Chemical interactions and mobility of species in fly ash-brine co-disposal systems

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Abstract

Fly ash is a waste product generated from the combustion of coal for power generation. South African coal-fired power stations, operated by ESKOM (Tutuka) and SASOL (Secunda) for instance, produced significant amounts (over 40 million tons (Mt)) of fly ash annually due to the high demand for electricity. Most of the fly ash generated is disposed of in landfills, slurry pond or ash dumps while only a small amount is productively used. Apart from the fly ash generated in the coal-fired station, the treatment of wastewaters with the aim of recovering water for reuse by using different methods such as reverse osmosis (RO), electro dialysis reversal (EDR), vapour compression (VC) and other membrane methods has led to the production of hyper-saline water called brine. The disposal of the brine and fly ash generated in the coal-fired power stations has been a major concern due to the large quantities produced, the cost of safe disposal and the environmental impact due to the possible ingress of salts and toxic elements in significant quantities into the surrounding soils and groundwater. The possibility of co-disposing fly ash and brine is being considered by some power stations in South Africa (ESKOM and SASOL) to save costs and reduce the negative environmental impacts of long term storage of these waste materials. The primary aim of these coal fired industries for co-disposing fly ash and brine was to use the fly ash as a sustainable salt sink. It is therefore important to study the interaction chemistry of the fly ash-brine systems to fully understand the leaching and mobility of the contaminant species, and to determine the possibility of capturing the salts from the brine solution when fly ash and brine are co-disposed. In order to achieve the aims and objectives of this study, several leaching procedures such as batch reaction tests, long-term fly ash-brