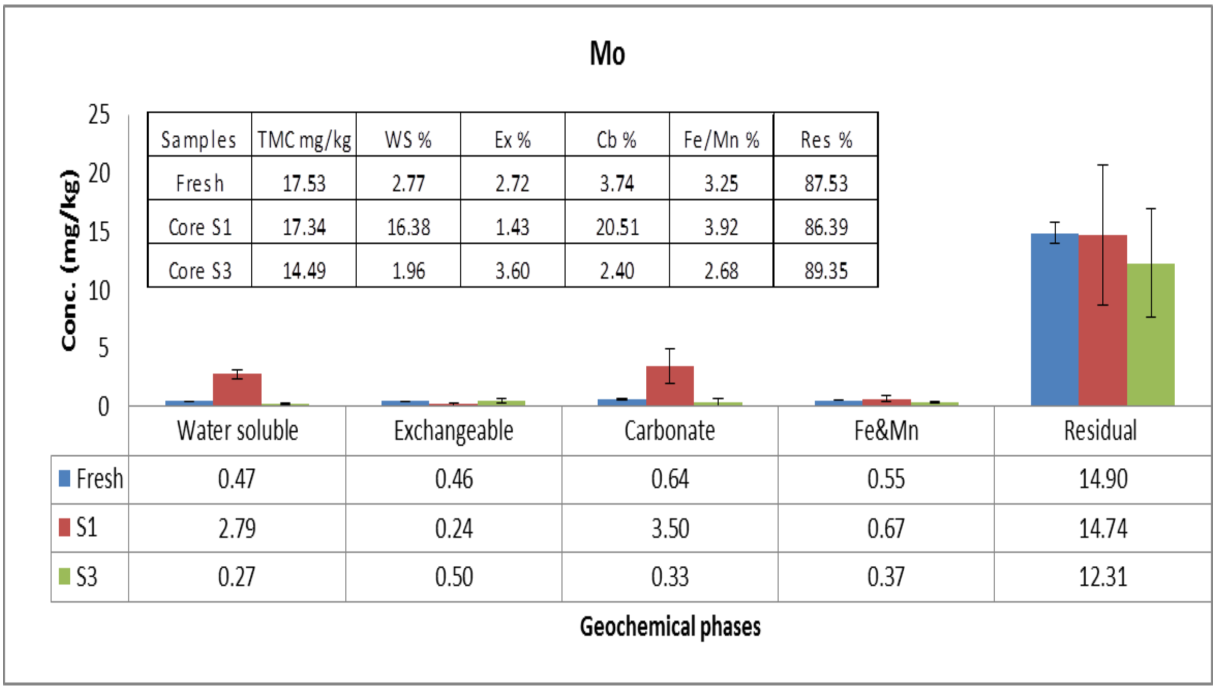
Figure 5.3.14: Distribution patterns of Ni in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations (n) for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

From Figure 5.3.14 it is observed that Ni as in the case of Zn in section 5.3.13 had significant proportions of the total Ni extracted from the water soluble fraction, exchangeable fraction, carbonate fraction and Fe and Mn fraction with the bulk of the extracted Ni reported in the residual fraction. The concentrations of Ni extracted in the residual fraction were 18.19 mg/kg (84.18 %) from the fresh fly ash; 17.74 mg/kg (72.16 %) in core S1 and 23.13 mg/kg (90.65 %) in core S3. In the water soluble fraction the concentration of Ni extracted was 0.34 mg/kg (1.57 %) from the fresh fly ash. The drilled ash core S1 had the highest mean concentration of Ni extracted from the two weathered drilled cores with a value of 1.49 mg/kg (6.04 %) while core S3 had a value of 0.44 mg/kg (1.72 %). The concentration of Ni extracted from the exchangeable fraction was 0.83 mg/kg (3.84 %) from the fresh fly ash while the mean concentration of Ni extracted from the two drilled cores were 1.87 mg/kg (7.59 %) and 0.33 mg/kg (1.27 %) for core S1 and S3 respectively. In the carbonate fraction the concentrations of Ni extracted were 1.27 mg/kg (5.90 %,) from the fresh fly ash; 2.08 mg/kg (8.47 %) from core S1 and 0.86 mg/kg (3.36 %) from core S3. A larger amount of Ni was released from the fresh fly ash and drilled ash core S1 and S3 in the carbonate fraction compared to the water soluble fraction and the exchangeable fraction. In the Fe and Mn fraction the concentration of Ni released in the fresh fly ash was 0.97 mg/kg (4.51 %) while the mean concentrations of Ni extracted for the two drilled cores were 1.41 mg/kg (5.74 %) for S1 and 0.76 mg/kg (3.00 %) for S3.

As in the case of Zn the amount of Ni that was extracted was predominant in the residual fraction. But the amount released in the water soluble fraction, exchangeable fraction and carbonate fraction were significant which also show that Ni in the fly ash samples is associated with mineral phases that may be easily dissolved and leached out of the dump under normal environmental conditions.

5.3.15 Molybdenum

Figure 5.3.15 and appendix 7 to 16 presents proportions of the total Mo extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn and residual fractions.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	17.53	2.77	2.72	3.74	3.25	87.53
Core S1	17.34	16.38	1.43	20.51	3.92	86.39
Core S3	14.49	1.96	3.60	2.40	2.68	89.35

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	0.47	0.46	0.64	0.55	14.90
🟥 S1	2.79	0.24	3.50	0.67	14.74
🟩 S3	0.27	0.50	0.33	0.37	12.31

Figure 5.3.15: Distribution patterns of Mo in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

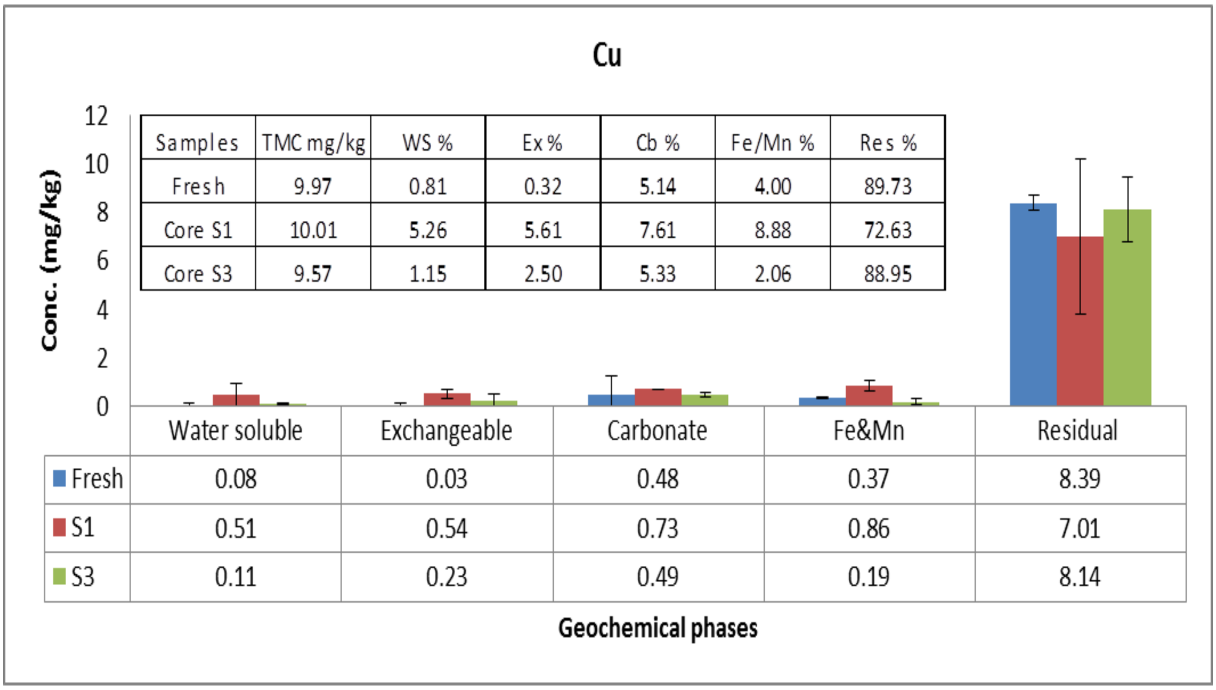
The trend of the extraction of Mo observed in figure 5.3.15 shows that the residual fraction, the carbonate fraction and the water soluble fraction had the largest proportions of the total Mo extracted in the fresh Secunda fly ash and drilled ash cores S1 and S3. In the residual fraction the concentration of Mo in the fresh fly ash was 14.90 mg/kg (87.53 %). The mean concentrations of Mo contained in the two drilled ash cores were 14.74 mg/kg (86.39 %) for core S1 and 12.31 mg/kg (89.35 %) for core S3. The concentration of Mo extracted in the Fe and Mn fraction was 0.55 mg/kg (3.25 %) in the fresh fly ash while the two drilled ash core were 0.67 mg/kg (3.92 %) and 0.19 mg/kg (2.68 %) from core S1 and S3 respectively It has been reported that Mo release can be controlled by Fe and Al in solution, which reduces Mo mobility substantially at acidic conditions as metal molybdates (Comans et al., 2000, Kukier et al., 2003).

The concentrations of Mo extracted water soluble fraction were 0.47 mg/kg (2.77 %) in the fresh ash; 0.38 mg/kg (16.38 %) in core S1 and 0.27 mg/kg (1.96 %) in core S3. The difference in the amounts of Mo released in the two drilled ash cores S1 and S3 show the inhomogeneity of the ash dump. The extraction of Mo in the exchangeable fraction released 0.46 mg/kg (2.72 %) in the fresh fly ash while the mean concentrations of Mo extracted for the two cores were 0.24 mg/kg (1.43 %) in S1 and 0.23 mg/kg (3.60 %) in S3. The significant concentration of Mo released in the water soluble fraction and exchangeable fraction may be attributed to Mo been highly soluble and mobile under alkaline conditions and can precipitate as MoO32- at high pH (Jankowski et al., 2006). It may also have resulted from the dissolution of the Si and Al matrix due to weathering.

In the carbonate fraction the concentration of Mo extracted in the fresh fly ash was 0.64 mg/kg (3.73 %) and the mean concentrations of Mo extracted for the two drilled cores were 3.50 mg/kg (6.04 %) for S1 and 0.49 mg/kg (3.73 %) for S3. Again the difference in the amounts of Mo released from core S1 and S3 indicates the inhomogeneity of the ash dump while the large amount of Mo released in the carbonate fraction may be due to the association of Mo with species in the carbonate phase. According to Fatoba, O., (2008), CaMoO4 was predicted by PHREEQC as one of the mineral phases that would precipitate and exert control on the release of Mo and Cr in the solution of the fly ashes.

5.3.16 Copper

The proportions of the total Mn extracted from the Secunda fresh fly ash and drilled core samples (cores S1 and S3) in the water soluble, exchangeable, carbonate, Fe and Mn, and residual fractions are presented in Figure 5.3.16 and appendix 7 to 16.



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	9.97	0.81	0.32	5.14	4.00	89.73
Core S1	10.01	5.26	5.61	7.61	8.88	72.63
Core S3	9.57	1.15	2.50	5.33	2.06	88.95

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
■ Fresh	0.08	0.03	0.48	0.37	8.39
■ S1	0.51	0.54	0.73	0.86	7.01
■ S3	0.11	0.23	0.49	0.19	8.14

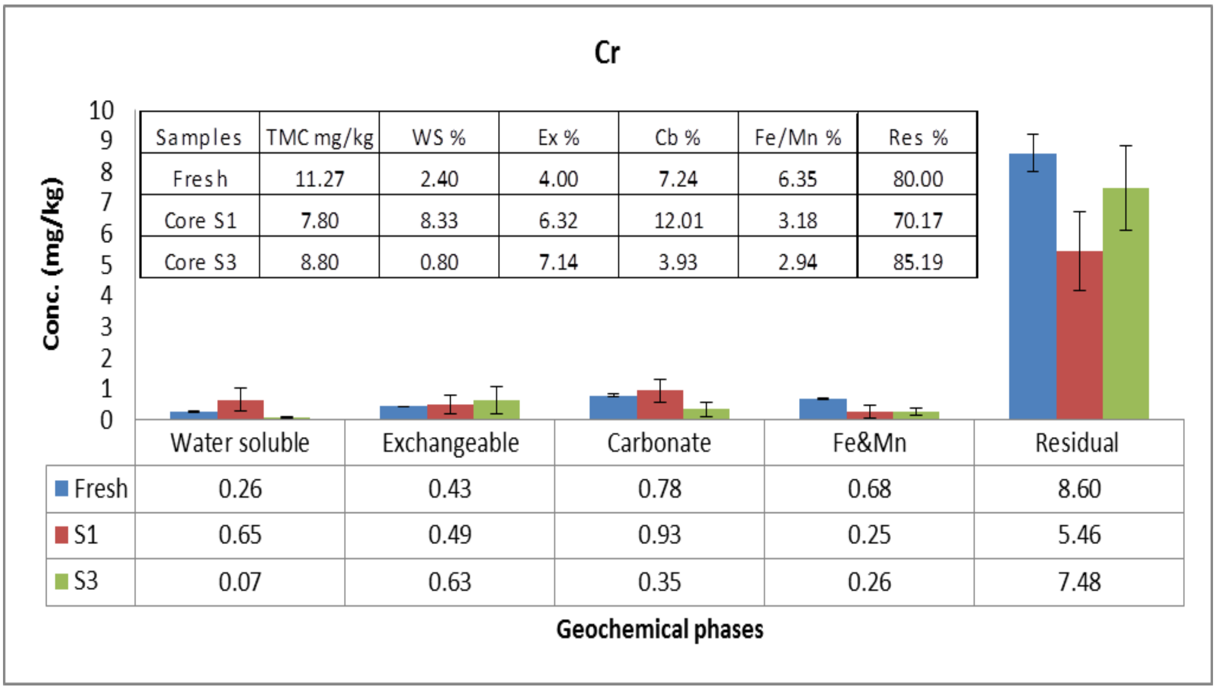
Figure 5.3.16: Distribution patterns of Cu in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

From Figure 5.3.16 it can be seen that Cu as in the case of Zn and Ni in sections 5.3.13 and5.3.14 had significant proportions of the total Cu extracted from the water soluble fraction, exchangeable fraction, carbonate fraction and Fe and Mn fraction with the bulk contained in the residual fraction. In the residual fraction the concentration of Cu in the fresh fly ash was 8.39 mg/kg (89.73 %) while the mean concentrations of Cu contained in the two drilled cores were 7.01 mg/kg (72.63 %) for core S1 and 8.14 mg/kg (88.95 %) for core S3. The concentrations of Cu extracted in Fe and Mn faction were 0.37 mg/kg (4%) in the fresh fly ash; 0.86 mg/kg (8.88 %) in core S1 and 0.19 mg/kg (2.06 %) in core S3. In the water soluble fraction the concentrations of Cu extracted from the fresh fly ash and drilled ash cores S1 and S3 were 0.08 mg/kg (0.81 %); 0.51 mg/kg (5.26 %) and 0.11 mg/kg (1.15 %) respectively. The concentration of Cu extracted in the exchangeable fraction from the fresh fly ash was 0.03 mg/kg (0.34 %) and the extracted mean concentrations from drilled ash cores S1 and S3 were 0.54 mg/kg (5.61 %) and 0.23 mg/kg (2.50 %) respectively. In the carbonate fraction the concentration of Cu released in the fresh fly ash was 0.37 mg/kg (4.00 %) and the mean concentrations of Cu extracted from the two drilled cores were 0.86 mg/kg (8.88 %) for S1 and 0.26 mg/kg (2.06 %) for S3. The high concentration of Cu released shows its association with the carbonate fraction. According to Jegadeesan et al., (2008) the bulk of labile Cu in fly ash was associated with the carbonate fraction.

This extraction study has shown that the amount of Cu released in the water soluble, exchangeable and carbonate fractions showed that the forms in which these species exist in the Secunda fly ash samples are easily soluble under normal environmental conditions. The high concentration of Cu in these fractions may have resulted from the interaction of the co-disposed brine with the fly ash.

5.3.17 Chromium

Figure 5.3.3 and appendix 7 to 16 presents the proportions of the total Ca, extracted in the five geochemical phases from the Secunda fresh fly ash and drilled core samples (cores S1 and S3).



Samples	TMC mg/kg	WS %	Ex %	Cb %	Fe/Mn %	Res %
Fresh	11.27	2.40	4.00	7.24	6.35	80.00
Core S1	7.80	8.33	6.32	12.01	3.18	70.17
Core S3	8.80	0.80	7.14	3.93	2.94	85.19

	Water soluble	Exchangeable	Carbonate	Fe&Mn	Residual
🟦 Fresh	0.26	0.43	0.78	0.68	8.60
🟥 S1	0.65	0.49	0.93	0.25	5.46
🟩 S3	0.07	0.63	0.35	0.26	7.48

Figure 5.3.17 Figure 5.3.17: Distribution patterns of Cr in the five geochemical phases of the fresh fly ash and weathered drilled core S1 and S3 [number of determinations for fresh ash, S1 and S3 are 3, 30 and 44 respectively] TMC = total metal content, WS = water soluble fraction, Ex = exchangeable fraction, Cb = carbonate fraction, Fe/Mn = Fe & Mn and Res = residual fraction.

It is observed from Figure 5.3.17 that the bulk proportion of the total Cr extracted are contained in the residual fraction though the water soluble fraction, exchangeable fraction, carbonate fraction and Fe and Mn fraction also had significant amounts of Cr released. In the residual fraction the concentration of Cr in the fresh fly ash was 8.60 mg/kg (80.00 %,) and the mean concentrations of Cr contained in the two drilled cores were 5.46 mg/kg (70.17 %) for core S1 and 7.48 mg/kg (85.19 %) for core S3. The mean values of the total concentration of Cr in the fresh and weathered fly ash that were extracted in the water soluble fraction were 0.26 mg/kg (2.40 %) in the fresh fly ash; 0.65 mg/kg (8.33%) in core S1 and 0.07 mg/kg in (0.80 %) core S3. In the exchangeable fraction the concentration of Cr released in the fresh fly ash was 0.43 mg/kg (4.00 %) and the extracted mean concentrations in the two drilled cores were 0.49 mg/kg (6.32 %) and 0.50 mg/kg (7.14 %) for S1 and S3 respectively. In the carbonate fraction the concentration of Cr extracted in the fresh fly ash was 0.78 mg/kg (7.24 %). The mean concentrations of Cr extracted from the two drilled cores were 0.93 mg/kg

(12.01 %) for S1 and 0.33 mg/kg (3.93 %) for S3. In the Fe and Mn fraction the concentration of Cr released in the fresh fly ash was 0.68 mg/kg (6.35 %) and the mean concentrations of Cr extracted from the two drilled cores were 0.25 mg/kg (3.18 %) for S1 and 0.37 mg/kg (2.94 %) for S3.

The high concentration of Cr that was released in the carbonate fraction as in the case of Mo in section 5.3.15 may indicate that these elements exist in association with the carbonate phase. As explained in the case of Mo, CaMoO4, and CaCrO4, are predicted by PHREEQC as some of the mineral phases that would precipitate and exert control on the release of Mo and Cr in the solution of the fly ashes (Fatoba, O., 2008). This may be the reason for the observed high release of Cr and Mo in the carbonate fraction. Also fairly high concentrations of Cr were extracted in the water soluble, exchangeable and carbonate fractions hence Cr and Mo are expected to leach considerably from the Secunda fly ash dump.

5.4 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 are summed up and compared with the total concentration of that particular element (Tessier et al., 1979). In the two drilled cores S1 and S3, the variability between the sums of the individual fractions versus the total metal content obtained from total acid digestion test 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 smaller concentration ranges Tables 5.1 and 5.2 shows the sum of the mean values of each major, minor and trace elements leached out from the four extraction steps and the residual and total metal contents for Secunda fresh fly ash vs. drilled core samples S1 and S3 respectively. Tables 5.1 and 5.2 also show the accuracy of the method used as shown in the calculated variance values.

Table 5.1. Mass balance for the major and minor elements in Secunda fresh fly ash vs. weathered fly ash from drilled ash cores S1 and S3

(mg/Kg)	**SUM**			**TMC**			**VARIANCE (%)**		
Majors	**Fresh**	**S1**	**S3**	**Fresh**	**S1**	**S3**	**Fresh**	**S1**	**S3**
Si	222903.57	239554.80	258578.90	230180.67	244662.66	264434.57	3.16	2.09	2.21
Al	132643.63	61716.99	117290.48	134015.28	62811.89	118566.14	1.02	1.74	1.08
Ca	62754.86	74280.56	51680.09	64096.73	75656.13	52210.04	2.09	1.82	1.02
Fe	15738.60	25333.60	28559.59	15874.44	25791.06	29328.18	0.86	1.77	2.62
Na	16306.30	18584.26	11600.17	16543.31	18817.10	11797.49	1.43	1.24	1.67
K	7903.05	9589.65	4409.24	7986.73	9726.40	4473.60	1.05	1.41	1.44
Mg	8570.60	9048.58	10650.49	8757.25	9199.82	10968.79	2.13	1.64	2.90
Sr	3846.26	4089.22	8906.59	3961.97	4153.33	9051.05	2.92	1.54	1.60
Ba	2528.47	2441.61	5706.62	2603.39	2489.94	5788.89	2.88	1.94	1.42
Mn	424.26	580.83	595.37	429.58	592.18	606.41	1.24	1.92	1.82

Table 5.3. Mass balance for the trace elements in Secunda fresh fly ash vs. weathered fly ash from drilled ash core S1 and S3

(mg/Kg)	**SUM**			**TMC**			**VARIANCE (%)**		
Traces	Fresh	S1	S3	Fresh	S1	S3	Fresh	S1	S3
As	59.65	82.04	82.28	60.20	83.13	87.67	0.91	1.31	6.15
Pb	26.63	30.68	29.75	26.99	31.96	30.77	1.30	4.00	3.33
Zn	25.71	32.00	27.40	25.77	32.57	28.57	0.24	1.75	4.09
Ni	21.61	24.59	25.52	22.03	25.35	27.22	1.90	3.00	6.23
Mo	17.02	17.06	13.78	17.53	17.34	14.49	2.89	1.61	4.87
Cu	9.35	9.65	9.15	9.97	10.01	9.57	6.17	3.63	4.44
Cr	10.75	7.78	8.78	11.27	7.80	8.80	4.65	0.24	0.22

SUM = water soluble + exchangeable + carbonate + Fe & Mn + residual, TMC = total metal content

From Table 5.1 and 5.2 it was observed that the extractability of the major elements Si, Al, Ca, Fe, Na, K and Mg; minor elements Sr, Ba and Mn and trace elements As, Pb, Zn, Ni, Mo, Cu and Cr from the five fractions (water soluble fraction, exchangeable fraction, carbonate fraction, Fe & Mn fraction and residual) of the fresh Secunda fly ash and drilled ash core S1 and S3 samples proved to be different. This is as a result of various distribution patterns and partitioning of the major elements between different fractions over time. All the major elements in the fresh Secunda fly ash and two drilled ash cores S1 and S3 had variability of less than 5 % while all the trace elements in the fresh Secunda fly ash and two drilled ash cores S1 and S3 had variability of less than 6.5 %. This affirms the accuracy of the method used. The water soluble, exchangeable and carbonate fractions were singled out as the most vulnerable to leaching at the ash dump; together they were referred to as the labile phase. The amount and percentage of each of the major, minor and trace element that were leached out in the labile phase are presented in Table 5.3 and 5.4.

Table 5.3: Element leachability chart for the major and minor elements in Secunda fresh fly ash vs. weathered fly ash from drilled ash core S1 and S3

mg/kg	SUM			LABILE PHASE		% LEACHED			
Major	**Fresh**	**Core S1**	**Core S3**	**Fresh**	**Core S1**	**Core S3**	**Fresh**	**Core S1**	**Core S3**
Si	222903.57	239554.80	258578.90	13704.12	17296.86	13684.70	6.15	7.22	5.29
Al	132643.63	61716.99	117290.48	10402.19	3588.21	6286.71	7.84	5.81	5.36
Ca	62754.86	63053.42	51680.09	6119.69	4669.12	5286.41	9.75	7.41	10.23
Fe	15738.60	25333.60	28559.59	249.10	216.95	103.20	1.58	0.86	0.36
Na	16306.30	18584.26	11600.17	1840.03	2454.62	1112.61	11.28	13.21	9.59
K	7903.05	9589.65	4409.24	1016.30	1113.61	503.28	12.86	11.61	11.41
Mg	8570.60	9048.58	10650.49	473.60	563.22	623.70	5.53	6.22	5.86
Sr	3846.26	4089.22	8906.59	216.05	219.91	940.98	5.62	5.38	10.56
Ba	2528.47	2441.61	5706.62	176.86	143.37	678.46	6.99	5.87	11.89
Mn	424.26	580.83	595.37	18.61	19.27	9.36	4.39	3.32	1.57

Table 5.4. Element leachability chart for the trace elements in Secunda fresh fly ash vs. weathered fly ash from drilled core S1 and S3

mg/kg	SUM			LABILE PHASE			% LEACHED		
Traces	**Fresh**	**Core S1**	**Core S3**	**Fresh**	**Core S1**	**Core S3**	**Fresh**	**Core S1**	**Core S3**
As	59.65	82.04	82.28	6.34	22.80	6.29	10.63	27.79	7.65
Pb	26.63	30.68	29.75	4.53	7.93	2.50	17.00	25.86	8.40
Zn	25.71	32.00	27.40	2.15	2.77	3.11	8.37	8.65	11.34
Ni	21.61	24.59	25.52	2.44	5.43	1.62	11.31	22.10	6.35
Mo	17.02	17.06	13.78	1.57	1.65	1.10	9.22	9.68	7.97
Cu	9.35	9.65	9.15	0.59	1.78	0.82	6.27	18.48	8.99
Cr	10.75	7.78	8.78	1.47	2.07	1.04	13.65	26.65	11.87

SUM = water soluble + exchangeable + carbonate + Fe & Mn + residual, TMC = total metal content, Labile phase = water soluble + exchangeable + carbonate.

The entire major, minor and trace elements analysed in the fresh Secunda fly ash and weathered drilled cores S1 and S3 showed the potential to leach as shown in tables 5.3 and 5.4. The sequential extraction procedures reported (section 5.3) that the bulk amount of the major and trace elements were contained in the residual fraction. The species in the residual fraction are locked up in the aluminosilicate matrix of fly ash and are only released upon the dissolution of the fly ash matrix. From Table 5.3 it can be seen that significant amounts of Si, Al, Ca, Na, K, Mg, Sr and Ba were leached out in the labile phase. Si had 7.22 % and 5.29 % leached out of the Secunda drilled ash cores S1 and S3 respectively while 5.81 % and 5.36 % of Al were respectively leached out of Secunda drilled ash core S1 and S3. This large amount of Si and Al leached out of the labile phase indicates the dissolution of the aluminosilicate matrix of the fly ash which may have a negative impact on the environment due to the release of other toxic species that are contained in the matrix (Choi et al., 2002). Also Na and K had the highest amounts leached out in the labile phase in the fresh Secunda fly ash and drilled ash core S1 and S3. Na leached out was 13.21 % and 9.59 % for core S1 and S3 respectively while the fresh fly ash leached out 11.28 % of Na. For K, core S1 and S3 leached out 11.61 % and 11.41 % respectively while the fresh fly ash leached out 12.86 % of K. This highlights the risk of these elements leaching out of the ash dump considering the effect of infiltrating rain water over time at the ash dump. It also points to the unsustainability of the dam as a salt sink.

Tables 5.4 show the mean values of the amount and the percentage of each trace element leached out in the labile phase fraction. Core S1 reported significant leaching of the trace elements in the labile phase while cores S3 had lower concentrations of elements leached out. In core S1, the proportions leached out for As, Pb, Zn, Ni, Mo, Cu and Cr were 18.76 %, 27.79 %, 25.86 %, 8.65 %, 22.10%, 38.33 %, 18.48 % and 26.65 % respectively. In core S3, the concentrations leached out for As, Pb, Zn, Ni, Mo, Cu and Cr were 7.65 %, 8.40 %, 11.34 %, 6.35 %, 7.97 %, 8.99 % and 11.87 % respectively. In the fresh fly ash sample, the concentrations leached out for As, Pb, Zn, Ni, Mo, Cu and Cr were 10.63 %, 17.00 %, 8.37 %, 11.31 %, 9.22 %, 6.27 % and 13.65 % respectively. XRF analysis in section 4.4.1 shows that the trace metals (As, Pb and Ni) were enriched in the Secunda drilled ash cores S1 and S3 when compared to the Secunda fresh fly ash. The enrichment of these elements is an indication that they were removed from the brine solution during the interaction of the co-disposed with the fly ash. The large amount of As, Pb, Zn, Ni, Mo, Cu and Cr leached out in the labile phase is an indication that these species were either co-precipitated or adsorbed on the surfaces of species like Al or Fe hydroxides which may have inhibited their solubility in the labile phase and not to be easily leached to the environment. The presence of Fe and Mn as Fe and Mn oxy-hydroxides has been observed to control the release of heavy metal such as Ni, Pb and Zn as these species adsorbed to the surface of the oxyhydroxides (Lee & Saunders, 2003; Cho et al. 2005; Steenari, 1999).The high amounts of these trace elements leached out of the labile may also have resulted from the dissolution of the aluminosilicate matrix and are of major concern in terms of toxicity.

5.5 Summary from sequential extraction scheme of weathered fine coal ash from cores S1 and S3 from Sasol Synfuels-Secunda ash dam

The sequential extraction results show that the major and minor elements Si, Al, Ca, Fe, Na, K, Mg, Sr, Ba, and Mn and trace elements As, Pb, Zn, Ni, Mo, Cu, and Cr are present in Secunda fresh and weathered fly ash and are partitioned between the water soluble, exchangeable, carbonate, iron and manganese, and residual fractions of the coal fly ash at different stages of weathering. The proportion of each elements total that could be extracted varied significantly in the weathered drilled cores (S1 and S3) and in the extraction fractions.

Generally, all the elements had the highest concentration in the residual fraction. It was evident that the labile phases (water soluble, exchangeable and carbonate fractions) had fairly high proportions of the total Ca, Mg, Ba, Sr, Na and K for the Secunda drilled core (S1 and S3) and fresh fly samples this indicates that the species can leach easily and will pose a danger to the environment. This has implications for the long-term durability of mineral phases thus drawing into question the sustainability of the ash dump and highlighting its potential for negatively impacting the environment over time.

The assessment of accuracy of the sequential extraction procedure shows that the extractability of the major elements from the five fractions of the three fly ash samples proved to be different, so various distribution patterns and partitioning of the major elements between different fractions over time have been observed. Sodium and potassium had the highest concentrations leached out in the labile phase in all the three cores which highlights the risk of these elements leaching down the ash dam considering the effect of infiltrating rain water over time at the ash dam and it’s unsustainability as a salt sink. In general, the study found that the major elements Si, Al and Ca; minor elements, Na, K, Mg, Sr and Ba and trace elements As, Pb, Zn, Ni, Mo, Cu and Cr in Sasol Secunda fly ash are capable of being lost due to leaching. The conclusions, findings and recommendation obtained from this study will be presented and discussed in chapter six.

Chapter Six

Conclusions and Recommendations

6 Introduction

This chapter gives a summary of the discussions, significant findings and conclusions of the results presented in the previous chapters. Recommendations for further research on some aspects are outlined.

6.1 Overview

The aim of the study was to determine the effects of weathering on the chemical composition, morphological properties and mineralogical composition of coal fly ash that was co-disposed with brine after some years of weathering. The purpose of co-disposing this ash with brine was originally aimed at using the ash as a sustainable salt sink. From the findings of this study some conclusions about the long term effect of weathering at the dump site were drawn to confirm if the ash dam could serve as a sustainable salt sink.

6.2 Site profile

The Secunda fly ash dam was created in 1989 and dumping stopped in 2009. The oldest layer at the bottom is 21 years old as at the time of study (2010) and the youngest at the top being 1 year old. The Secunda fly ash is made up of 87% fly ash from the combustion of pulverized coal to produce steam and electric power and 13% fine ash from the gasification process. The particle size of the fine ash being dumped ranges between $20 \leq 50$ µm. The ash was pumped to the ash dam as slurry of 5:1 water/ash ratio using the highly saline stream that was generated from the water treatment processes in the Secunda plant. Samples were taken along the depth of two drilled cores (S1 and S3) from the weathered ash dam and analysed in conjunction with the fresh (un-weathered) fly ash taken from the hoppers for comparative analysis.

6.3 pH, EC, TDS and moisture profile

The Sasol Secunda fresh fly ash and weathered drilled core samples exhibited alkaline pH due to the lime content of the ash. The significant decrease in pH of the weathered drilled cores (9.33 – 11.32 for S1 and 9.32 – 11.287 forS3) in comparison to the fresh fly ash sample (12.38) was due to the formation of calcite in the weathered fly ash as result of infiltration of CO_2 over time in the fly ash dump. The changes in pH values can also be attributed to the dissolution and flushing out from the dump basic alkaline oxides like CaO and MgO.

The EC (Electrical Conductivity) and TDS (total dissolved solid) values essentially follow the same trend. The EC value of the fresh Secunda fly ash sample was observed to be 4.92 mS/cm. For the drilled Secunda ash core S1, the EC values were between 0.83 mS/cm at surface and 22.5 m, and 1.28 mS/cm at 7.5 m while for the drilled Secunda ash core S3, the EC values range from 0.32 - 1.08 mS/cm. A TDS value of 2.68 ppt (parts per thousand) was observed for the fresh Secunda fly ash sample. The drilled Secunda ash core S1 had TDS values ranging from 0.49 ppt 0.76 ppt and for drilled Secunda ash core S3 the TDS values were between 0.19 – 0.68 ppt. The pH EC and TDS of the drilled cores show a large decrease in value when compared to the values of the fresh Secunda fresh fly ash. This shows the extent of leaching and poor salt sink capacity of the fly ash dam because the EC and TDS values would have been considerably higher in the drilled cores if the fly ash dam was holding salts. Usually ionic species from salts are responsible for high EC and TDS readings.

Though the core S1 and S3 fly ash samples from the surface of the dump appeared dry, moisture content analysis showed that there is considerable water remaining within the fly ash dump. The fresh ash MC was 1.8 % while weathered drilled core S1 ranged from 41.4 – 73.2 % and core S3 ranged from 21.7 – 76.4 % with higher moisture values at lower depths of the ash embankment. The wet method of disposal employed at the dump accounts for the high moisture content observed in the Secunda weathered fly ash drilled core samples when compared to the fresh fly ash samples.

6.4 Morphological analysis

The morphology of the fresh fly ash and weathered drilled core samples showed spherical rounded particles and some agglomerations. The smooth outer surfaces of the fresh ash particles are mainly aluminosilicate structure. The surfaces of the particles from the drilled core samples appeared to be etched, corroded and encrusted due to the formation of new mineral phases in the weathered fly ash as shown in the XRD results. Qualitatively, the elements in the fly ashes were predominantly Si, Al and Ca in all the samples, while Mg and S were also detected in all the samples but in lower quantities as determined by EDS.

6.5 Chemical analysis

Based on the concentrations of the elements determined by the XRF analysis for the fresh fly ash and drilled core samples, the major oxides identified were SiO_2, Al_2O_3, CaO, Fe_2O_3, MgO, Na_2O and TiO_2, minor elements were K, P, S and Mn and trace elements in the samples were As, Ba, Ce, Co, Cu, Nb, Ni, Pb, Rb, Sr, U, V, Y, Zr and Th. Sr (4465 ppm and 4864 ppm in core S1 and S3 respectively), Ba (2682 ppm and 3014 ppm in core S1 and S3 respectively) and Th (2075 ppm and 2283 ppm in core S1 and S3 respectively) recorded the highest levels among the trace elements in the ash dump cores while Rb (16 ppm and 25 ppm in core S1 and S3 respectively) and Ni (29 and 32 in core S1 and S3 respectively) recorded the lowest levels. The sum of the SiO_2, Al_2O_3, and Fe_2O_3 content present in the Secunda weathered drilled fly ash and fresh ash samples were > 70 % in each of the respective sample, making the Secunda fly ash samples class F fly ash according to ASTM C 618, 1993. The XRF analysis further indicated how the species were enriched and (or) depleted along the depths of the drilled core samples when compared to the fresh ash samples showing considerable mobility and inconsistency/ inhomogeneity of the ash dump. From the enrichment and depletion table no significant enrichment or accumulation of any particular element was observed down the two drilled Secunda ash cores. This shows that the dump is not holding or encapsulating any particular element to any significant extent. There was no significant enrichment of Na in the drilled Secunda ash cores S1 and S3 only (0.26 % and 0.55 % in drilled ash cores S1 and S3 respectively) which highlights the unsustainability of the Secunda ash dump as a salt sink.

6.6 Mineralogical analysis

The XRD analysis revealed the primary minerals present in the weathered drilled core samples to be quartz and mullite. Lime and calcite were also identified but as minor peaks. The ingress of CO_2 in the ash over time upon disposal led to the formation of calcite in the weathered drilled core samples. Halite (NaCl), bassanite ($CaSO_4.2H_2O$), nitratine ($NaNO_3$), hydrophitte ($CaCl_2$), microline and ($KAlSi_3O_8$) are considered as transient mineral that were identified in low quantities in the weathered drilled core samples but not in the Secunda fresh fly ash sample. These transient mineral phases may have formed from the interaction of brine with the fly ash. This is based on the chemical composition of these mineral phases which can be linked to the chemical composition of the co-disposed brine. Since halite, bassanite and nitratine could be formed at high temperatures during evolution in complex aqueous systems, these transient mineral may also have formed at the point of analysis due to the drying process used. EC and TDS values showed high salt content in the pore-water of Secunda fly ash samples. The XRD analysis of the Secunda fresh fly ash sample showed quartz and mullite as the major crystalline mineral phases. Lime was also identified but was present in low amounts.

6.7 Total metal content

The total metal content analysis showed the total concentration of the elements Si, Al, Ca, Fe, Na, Mg, Sr, Ba, Mn, As, Pb, Zn, Ni, Mo, Cu and Cr that were analysed in the Secunda fly ash samples. The concentrations of the elements (Si, Al, Ca, Fe, Na, Mg, Sr, Ba and Mn) accounted for 99.96 % of the total elemental components analysed in the fresh Secunda fly ash; 99.95 % and 99.96 % in drilled Secunda ash cores S1 and S3 respectively. The concentrations of the trace elements (As, Pb, Zn, Ni, Mo, Cu and Cr), accounted for 0.04 % of the total elemental components analysed in the fresh Secunda fly ash and drilled ash core S3 and 0.05 % of drilled Secunda ash core S1.

6.8 Anionic Species

The study also revealed that there was significant enrichment of sulphate anions which were associated with the water soluble phases as shown in the pore water analysis though negligible in the chloride anions in the Secunda weathered fly ash from drilled ash core (S1 and S3) compared to the Secunda fresh fly ash. This observed enrichment of sulphates and chlorides anions may have resulted from the co-disposal of the fly ash with brine that is rich in sulphates and chlorides.

6.9 Sequential extraction

From the results of the concentration profile of the investigated major and trace chemical species in the Secunda weathered drilled cores (S1 and S3) and fresh fly ash samples using the sequential extraction scheme. The study showed that the mobility of major and trace elements in fly ashes depended on the pH and the elements concentration. The major elements (Al, Si, Ca, Mg, Ba, Sr, Fe and Mn) were found to be associated with the carbonate, iron and manganese and residual fraction phases. Furthermore the solubility of fly ash matrix major components such as Al, and Si are pH dependent as there is more release of these elements as the pH decreases. Ca Na and K were also found to be associated with the water soluble and exchangeable fractions showing their presence in readily soluble forms. It was also observed that the trace elements As, Pb, Cr, Mo, Cu, Ni and Zn do not show permanent association with particular mineral phases as a continuous partitioning between different mineral phases was observed in the weathered drilled core. It is also noteworthy that the labile fractions (water soluble, exchangeable and carbonate) of the major and trace elements in Secunda fly ash dam were high. Thus highlighting the inhomogeneity of the ash dam and the potential of the dump to negatively impact the surface and groundwater in the ash dump vicinity over time

Furthermore there was no indication of Na retention in the ash dam. Although brine enriched the fly ash with Na, there was no accumulation of Na along the cores at the ash dam despite the continuous addition of brine over the 20 year period. It was noted that Sasol Secunda fly ash seems to reach a saturation point of holding Na at about 0.26 % above which the fly ash holds no more Na.

6.10 Significance of the study

The study showed that chemical weathering as a result of ingress of CO_2, atmospheric O_2, infiltrating rainwater and co-disposed brine resulted in changes in the physical, chemical and mineralogical properties of the weathered Secunda fly ash compared to fresh Secunda fly ash. This study also showed how the major (Si, Al, Ca and Fe), minor (Na, K, Mg, Sr, Ba and Mn) and trace (As, Pb, Zn, Ni, Mo, Cu and Cr) elements are distributed in the five geochemical phases of the Secunda fly ash samples. Furthermore it was observed from the study that elements were leached out of the Secunda fly ashes at both alkaline and acidic pH and their mobility through the dump is correlated with their association with different mineralogical phases at certain depths within the dump. But over time, with high moisture and a low pH, the mineralogical association of all the elements in the ash varied considerably showing their high mobility. Hence the Secunda fly ash dump is not a sustainable salt sink because there is continuous mobilization and migration of species present in the ash and co-disposed brine through the dump.

6.11 Recommendations

This study has shown that the co-disposal of brine and coal fly ash is not sustainable. It is therefore recommended that alternative methods of disposing brine generated by the Sasol Secunda syngas plant should be adopted. If brine is to be co-disposed with fly ash the excessive flow of brine and rainwater through the ash dump should be circumvented.

Also the sequential extraction procedures used in this study proved valid, replicable and can therefore be applied in similar research studies. It also proved to be adequate for the defined purpose of understanding mineralogical association and can therefore be applied in similar research studies. The limitation of the present study is that the presence of sulphur as various metal sulphides would be expected in fly ashes.

Therefore, it seems to be necessary to add more extraction steps with properly selected extractants, including more aggressive reagents.

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APPENDIX 1

The chemical composition of the major and trace elements of Secunda core S1 as obtained from XRF analysis

	Fresh ash	0m	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	16.5m	18m	19m	21m	22.5m
Major/wt%																
SiO_2	50.91	47.05	49.66	47.96	47.86	46.74	46.08	46.17	42.57	44.87	43.42	43.98	34.57	41.10	37.02	32.87
Al_2O3	25.49	24.30	25.36	25.41	25.57	25.01	24.66	24.87	22.53	23.43	22.71	23.56	18.80	21.83	20.19	17.58
CaO	8.95	6.15	6.82	7.71	8.28	8.63	8.79	8.58	8.53	8.67	9.87	9.14	7.25	7.55	7.37	6.85
Fe_2O_3	2.27	4.50	3.73	2.32	2.88	2.99	3.95	3.24	2.97	4.31	6.60	4.31	3.61	3.03	3.39	3.27
Na_2O	2.21	2.42	2.32	2.51	2.53	2.70	2.57	2.65	2.48	2.60	2.51	2.48	2.33	2.44	2.31	2.18
MgO	1.87	2.64	2.32	2.62	2.66	2.88	2.64	2.64	2.39	2.66	2.59	2.55	1.83	2.28	2.14	1.78
TiO_2	1.78	1.74	1.54	1.82	1.82	1.87	1.75	1.77	1.75	1.77	1.66	1.77	1.53	1.68	1.53	1.44
K_2O	0.95	0.90	0.75	1.07	0.96	1.00	0.94	0.98	0.97	0.95	0.99	1.06	0.96	1.08	0.96	0.92
P_2O_5	0.71	0.54	0.52	0.82	0.76	0.77	0.73	0.74	0.68	0.69	0.66	0.72	0.57	0.69	0.63	0.55
MnO	0.05	0.06	0.05	0.05	0.07	0.07	0.07	0.07	0.07	0.08	0.08	0.07	0.06	0.06	0.06	0.06
SO_3	0.03	0.05	0.08	0.11	0.11	0.12	0.12	0.11	0.11	0.12	0.12	0.11	0.11	0.10	0.11	0.11
LOI	4.78	9.62	6.87	7.60	6.47	7.19	7.67	8.16	14.91	9.81	8.74	10.18	28.62	18.17	24.62	33.15
Sum	100.00	99.96	100.03	100.00	99.98	99.97	99.98	99.97	99.95	99.96	99.95	99.94	100.26	100.01	100.32	100.76
Trace/ppm																
Sr	4160	3352	3555	4755	4546	4580	4323	4437	4668	4450	4235	4665	4744	4886	4717	4933
Ba	2749	2089	2118	3059	2850	3009	2593	2659	2770	2700	2560	2710	2685	2880	2792	2754
Th	1922	1527	1625	2224	2122	2140	2007	2066	2178	2070	1952	2180	2220	2298	2201	2314
Zr	664	600	582	678	686	674	672	674	713	693	647	685	675	681	682	665
Ce	177	172	158	175	158	193	146	159	198	194	178	200	243	189	189	211
Y	156	151	153	173	168	173	163	166	172	169	150	166	167	173	169	169
Nb	109	104	104	149	120	140	107	117	143	134	106	114	133	144	137	143
As	61	74	49	66	60	71	65	72	92	76	75	82	158	106	132	185
Co	32	26	35	31	35	38	20	39	29	28	36	31	35	26	32	50
Pb	28	29	42	38	45	48	41	43	38	38	31	33	29	34	34	26
Ni	23	24	27	25	28	29	29	28	28	35	33	30	31	31	31	28
Rb	16	31	32	5	13	5	31	15	5	8	36	21	12	13	4	12
V	15	93	104	91	83	66	69	81	74	69	40	54	70	110	75	70

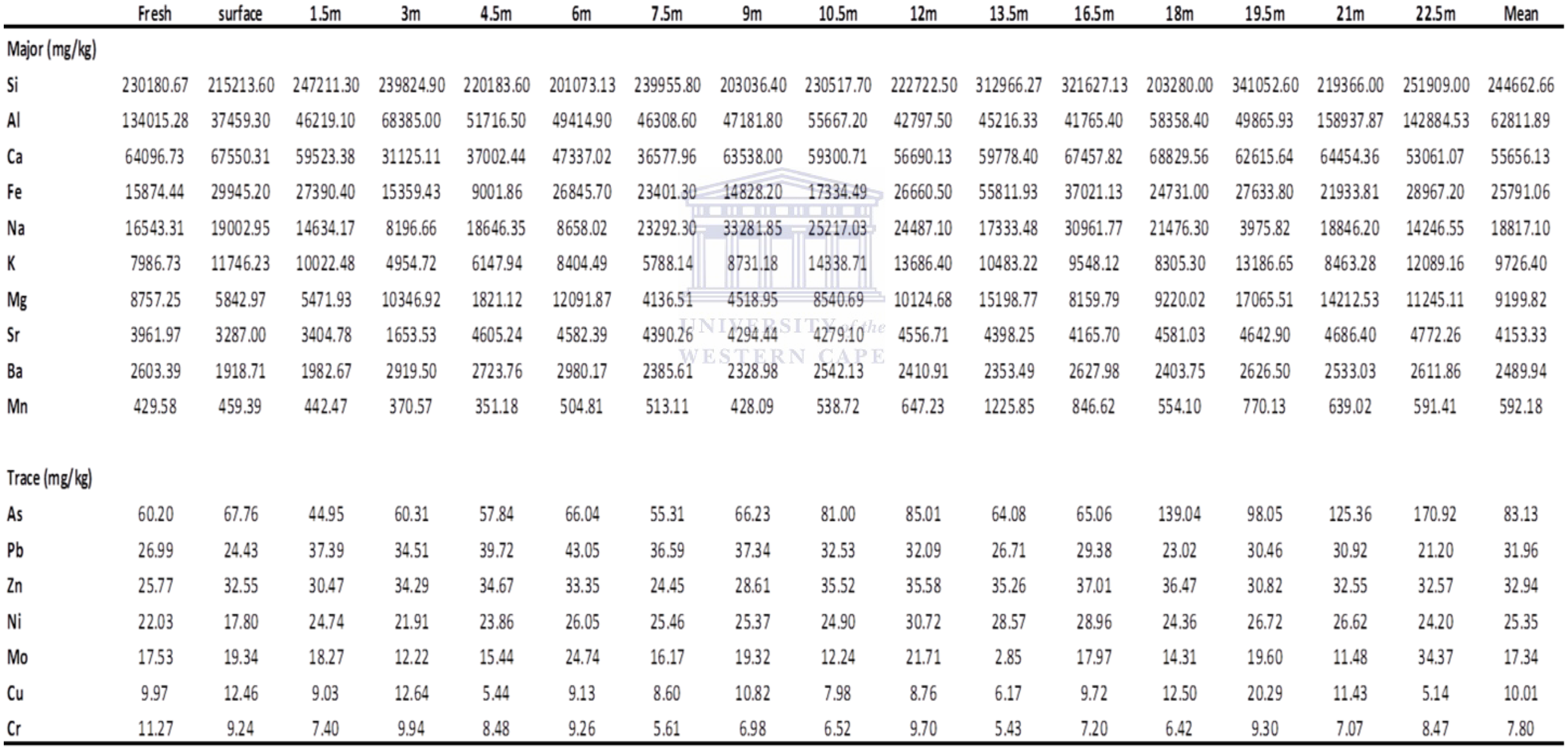
APPENDIX 2

The chemical composition of the major and trace elements of Secunda core S3 as obtained from XRF analysis

	Fresh ash	0m	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5M	27m	28.5m	30m	31.5m
Major / wt%																							
SiO_2	50.91	46.16	47.47	47.52	47.44	45.43	45.08	45.75	47.88	49.65	41.44	45.89	45.64	47.77	47.74	48.12	47.04	46.62	40.65	45.03	44.74	43.53	58.86
Al_2O_3	25.49	23.43	25.70	24.71	25.50	24.43	23.59	20.69	22.08	21.27	21.52	23.59	21.53	22.32	22.91	22.51	25.42	21.21	23.27	21.35	20.08	24.54	11.87
CaO	8.95	8.45	8.10	8.14	7.40	8.89	8.57	9.90	8.93	8.51	9.22	7.75	8.76	8.69	9.34	9.60	8.64	9.98	10.39	9.81	11.24	9.76	6.69
Fe_2O_3	2.27	3.18	2.73	3.12	2.87	3.50	4.99	4.30	3.16	3.39	10.41	5.10	4.21	3.33	3.19	2.94	2.19	2.47	5.50	2.92	2.90	2.63	6.81
Na_2O	2.21	2.36	2.45	2.56	2.57	2.79	2.61	3.00	2.85	2.90	2.53	2.38	2.66	2.88	2.72	2.80	2.57	3.02	2.81	3.13	3.16	2.74	3.17
MgO	1.87	3.31	2.78	2.55	2.60	2.58	2.56	2.77	2.93	3.00	2.57	2.44	2.76	2.90	2.81	2.91	2.74	3.10	2.74	3.19	3.31	2.83	2.91
TiO_2	1.78	1.91	1.83	1.91	1.74	1.90	1.75	2.10	2.04	2.08	1.68	1.74	1.88	1.98	1.97	2.08	1.85	2.11	1.79	2.05	2.12	1.85	1.51
K_2O	0.95	1.14	1.09	1.22	1.25	1.24	1.15	1.29	1.34	1.39	0.98	1.15	1.24	1.27	1.26	1.21	0.98	1.10	0.90	1.00	0.88	0.95	4.41
P_2O_5	0.71	0.83	0.75	0.71	0.74	0.78	0.72	0.81	0.82	0.83	0.67	0.71	0.75	0.84	0.76	0.81	0.80	0.84	0.79	0.89	0.95	0.85	0.36
MnO	0.05	0.07	0.06	0.07	0.06	0.07	0.07	0.08	0.07	0.07	0.10	0.07	0.08	0.07	0.08	0.08	0.07	0.08	0.09	0.08	0.09	0.08	0.12
SO_3	0.03	0.05	0.12	0.09	0.09	0.10	0.12	0.11	0.10	0.10	0.09	0.08	0.09	0.09	0.09	0.09	0.08	0.10	0.10	0.11	0.09	0.10	0.04
LOI	4.78	9.05	6.90	7.33	7.72	8.22	8.76	9.04	7.71	6.73	8.76	9.07	10.32	7.80	7.08	6.78	7.60	9.28	10.90	10.34	10.27	10.11	3.18
Sum	100.00	99.95	99.98	99.94	99.99	99.93	99.96	99.85	99.93	99.94	99.97	99.97	99.91	99.94	99.94	99.93	99.98	99.90	99.93	99.90	99.84	99.95	99.93
Trace/ppm																							
Sr	4160	4769	4801	4570	4494	5025	4388	5463	5257	4789	4874	4686	5018	5209	4870	4832	5007	5595	5742	5636	5590	5465	919
Ba	2749	3141	3110	2808	3077	3174	2809	3177	3218	3096	2657	2703	2985	3241	2920	3105	3058	3320	3108	3319	3476	3138	1674
Th	1922	2237	2253	2141	2103	2369	2028	2591	2486	2252	2249	2179	2354	2457	2279	2264	2355	2657	2718	2674	2649	2587	351
Zr	664	724	709	701	645	703	689	780	744	730	719	692	749	757	751	768	737	806	741	817	833	772	266
Y	156	174	173	164	158	172	162	186	182	174	150	168	176	184	176	178	175	194	188	205	202	186	39
Ce	177	190	160	188	163	175	169	247	211	226	248	217	200	203	199	224	167	214	225	232	218	226	142
Nb	109	146	144	141	139	144	113	158	161	148	114	130	134	157	132	148	157	169	159	164	163	153	27
As	61	95	81	77	61	93	73	104	92	80	112	80	79	84	78	82	77	87	109	86	92	78	153
Co	32	37	24	32	37	33	23	38	27	41	26	51	38	34	32	26	18	35	31	42	36	28	49
Pb	28	33	24	34	42	42	34	45	34	34	24	36	37	34	25	35	33	31	32	41	30	32	47
Ni	23	28	24	29	30	29	30	31	32	34	31	23	29	32	29	30	31	33	39	36	37	32	61
Rb	16	12	ND	23	24	13	18	17	19	30	33	9	25	22	29	11	2	2	ND	ND	ND	ND	135
V	15	48	72	112	74	116	57	90	69	81	53	61	60	122	63	41	85	101	58	70	54	48	30

APPENDIX 3

Analysis of the extractions in the total acid digestion test for the Secunda fresh fly ash and the drilled core samples (S1) as a function of depth



	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	16.5m	18m	19.5m	21m	22.5m	Mean
Major (mg/kg)																	
Si	230180.67	215213.60	247211.30	239824.90	220183.60	201073.13	239955.80	203036.40	230517.70	222722.50	312966.27	321627.13	203280.00	341052.60	219366.00	251909.00	244662.66
Al	134015.28	37459.30	46219.10	68385.00	51716.50	49414.90	46308.60	47181.80	55667.20	42797.50	45216.33	41765.40	58358.40	49865.93	158937.87	142884.53	62811.89
Ca	64096.73	67550.31	59523.38	31125.11	37002.44	47337.02	36577.96	63538.00	59300.71	56690.13	59778.40	67457.82	68829.56	62615.64	64454.36	53061.07	55656.13
Fe	15874.44	29945.20	27390.40	15359.43	9001.86	26845.70	23401.30	14828.20	17334.49	26660.50	55811.93	37021.13	24731.00	27633.80	21933.81	28967.20	25791.06
Na	16543.31	19002.95	14634.17	8196.66	18646.35	8658.02	23292.30	33281.85	25217.03	24487.10	17333.48	30961.77	21476.30	3975.82	18846.20	14246.55	18817.10
K	7986.73	11746.23	10022.48	4954.72	6147.94	8404.49	5788.14	8731.18	14338.71	13686.40	10483.22	9548.12	8305.30	13186.65	8463.28	12089.16	9726.40
Mg	8757.25	5842.97	5471.93	10346.92	1821.12	12091.87	4136.51	4518.95	8540.69	10124.68	15198.77	8159.79	9220.02	17065.51	14212.53	11245.11	9199.82
Sr	3961.97	3287.00	3404.78	1653.53	4605.24	4582.39	4390.26	4294.44	4279.10	4556.71	4398.25	4165.70	4581.03	4642.90	4686.40	4772.26	4153.33
Ba	2603.39	1918.71	1982.67	2919.50	2723.76	2980.17	2385.61	2328.98	2542.13	2410.91	2353.49	2627.98	2403.75	2626.50	2533.03	2611.86	2489.94
Mn	429.58	459.39	442.47	370.57	351.18	504.81	513.11	428.09	538.72	647.23	1225.85	846.62	554.10	770.13	639.02	591.41	592.18
Trace (mg/kg)																	
As	60.20	67.76	44.95	60.31	57.84	66.04	55.31	66.23	81.00	85.01	64.08	65.06	139.04	98.05	125.36	170.92	83.13
Pb	26.99	24.43	37.39	34.51	39.72	43.05	36.59	37.34	32.53	32.09	26.71	29.38	23.02	30.46	30.92	21.20	31.96
Zn	25.77	32.55	30.47	34.29	34.67	33.35	24.45	28.61	35.52	35.58	35.26	37.01	36.47	30.82	32.55	32.57	32.94
Ni	22.03	17.80	24.74	21.91	23.86	26.05	25.46	25.37	24.90	30.72	28.57	28.96	24.36	26.72	26.62	24.20	25.35
Mo	17.53	19.34	18.27	12.22	15.44	24.74	16.17	19.32	12.24	21.71	2.85	17.97	14.31	19.60	11.48	34.37	17.34
Cu	9.97	12.46	9.03	12.64	5.44	9.13	8.60	10.82	7.98	8.76	6.17	9.72	12.50	20.29	11.43	5.14	10.01
Cr	11.27	9.24	7.40	9.94	8.48	9.26	5.61	6.98	6.52	9.70	5.43	7.20	6.42	9.30	7.07	8.47	7.80

APPENDIX 4

Analysis of the extractions in the total acid digestion test for the Secunda fresh fly ash and the drilled core samples (S3) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5m	27m	28.5m	30m	31.5m	Mean
Major(mg/kg)																								
Si	230180.67	251992.00	271694.00	257290.67	121177.90	274564.00	281973.00	275391.00	257203.00	269524.00	226085.00	272750.00	292880.00	270430.00	299296.00	269493.00	222102.00	286468.00	279431.00	261722.00	286287.00	307030.00	282777.00	264434.57
Al	134015.28	102716.80	132763.60	109812.87	78911.47	111929.00	135576.00	129289.13	98467.87	133422.53	91064.93	111019.90	130122.07	98443.40	133107.00	95928.47	239209.33	119444.47	105122.10	102363.22	138337.80	141032.00	70371.10	118566.14
Ca	64096.73	25240.18	40516.67	20789.71	18931.83	88670.60	84104.27	52833.73	47310.93	33112.47	23262.18	29896.07	45229.33	22356.64	103738.53	37087.60	71045.00	75704.27	60354.15	45404.81	108381.53	106826.13	7824.30	52210.04
Fe	15874.44	13729.69	19770.81	15792.07	8709.80	37377.33	65419.53	33390.93	21423.27	19098.28	63018.40	36886.80	35820.87	20474.91	40519.40	23295.33	25289.67	22388.16	36367.51	15786.03	27744.53	30293.47	32623.20	29328.18
Na	16543.31	7138.83	10561.79	7838.52	6425.21	19911.96	18396.96	13688.26	12990.19	12271.18	9340.85	6775.63	8467.22	6332.93	18506.81	9386.60	11792.25	11052.82	8937.25	7433.55	13547.75	10345.62	28402.50	11797.49
Mg	8757.25	13505.77	10991.78	8931.37	5437.47	7197.67	11455.21	7451.89	8092.16	10255.99	3958.28	12996.14	15355.36	10335.53	33502.53	8129.88	11113.50	11751.26	11186.01	7245.37	9654.60	14604.95	8160.57	10968.79
K	7986.73	2296.48	2524.11	2850.47	2508.02	11372.69	7901.19	1620.82	408.46	1189.02	2743.97	2657.36	3602.12	1891.13	15741.62	1709.04	1992.72	2256.12	4344.43	2504.23	7822.75	5016.25	13466.24	4473.60
Sr	3961.97	9315.89	9765.88	8838.86	8724.70	9849.32	8591.39	10755.92	10543.83	9297.53	9546.54	9105.21	9949.01	10285.49	9459.16	9302.22	1054.93	9981.41	10962.15	10802.19	10794.33	10444.88	1752.34	9051.05
Ba	2603.39	6154.55	6182.25	5552.80	6006.61	6223.64	5422.23	6190.09	6341.59	6041.38	4753.69	5197.03	5631.77	5643.57	5624.80	6007.95	5944.44	6467.88	6026.17	6593.85	6595.74	6031.11	2722.45	5788.89
Mn	429.58	455.26	538.34	447.10	203.87	598.80	763.24	538.17	380.49	339.63	456.66	547.45	750.78	500.10	1270.13	785.02	1016.36	743.05	565.51	371.51	732.65	724.03	612.77	606.41
Trace (mg/kg)																								
As	60.20	87.14	77.43	74.69	56.71	86.64	68.75	98.84	88.16	75.63	106.05	73.39	78.45	77.41	73.31	77.63	70.15	81.81	101.13	179.03	81.31	71.53	143.49	87.67
Pb	26.99	28.40	19.44	29.77	38.47	37.99	28.15	39.15	29.11	29.16	19.75	30.18	30.61	30.39	22.84	31.76	29.70	29.07	28.71	38.29	38.35	27.61	40.10	30.77
Zn	25.77	30.83	37.24	33.88	37.19	21.89	29.93	32.36	33.29	31.62	24.51	30.64	26.69	29.98	26.76	27.61	27.64	29.52	26.17	29.36	27.79	10.09	23.55	28.57
Ni	22.03	25.71	20.04	25.23	26.59	24.82	25.72	26.26	27.02	27.03	20.05	29.59	32.29	30.32	20.50	26.86	26.46	26.68	32.40	30.93	30.77	26.82	36.68	27.22
Mo	17.53	20.94	22.71	8.08	20.05	9.56	20.22	21.15	20.57	9.76	16.26	15.10	11.06	6.89	6.12	15.08	13.31	13.04	22.58	10.87	16.75	8.76	9.87	14.49
Cu	9.97	8.72	9.78	10.16	10.04	8.80	11.00	9.70	8.61	9.41	12.00	12.06	13.50	11.21	8.90	7.99	9.02	8.64	7.17	8.61	8.28	9.62	7.41	9.57
Cr	11.27	7.62	8.87	8.09	8.65	9.49	9.95	6.37	9.25	9.57	8.36	7.83	7.37	10.85	9.76	7.87	6.93	7.95	7.71	6.88	12.41	12.00	9.79	8.80

APPENDIX 5

Anions (mg/kg)	Fresh	1.5m	3m	4.5m	6m	7.5m	9m	12m	13.5m	16.5m	18m	19.5m	21m	22.5m
Core S1														
Cl^-	4.05	20.50	21.89	27.22	20.61	7.62	20.31	28.86	20.73	20.11	19.88	34.34	18.73	23.33
SO_4^{2-}	13.64	253.58	208.42	208.62	355.30	59.40	219.23	191.63	229.01	359.87	195.40	285.65	262.46	280.49

APPENDIX 6

Anions (mg/kg)	Fresh	Surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5m	27m	28.5m	30m	31.5m
Core S3																							
Cl^-	4.05	2.56	8.04	8.35	15.44	51.32	24.29	33.03	22.00	7.72	22.04	21.02	29.94	11.72	35.22	20.29	13.98	7.20	18.80	19.70	8.45	11.56	9.02
SO_4^{2-}	13.64	70.08	459.41	108.94	176.80	594.13	325.93	509.29	379.13	98.81	286.25	217.52	269.24	138.45	273.20	193.35	174.24	82.70	225.55	200.20	103.94	144.67	27.98

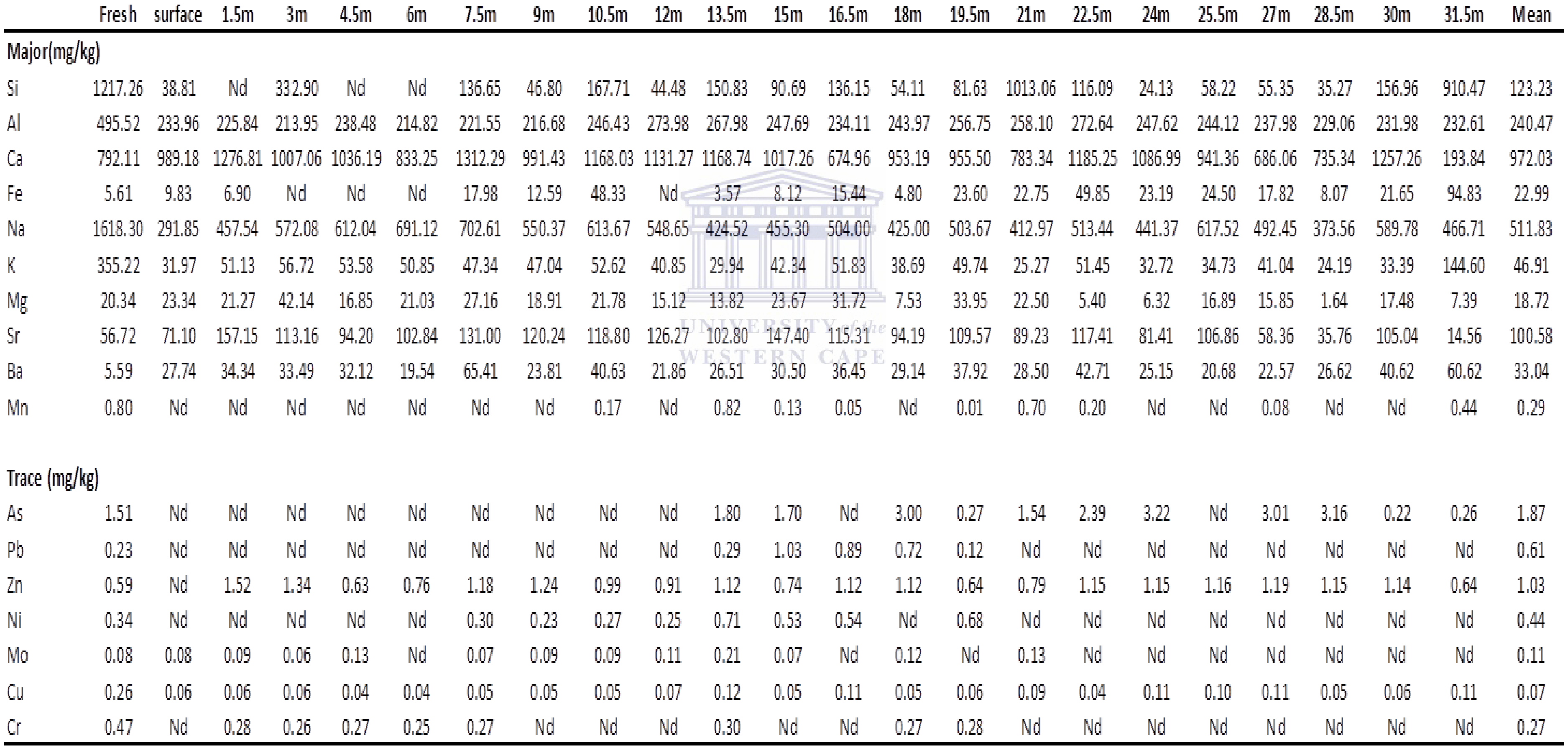
APPENDIX 7

Analysis of the extractions in the water soluble fraction for the Secunda fresh fly ash and the drilled core samples (S1) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	16.5m	18m	19.5m	21m	22.5m	Mean
Major(mg/kg)																	
Si	1217.26	3481.31	3407.70	2041.24	1313.55	1216.92	2638.17	1703.72	3554.26	4139.80	4573.63	3328.12	1656.61	1147.54	514.53	783.81	2366.73
Al	495.52	512.70	1056.85	439.40	90.99	153.58	76.88	496.58	649.46	704.80	208.06	17.64	225.32	499.43	206.59	425.93	384.28
Ca	792.11	323.01	361.07	1445.56	2510.36	828.38	344.73	1308.60	2108.90	708.94	758.53	1851.23	1197.86	619.48	1050.11	2901.05	1221.19
Fe	5.61	Nd	42.75	1.42	8.25	6.10	18.20	8.44	20.09	48.06	36.76	21.27	11.17	18.42	19.78	27.07	20.56
Na	1618.30	1100.94	1155.43	1654.92	1340.88	1387.71	1410.09	1072.25	1251.81	1523.15	600.53	841.07	1195.69	1818.74	1153.12	1744.05	1283.36
K	355.22	429.91	448.36	391.86	389.52	528.78	458.09	362.47	405.19	422.23	703.34	440.52	636.09	620.30	516.32	763.10	501.07
Mg	20.34	35.64	73.47	30.55	6.33	10.68	5.34	34.52	45.15	49.00	14.46	1.23	15.66	34.72	14.36	29.61	26.72
Sr	56.72	28.24	108.67	109.15	71.29	75.72	67.13	51.03	79.77	94.23	51.18	48.94	Nd	Nd	Nd	Nd	71.40
Ba	5.59	5.98	13.87	7.67	4.81	6.77	5.95	3.26	10.82	13.91	11.54	5.80	0.81	1.18	0.23	1.21	6.25
Mn	0.80	Nd	Nd	Nd	Nd	Nd	2.24	0.71	1.04	Nd	Nd	0.43	1.54	1.23	0.47	0.24	0.99
Trace (mg/kg)																	
As	1.51	Nd	Nd	Nd	Nd	Nd	11.57	Nd	27.36	18.45	23.08	17.83	4.57	Nd	5.70	4.78	14.17
Pb	0.23	Nd	Nd	Nd	Nd	Nd	3.13	2.64	5.10	7.60	20.03	Nd	4.29	2.85	1.59	4.41	5.74
Zn	0.59	Nd	2.18	1.83	2.59	0.90	0.31	0.80	0.60	0.24	1.25	0.29	3.00	1.99	1.22	3.17	1.46
Ni	0.34	1.60	Nd	0.20	Nd	Nd	Nd	Nd	2.62	Nd	1.52	Nd	Nd	Nd	Nd	Nd	1.49
Mo	0.47	0.02	0.05	0.88	0.09	0.09	Nd	1.32	Nd	Nd	0.78	0.04	0.56	0.36	0.02	0.31	0.38
Cu	0.08	0.15	0.14	0.38	0.21	0.40	0.07	0.28	0.33	0.66	Nd	Nd	0.51	1.00	0.75	1.71	0.51
Cr	0.26	1.00	0.58	0.67	0.48	0.05	Nd	Nd	Nd	Nd	Nd	1.10	Nd	Nd	Nd	Nd	0.65

APPENDIX 8

Analysis of the extractions in the water soluble fraction for the fresh Secunda fly ash and the drilled ash core samples (S3) as a function of depth



	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5m	27m	28.5m	30m	31.5m	Mean
Major(mg/kg)																								
Si	1217.26	38.81	Nd	332.90	Nd	Nd	136.65	46.80	167.71	44.48	150.83	90.69	136.15	54.11	81.63	1013.06	116.09	24.13	58.22	55.35	35.27	156.96	910.47	123.23
Al	495.52	233.96	225.84	213.95	238.48	214.82	221.55	216.68	246.43	273.98	267.98	247.69	234.11	243.97	256.75	258.10	272.64	247.62	244.12	237.98	229.06	231.98	232.61	240.47
Ca	792.11	989.18	1276.81	1007.06	1036.19	833.25	1312.29	991.43	1168.03	1131.27	1168.74	1017.26	674.96	953.19	955.50	783.34	1185.25	1086.99	941.36	686.06	735.34	1257.26	193.84	972.03
Fe	5.61	9.83	6.90	Nd	Nd	Nd	17.98	12.59	48.33	Nd	3.57	8.12	15.44	4.80	23.60	22.75	49.85	23.19	24.50	17.82	8.07	21.65	94.83	22.99
Na	1618.30	291.85	457.54	572.08	612.04	691.12	702.61	550.37	613.67	548.65	424.52	455.30	504.00	425.00	503.67	412.97	513.44	441.37	617.52	492.45	373.56	589.78	466.71	511.83
K	355.22	31.97	51.13	56.72	53.58	50.85	47.34	47.04	52.62	40.85	29.94	42.34	51.83	38.69	49.74	25.27	51.45	32.72	34.73	41.04	24.19	33.39	144.60	46.91
Mg	20.34	23.34	21.27	42.14	16.85	21.03	27.16	18.91	21.78	15.12	13.82	23.67	31.72	7.53	33.95	22.50	5.40	6.32	16.89	15.85	1.64	17.48	7.39	18.72
Sr	56.72	71.10	157.15	113.16	94.20	102.84	131.00	120.24	118.80	126.27	102.80	147.40	115.31	94.19	109.57	89.23	117.41	81.41	106.86	58.36	35.76	105.04	14.56	100.58
Ba	5.59	27.74	34.34	33.49	32.12	19.54	65.41	23.81	40.63	21.86	26.51	30.50	36.45	29.14	37.92	28.50	42.71	25.15	20.68	22.57	26.62	40.62	60.62	33.04
Mn	0.80	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.17	Nd	0.82	0.13	0.05	Nd	0.01	0.70	0.20	Nd	Nd	0.08	Nd	Nd	0.44	0.29
Trace (mg/kg)																								
As	1.51	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	1.80	1.70	Nd	3.00	0.27	1.54	2.39	3.22	Nd	3.01	3.16	0.22	0.26	1.87
Pb	0.23	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.29	1.03	0.89	0.72	0.12	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.61
Zn	0.59	Nd	1.52	1.34	0.63	0.76	1.18	1.24	0.99	0.91	1.12	0.74	1.12	1.12	0.64	0.79	1.15	1.15	1.16	1.19	1.15	1.14	0.64	1.03
Ni	0.34	Nd	Nd	Nd	Nd	Nd	0.30	0.23	0.27	0.25	0.71	0.53	0.54	Nd	0.68	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.44
Mo	0.08	0.08	0.09	0.06	0.13	Nd	0.07	0.09	0.09	0.11	0.21	0.07	Nd	0.12	Nd	0.13	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.11
Cu	0.26	0.06	0.06	0.06	0.04	0.04	0.05	0.05	0.05	0.07	0.12	0.05	0.11	0.05	0.06	0.09	0.04	0.11	0.10	0.11	0.05	0.06	0.11	0.07
Cr	0.47	Nd	0.28	0.26	0.27	0.25	0.27	Nd	Nd	Nd	0.30	Nd	Nd	0.27	0.28	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.27

APPENDIX 9

Analysis of the extractions in the exchangeable fraction for the Secunda fresh fly ash and the drilled core samples (S1) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	16.5m	18m	19.5m	21m	22.5m	Mean
Major (mg/kg)																	
Si	47.85	928.25	1316.09	1152.91	1010.37	2079.01	1466.30	1116.28	581.46	607.44	2199.50	949.71	68.86	358.66	1162.95	2435.02	1162.19
Al	46.20	108.08	556.38	252.78	248.37	256.70	372.59	369.53	367.06	422.95	497.30	532.69	250.77	726.38	582.77	438.72	398.87
Ca	1399.64	735.87	592.91	1705.52	2138.00	1809.27	2288.24	2105.05	1040.08	1302.93	1444.72	2666.36	1452.86	1103.74	2197.00	1317.86	1593.36
Fe	53.79	80.75	98.32	39.19	48.29	35.91	40.81	37.30	72.72	78.61	249.33	171.84	55.65	65.83	48.76	78.86	80.14
Na	14.43	1037.65	1258.28	786.86	690.57	770.06	902.29	940.12	1176.97	1187.51	1327.14	985.30	845.51	863.39	655.28	655.48	938.83
K	513.61	1304.97	1161.51	516.48	652.07	806.51	250.70	274.80	447.44	457.67	586.29	379.65	297.66	567.40	268.88	267.49	549.30
Mg	251.11	261.84	310.54	142.53	112.81	137.90	139.15	138.94	287.54	417.80	261.45	214.10	169.33	144.32	69.88	280.82	205.93
Sr	45.67	19.47	19.23	47.32	53.69	42.34	54.26	47.15	29.95	29.11	32.61	62.28	40.96	45.62	75.55	40.74	42.69
Ba	59.43	15.76	22.06	33.04	35.99	31.90	38.53	28.31	25.45	24.34	31.12	37.76	24.95	34.23	41.69	26.32	30.10
Mn	0.61	4.43	1.91	1.44	2.24	3.45	3.21	3.88	3.69	2.92	2.62	1.45	0.99	1.29	2.21	3.86	2.64
Trace (mg/kg)																	
As	1.93	Nd	Nd	Nd	Nd	Nd	1.07	4.28	2.27	0.79	0.66	0.99	0.64	0.26	0.05	Nd	1.22
Pb	0.45	0.38	0.26	0.25	Nd	0.04	Nd	Nd	Nd	Nd	1.00	0.24	0.01	0.27	Nd	Nd	0.31
Zn	0.78	1.20	1.26	0.66	0.51	0.60	0.52	0.53	1.03	1.22	2.03	1.17	0.77	1.32	0.57	1.06	0.96
Ni	0.83	1.60	Nd	1.30	0.88	1.22	1.06	1.08	2.48	2.59	4.42	2.06	1.79	2.70	1.00	1.95	1.87
Mo	0.46	Nd	Nd	Nd	Nd	Nd	0.30	0.22	Nd	Nd	Nd	Nd	0.39	Nd	0.07	Nd	0.24
Cu	0.03	0.87	Nd	Nd	0.43	0.29	Nd	Nd	Nd	Nd	Nd	0.56	0.61	Nd	0.48	Nd	0.54
Cr	0.43	Nd	0.77	0.06	0.64	0.11	0.86	0.38	Nd	Nd	0.85	0.09	0.36	0.83	0.25	0.70	0.49

APPENDIX 10

Analysis of the extractions in the exchangeable fraction for the Secunda fresh fly ash and the drilled core samples (S3) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5m	27m	28.5m	30m	31.5m	Mean
Major(mg/kg)																								
Si	47.85	1163.71	344.79	54.70	163.71	1340.73	627.82	945.98	622.18	1276.73	821.79	941.62	539.66	1757.94	1258.95	1047.42	1244.72	778.83	1702.54	1031.56	1363.07	876.84	1289.15	963.38
Al	46.20	103.61	354.52	175.89	163.97	161.65	298.85	201.68	313.67	185.97	214.94	207.96	197.82	280.55	227.90	213.57	505.08	199.20	303.39	143.34	273.15	284.96	278.58	240.47
Ca	1399.64	1449.13	1183.90	1723.53	1237.65	1505.76	911.53	1451.14	1459.17	1730.80	1704.62	1798.41	1339.34	1112.55	1290.63	1170.94	1259.56	29.39	102.24	88.76	58.08	25.79	75.57	1032.20
Mg	251.11	283.38	258.36	246.11	282.79	228.04	264.93	174.96	208.27	183.51	185.28	181.67	204.14	170.68	170.03	150.87	178.16	169.19	188.64	155.87	181.34	170.81	162.38	199.97
Ba	59.43	176.81	127.71	72.99	77.73	73.25	40.10	106.51	74.53	69.08	60.46	72.64	38.75	92.76	117.74	103.74	102.14	125.43	112.16	109.49	155.16	89.04	85.75	94.73
Sr	45.67	192.36	175.77	132.65	111.81	126.91	66.44	178.43	133.02	115.13	127.95	132.83	66.31	129.60	162.46	149.69	159.36	248.79	258.29	237.94	253.71	214.75	110.02	158.37
Fe	53.79	14.22	14.07	14.04	11.75	33.25	40.96	31.25	17.01	12.53	20.32	33.36	31.70	18.40	2.92	18.85	8.44	10.69	14.84	19.84	3.30	9.24	9.99	17.77
Mn	0.61	0.74	1.43	1.47	1.37	0.94	0.51	1.69	1.08	1.17	1.28	1.45	0.47	1.58	2.07	1.62	1.51	3.93	4.09	4.16	4.69	3.67	2.78	1.99
Na	14.43	68.53	85.10	112.15	127.64	186.56	85.86	220.79	137.64	53.70	36.25	31.15	17.05	102.69	129.97	42.43	86.37	271.43	379.79	395.14	346.22	361.13	149.30	155.77
K	513.61	237.13	188.24	197.93	203.25	212.84	101.73	268.95	190.19	123.37	89.93	99.21	69.13	142.78	222.94	124.18	170.77	290.91	515.11	405.61	501.96	506.38	622.14	249.30
Trace (mg/kg)																								
As	1.93	4.61	Nd	1.32	0.17	Nd	Nd	0.21	Nd	1.17	Nd	1.36	Nd	5.00	6.48	7.02	1.72	4.73	Nd	Nd	Nd	Nd	Nd	3.07
Pb	0.45	Nd	Nd	Nd	Nd	0.93	1.40	2.28	2.89	0.15	Nd	Nd	Nd	1.19	0.82	0.56	Nd	Nd	0.67	1.04	1.84	1.20	Nd	1.25
Zn	0.78	1.73	1.46	1.38	1.50	1.59	1.60	1.70	1.75	1.04	0.89	0.71	0.71	1.04	1.04	1.03	1.02	0.08	1.49	0.02	0.49	0.31	0.23	1.04
Ni	0.83	0.31	0.27	Nd	0.43	0.28	0.62	0.65	0.65	0.07	0.37	0.27	0.20	Nd	Nd	Nd	0.20	Nd	Nd	0.02	0.46	0.09	Nd	0.33
Mo	0.03	0.05	Nd	Nd	Nd	0.57	0.10	0.32	0.28	0.19	0.10	0.41	0.22	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.05	Nd	0.23
Cu	0.03	0.27	Nd	0.22	Nd	Nd	0.81	Nd	0.25	0.50	0.31	0.74	0.80	Nd	Nd	Nd	Nd	Nd	0.89	0.90	0.64	0.95	0.86	0.63
Cr	0.46	0.10	0.48	0.75	0.59	Nd	Nd	Nd	Nd	0.56	0.15	0.40	0.22	0.03	0.58	0.08	0.01	0.70	0.20	1.22	1.63	1.08	0.16	0.50

APPENDIX 11

Analysis of the extractions in the carbonate fraction for the Secunda fresh fly ash and the drilled core samples (S1) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	16.5m	18m	19.5m	21m	22.5m	Mean
Major (mg/kg)																	
Si	12439.00	18056.07	18485.11	8685.94	6241.21	8733.30	8680.74	9081.70	14938.76	13774.49	29416.95	16985.00	12788.63	23873.44	6457.69	10320.14	13767.94
Al	9860.47	2713.27	2791.33	2367.21	1504.18	1256.72	1681.95	1573.83	3182.82	3299.75	10072.41	5746.60	557.94	1925.49	851.35	2551.01	2805.06
Ca	3927.94	3035.34	2522.66	1022.45	1269.59	1276.16	1177.38	1201.23	3077.37	3210.35	2668.46	1705.91	1038.78	1734.39	2847.22	31.14	1854.56
Fe	189.70	nd	295.23	180.26	152.81	nd	nd	0.01	108.51	nd	nd	nd	59.73	93.53	71.42	84.73	116.25
Na	207.30	227.15	237.73	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	232.44
K	147.47	52.45	101.21	55.08	53.27	3.25	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	114.17	63.24
Mg	202.16	131.87	266.26	349.34	442.77	367.28	514.17	392.01	262.33	276.94	321.38	542.14	235.63	243.94	364.68	247.88	330.57
Sr	113.66	30.41	49.80	62.08	57.00	52.80	114.76	153.84	104.94	130.63	107.69	168.13	115.27	144.10	142.27	153.66	105.83
Ba	111.84	47.99	67.20	51.44	62.70	79.30	80.68	122.45	120.49	157.25	147.96	159.39	91.58	136.74	127.16	152.97	107.02
Mn	17.20	5.51	14.30	12.08	17.04	14.70	20.32	18.71	11.13	11.95	17.33	23.99	15.24	14.87	21.67	15.79	15.64
Trace (mg/kg)																	
As	2.90	Nd	4.54	Nd	Nd	Nd	42.06	2.24	1.69	1.41	2.37	Nd	1.31	3.63	Nd	Nd	7.41
Pb	3.84	Nd	2.13	0.77	Nd	2.24	1.20	2.00	5.37	1.47	Nd	0.85	0.99	Nd	Nd	Nd	1.89
Zn	0.78	Nd	Nd	Nd	0.08	Nd	Nd	0.62	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.35
Ni	1.27	Nd	2.24	Nd	Nd	1.12	3.94	1.65	Nd	2.88	Nd	Nd	Nd	1.83	0.91	Nd	2.08
Mo	0.64	Nd	Nd	Nd	Nd	0.49	0.22	0.28	0.58	0.93	0.32	Nd	Nd	4.39	Nd	Nd	1.03
Cu	0.48	Nd	Nd	Nd	Nd	Nd	Nd	0.73	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	0.73
Cr	0.78	1.45	1.04	0.67	1.20	1.28	0.58	0.62	1.06	0.85	1.28	Nd	0.05	1.23	0.84	Nd	0.93

APPENDIX 12

Analysis of the extractions in the Carbonate fraction for the Secunda fresh fly ash and the drilled core samples (S3) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5m	27m	28.5m	30m	31.5m	Mean
Major(mg/kg)																								
Si	12439.00	11664.20	24051.54	22801.20	26194.41	17215.50	21663.42	8196.06	4710.36	2989.24	4652.22	3733.14	3127.20	10510.62	10738.44	7226.70	12891.06	15155.64	11903.46	16975.14	23383.20	13636.20	3739.04	12598.09
Al	9860.47	3173.22	3911.07	3902.78	3748.00	3562.26	4713.18	4359.64	4063.47	3912.74	4259.76	3621.96	3566.04	6561.07	10219.05	7827.10	11058.10	13878.88	12000.40	8502.47	6073.62	5554.64	3908.40	6017.18
Ca	3927.94	2587.29	2825.58	3031.27	2862.67	1817.54	4088.96	4547.89	2942.86	1132.12	3240.69	2769.47	2480.67	2269.89	3143.50	2382.75	3443.90	4680.20	5984.16	4800.32	5935.22	4472.33	768.61	3282.17
Fe	189.70	31.74	78.81	27.31	81.65	55.48	174.65	75.06	62.10	49.07	42.65	91.36	54.79	39.15	99.66	45.69	94.63	14.48	71.32	72.76	16.26	68.74	26.29	62.44
Na	207.30	304.79	337.16	355.47	387.13	358.40	444.24	571.05	349.66	368.15	448.04	454.19	451.98	540.11	644.32	399.08	539.66	575.33	551.31	492.36	480.33	435.85	301.64	445.01
K	147.47	127.25	115.78	158.58	133.31	112.65	203.65	260.61	161.62	83.91	167.79	120.67	170.68	220.83	271.63	94.32	175.37	278.94	375.40	375.83	350.62	342.53	253.41	207.06
Mg	202.16	293.54	345.88	354.67	322.82	361.06	323.75	474.98	348.03	316.16	380.45	387.04	297.66	404.88	551.16	438.32	447.02	422.64	480.57	497.80	453.21	463.42	435.08	400.01
Sr	113.66	487.23	634.39	612.30	580.94	320.29	701.23	998.80	689.13	361.94	706.46	673.42	537.69	484.54	636.02	455.22	788.31	1044.23	1232.48	951.72	1171.46	798.89	137.88	682.03
Ba	111.84	337.02	632.13	599.43	568.58	299.21	698.57	751.05	479.11	319.81	547.98	472.35	422.97	387.75	557.20	422.59	628.67	747.37	712.86	631.44	1120.20	607.61	171.21	550.69
Mn	17.20	5.70	11.61	11.67	9.34	6.61	5.46	5.62	5.88	4.25	9.40	8.00	5.95	6.87	8.60	10.38	9.85	1.80	6.09	1.81	5.46	9.93	5.52	7.08
Trace (mg/kg)																								
As	2.90	2.79	1.08	Nd	1.52	3.43	1.28	0.56	1.94	Nd	1.31	0.28	0.29	0.18	1.36	0.84	2.07	2.07	0.22	2.39	1.52	1.31	0.55	1.35
Pb	3.84	Nd	0.64	0.07	0.06	0.16	Nd	Nd	Nd	0.31	Nd	0.53	0.83	0.24	0.51	0.85	0.81	0.98	0.62	1.58	0.62	0.62	1.41	0.64
Zn	0.78	0.99	1.01	1.03	0.99	0.97	1.05	1.15	0.98	1.03	1.00	0.99	1.04	1.01	1.13	1.10	1.09	1.02	1.01	1.02	1.09	1.06	1.05	1.04
Ni	1.27	2.45	1.90	1.12	1.70	2.38	0.83	0.35	0.34	0.75	0.39	0.42	0.39	0.37	0.74	1.52	0.46	0.32	0.36	0.41	0.66	0.51	0.55	0.86
Mo	0.48	0.10	0.18	0.07	0.46	0.28	0.51	0.69	0.01	0.57	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	Nd	1.29	1.23	Nd	0.49
Cu	0.78	0.45	0.49	0.24	0.57	0.34	0.38	0.23	0.39	0.53	0.39	0.27	0.42	0.26	0.30	0.27	0.22	0.17	0.25	0.28	0.29	0.47	0.40	0.35
Cr	0.64	0.69	0.42	0.35	0.31	0.30	0.17	0.56	0.83	0.21	0.85	0.67	0.34	0.19	0.11	0.12	0.11	0.23	0.16	0.17	0.20	0.09	0.23	0.33

APPENDIX 13

Analysis of the extractions in the Fe/Mn fraction for the Secunda fresh fly ash and the drilled core samples (S1) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	16.5m	18m	19.5m	21m	22.5m	Mean
Major (mg/kg)																	
Si	13545.89	18571.49	3515.56	17567.22	6990.53	550.71	656.64	20394.69	22206.44	17772.37	22788.55	14030.63	21280.08	24833.66	7822.76	15439.08	14294.70
Al	8328.45	5082.05	92.57	6190.17	3706.50	619.56	483.42	5724.28	13095.70	2604.28	3053.52	6547.47	4827.30	5057.40	816.41	13169.63	4738.02
Ca	2152.95	687.37	3178.90	5674.96	3530.52	4559.73	4162.38	3419.05	3712.90	5170.91	1705.83	2814.70	2211.04	2854.66	1913.59	2459.41	3203.73
Fe	1996.23	3955.33	3370.00	4063.21	1720.28	15.30	32.77	1860.30	4425.38	3741.37	4209.29	2527.04	3130.88	3879.30	728.64	10251.84	3194.06
Na	404.45	71.67	79.31	Nd	Nd	72.60	186.77	Nd	Nd	169.87	292.47	Nd	Nd	98.36	109.76	Nd	135.10
K	98.03	90.15	111.45	Nd	37.83	351.11	277.48	Nd	Nd	335.82	816.57	Nd	45.42	22.55	195.22	11.03	208.60
Mg	653.33	358.56	3.93	1042.04	1298.87	12.65	64.23	645.44	787.47	915.83	310.20	1392.87	1155.43	262.33	293.66	1439.83	665.56
Sr	262.53	309.82	559.66	209.68	207.78	353.20	320.83	347.90	460.93	449.62	450.47	340.32	411.09	416.13	203.43	34.16	338.34
Ba	138.72	205.46	303.00	144.66	78.59	186.32	172.33	168.01	234.60	247.50	194.66	154.73	184.71	272.48	86.30	93.52	181.79
Mn	40.51	145.73	11.13	199.24	271.09	4.75	6.45	144.39	145.84	81.57	81.54	254.63	167.15	31.21	42.35	181.40	117.90
Trace (mg/kg)																	
As	1.96	0.49	1.44	1.04	0.35	0.90	1.06	0.30	1.05	1.61	1.46	Nd	Nd	1.91	0.96	Nd	1.05
Pb	0.41	0.40	0.38	0.45	0.49	0.03	0.10	0.25	Nd	0.22	0.28	0.34	0.26	1.03	0.17	0.88	0.38
Zn	1.65	2.35	2.51	1.67	1.34	1.58	0.94	1.54	1.29	1.71	1.24	1.07	1.52	2.13	1.10	1.22	1.55
Ni	0.97	0.85	Nd	1.71	0.50	1.40	1.57	2.11	1.39	Nd	Nd	Nd	1.38	1.79	Nd	Nd	1.41
Mo	0.55	0.67	0.77	0.40	0.53	Nd	Nd	Nd	0.84	0.31	0.27	Nd	0.88	0.90	0.62	1.16	0.67
Cu	0.37	0.88	1.01	Nd	Nd	0.43	0.84	nd	Nd	1.09	0.75	Nd	Nd	1.05	0.80	Nd	0.86
Cr	0.68	Nd	Nd	0.07	0.50	0.03	Nd	Nd	0.43	Nd	Nd	Nd	0.04	0.21	0.19	0.51	0.25

APPENDIX 14

Analysis of the extractions in the Fe and Mn fraction for the Secunda fresh fly ash and the drilled core samples (S3) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5m	27m	28.5m	30m	31.5m	Mean
Major(mg/kg)																								
Si	13545.89	19907.79	8333.15	9202.16	11015.38	12295.33	35558.62	27987.43	19702.84	26877.03	13596.66	29150.09	30598.78	15713.68	19950.69	22020.16	18551.08	9930.70	38283.58	24418.18	17737.18	13430.98	18484.30	20124.81
Al	8328.45	6378.53	5580.66	5298.86	4255.76	5368.84	12835.60	11432.28	8755.73	9882.66	7252.62	10802.60	13826.93	10246.57	13473.07	13538.15	11484.70	10568.76	9691.09	15461.72	11603.05	12026.98	15130.99	10222.55
Ca	2152.95	938.78	1264.33	1448.14	906.20	1218.37	1446.14	1444.96	1698.08	1660.93	1519.89	3062.35	1646.58	1907.10	3950.85	2414.22	2964.48	1703.94	2181.90	3021.73	2196.82	2875.73	2861.76	2015.15
Fe	1996.23	2396.73	4018.03	4157.61	5151.71	5572.25	5884.41	2817.66	2225.56	3399.30	3595.97	5198.46	7013.71	3516.43	3377.75	3888.54	2790.43	1492.40	1259.41	2345.64	1676.73	2095.77	3728.97	3527.43
Na	404.45	442.16	402.73	544.11	559.13	625.70	960.35	696.93	601.96	496.30	210.89	1597.67	494.40	651.05	129.78	343.25	247.22	249.98	199.83	46.91	179.69	211.97	221.33	459.70
K	98.03	124.59	99.00	79.85	117.41	117.11	205.49	196.02	129.66	138.76	141.33	204.15	66.79	165.55	12.35	50.56	103.76	107.61	21.96	24.31	17.05	47.13	114.99	103.88
Mg	653.33	891.96	830.77	492.09	786.30	789.63	755.29	743.79	637.24	525.90	491.49	754.06	747.91	809.45	360.14	943.15	589.59	937.09	598.70	749.29	845.58	913.96	273.60	703.04
Sr	262.53	16.90	46.27	158.55	300.62	663.35	449.00	498.32	314.99	150.04	201.01	150.95	369.51	149.67	173.99	88.00	269.23	311.88	354.04	560.13	264.39	402.52	95.42	272.22
Ba	138.72	4.00	14.81	47.38	126.64	182.43	163.59	156.06	111.34	87.66	56.36	53.86	158.39	62.49	83.10	52.91	98.94	133.22	97.31	223.15	158.86	105.70	189.22	107.61
Mn	40.51	76.84	64.28	52.57	55.71	59.75	87.17	80.10	70.27	73.71	84.72	81.81	61.81	47.12	42.40	66.45	50.75	60.70	51.44	68.72	61.68	59.34	195.25	70.57
Trace (mg/kg)																								
As	1.96	1.66	1.86	1.71	1.68	1.75	0.40	1.59	0.56	1.35	Nd	2.24	1.32	1.05	0.65	Nd	2.73	2.75	0.46	Nd	0.70	1.94	Nd	1.47
Pb	0.41	2.35	2.51	2.27	1.63	0.47	1.04	Nd	Nd	Nd	Nd	0.78	Nd	0.18	Nd	Nd	0.02	1.05	Nd	Nd	0.33	Nd	0.47	1.09
Zn	1.65	0.03	Nd	Nd	Nd	0.01	0.01	0.01	0.01	0.01	0.01	0.05	0.01	0.01	0.01	0.01	0.00	0.00	0.01	0.01	0.02	0.00	0.01	0.01
Ni	0.97	1.05	0.81	0.55	0.62	0.52	0.61	0.89	0.93	0.85	1.84	0.52	0.82	0.69	0.92	0.71	0.57	0.75	0.24	0.99	0.68	0.54	0.71	0.76
Mo	0.37	0.38	Nd	Nd	Nd	0.15	0.11	0.15	0.19	0.11	0.38	0.13	0.18	0.12	0.16	0.15	0.16	0.20	0.14	0.22	0.31	0.20	0.13	0.19
Cu	0.68	0.32	0.12	0.53	0.39	0.29	0.37	0.17	0.20	0.50	0.32	0.18	0.24	0.21	0.30	0.15	0.12	0.18	0.13	0.17	Nd	Nd	Nd	0.26
Cr	0.55	0.54	0.34	0.41	0.23	0.30	0.39	Nd	0.39	0.29	0.29	0.37	0.33	0.44	0.31	0.16	0.59	0.61	0.45	Nd	0.27	0.31	Nd	0.37

APPENDIX 15

Analysis of the extractions in the residual fraction for the Secunda fresh fly ash and the drilled core samples (S1) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	16.5m	18m	19.5m	21m	22.5m	Mean
Major (mg/kg)																	
Si	195653.57	182931.56	210129.61	203851.17	187156.06	170912.16	203962.43	172580.94	195940.05	189314.13	266021.33	273383.06	172788.00	289894.71	186461.10	214122.65	207963.26
Al	113912.99	31840.41	39286.24	58127.25	43959.03	42002.67	39362.31	40104.53	47317.12	36377.88	38433.88	35500.59	49604.64	42386.04	135097.19	121451.85	53390.11
Ca	54482.22	57417.76	50594.87	26456.34	31452.08	40236.47	31091.26	54007.30	50405.60	48186.61	50811.64	57339.15	58505.12	53223.30	54786.20	45101.91	47307.71
Fe	13493.27	25453.42	23281.84	13055.51	7651.58	22818.85	19891.11	12603.97	14734.32	22661.43	47440.14	31467.96	21021.35	23488.73	18643.74	24622.12	21922.40
Na	14061.82	16152.51	12439.04	6967.16	15849.40	7359.31	19798.46	28289.57	21434.48	20814.04	14733.46	26317.50	18254.86	3379.45	16019.27	12109.57	15994.54
K	6788.72	9984.30	8519.11	4211.51	5225.75	7143.82	4919.92	7421.50	12187.90	11633.44	8910.74	8115.90	7059.51	11208.65	7193.78	10275.79	8267.44
Mg	7443.67	4966.52	4651.14	8794.88	1547.95	10278.09	3516.04	3841.10	7259.58	8605.98	12918.95	6935.82	7837.02	14505.69	12080.65	9558.34	7819.85
Sr	3367.67	2793.95	2894.06	1405.50	3914.45	3895.03	3731.72	3650.27	3637.24	3873.21	3738.51	3540.85	3893.87	3946.47	3983.44	4056.42	3530.33
Ba	2212.88	1630.90	1685.27	2481.58	2315.20	2533.15	2027.76	1979.64	2160.81	2049.28	2000.46	2233.78	2043.18	2232.52	2153.08	2220.08	2116.45
Mn	365.15	344.54	331.85	277.93	263.38	378.61	384.83	321.06	404.04	485.42	919.38	634.97	415.58	577.60	479.27	443.56	444.13
Trace (mg/kg)																	
As	51.36	57.59	38.21	51.26	49.16	56.13	47.01	56.29	68.85	72.26	54.47	55.30	118.18	83.34	106.56	145.29	70.66
Pb	21.70	20.76	31.78	29.33	33.76	36.59	31.10	31.74	27.65	27.27	22.70	24.98	19.57	25.89	26.28	18.02	27.16
Zn	21.90	27.67	25.90	29.15	29.47	28.35	20.78	24.32	30.19	30.24	29.97	31.46	31.00	26.20	27.67	27.68	28.00
Ni	18.19	15.13	21.03	18.62	20.28	22.14	21.64	21.56	21.16	26.11	24.28	24.62	20.71	22.72	22.63	20.57	21.55
Mo	8.39	16.44	15.53	10.39	13.13	21.03	13.75	16.42	10.40	18.45	2.42	15.27	12.17	16.66	9.76	29.21	14.74
Cu	8.60	10.59	7.68	10.75	4.63	7.76	7.31	9.20	6.78	7.45	5.24	8.26	10.63	17.25	9.72	4.37	8.51
Cr	14.90	7.85	6.29	8.45	7.21	7.88	4.77	5.94	5.54	8.25	4.61	6.12	5.46	7.90	6.01	7.20	6.63

APPENDIX 16

Analysis of the extractions in the residual fraction for the Secunda fresh fly ash and the drilled core samples (S3) as a function of depth

	Fresh	surface	1.5m	3m	4.5m	6m	7.5m	9m	10.5m	12m	13.5m	15m	16.5m	18m	19.5m	21m	22.5m	24m	25.5m	27m	28.5m	30m	31.5m	MEAN
Major(mg/kg)																								
Si	195653.57	214193.20	230939.90	218697.07	103001.22	233379.40	239677.05	234082.35	218622.55	229095.40	192172.25	231837.50	248948.00	229865.50	254401.60	229069.05	188786.70	243497.80	237516.35	222463.70	243343.95	260975.50	240360.45	224769.39
Al	113912.99	87309.28	112849.06	93340.94	67074.75	95139.65	115239.60	109895.76	83697.69	113409.15	77405.19	94366.92	110603.76	83676.89	113140.95	81539.20	203327.93	101527.80	89353.79	87008.74	117587.13	119877.20	59815.44	100781.22
Ca	54482.22	21454.15	34439.17	17671.26	16092.05	75370.01	71488.63	44908.67	40214.29	28145.60	19772.85	25411.66	38444.93	19003.14	88177.75	31524.46	60388.25	64348.63	51301.02	38594.09	92124.30	90802.21	6650.66	44378.54
Fe	13493.27	11670.23	16805.19	13423.26	7403.33	31770.73	55606.60	28382.29	18209.78	16233.54	53565.64	31353.78	30447.74	17403.67	34441.49	19801.03	21496.22	19029.94	30912.38	13418.12	23582.85	25749.45	27729.72	24928.95
Na	14061.82	6068.01	8977.52	6662.74	5461.43	16925.17	15637.42	11635.02	11041.66	10430.50	7939.73	5759.28	7197.14	5382.99	15730.79	7978.61	10023.41	9394.90	7596.66	6318.51	11515.59	8793.78	24142.13	10027.86
K	6788.72	1952.01	2145.49	2422.90	2131.82	9666.78	6716.01	1377.70	347.19	1010.67	2332.38	2258.76	3061.80	1607.46	13380.38	1452.68	1693.82	1917.70	3692.76	2128.60	6649.33	4263.82	11446.30	3802.56
Mg	7443.67	11479.91	9343.01	7591.67	4621.85	6118.02	9736.93	6334.11	6878.34	8717.59	3364.54	11046.72	13052.06	8785.20	28477.15	6910.40	9446.48	9988.57	9508.11	6158.57	8206.41	12414.21	6936.48	9323.47
Sr	3367.67	7918.50	8301.00	7513.03	7416.00	8371.92	7302.68	9142.53	8962.25	7902.90	8114.56	7739.43	8456.66	8742.67	8040.29	7906.89	896.69	8484.20	9317.83	9181.86	9175.18	8878.15	1489.49	7693.40
Ba	2212.88	5231.36	5254.92	4719.88	5105.62	5290.09	4608.89	5261.57	5390.35	5135.17	4040.64	4417.48	4787.00	4797.03	4781.08	5106.75	5052.77	5497.70	5122.24	5604.77	5606.38	5126.44	2314.08	4920.56
Mn	365.15	386.97	457.59	380.04	173.29	508.98	648.76	457.45	323.42	288.68	388.16	465.34	638.16	425.09	1079.61	667.27	863.91	631.59	480.68	315.78	622.75	615.43	520.86	515.45
Trace (mg/kg)																								
As	51.36	74.07	65.82	63.49	48.21	73.64	58.44	84.02	74.94	64.29	90.14	62.38	66.68	65.80	62.31	65.99	59.63	69.54	85.96	152.17	69.11	60.80	121.97	74.52
Pb	21.70	24.14	16.52	25.31	32.70	32.29	23.93	33.28	24.74	24.79	16.78	25.65	26.02	25.83	19.41	27.00	25.24	24.71	24.40	32.54	32.60	23.47	34.08	26.16
Zn	21.90	26.20	31.66	28.80	31.61	18.60	25.44	27.50	28.30	26.87	20.84	26.04	22.69	25.48	22.74	23.47	23.50	25.09	22.24	24.95	23.62	8.57	20.02	24.28
Ni	18.19	21.85	17.04	21.45	22.60	21.10	21.86	22.32	22.96	22.98	17.04	25.15	27.45	25.77	17.43	22.83	22.49	22.68	27.54	26.29	26.15	22.79	31.18	23.13
Mo	14.90	17.80	19.31	6.86	17.04	8.13	17.19	17.97	17.48	8.30	13.83	12.83	9.40	5.86	5.20	12.82	11.32	11.09	19.19	9.24	14.23	7.45	8.39	12.31
Cu	8.39	7.41	8.31	8.64	8.53	7.48	9.35	8.25	7.32	8.00	10.20	10.26	11.48	9.53	7.57	6.79	7.67	7.34	6.09	7.32	7.04	8.18	6.30	8.14
Cr	8.60	6.48	7.54	6.88	7.36	8.07	8.45	5.42	7.86	8.13	7.11	6.66	6.27	9.22	8.30	6.69	5.89	6.76	6.56	5.85	10.55	10.20	8.32	7.48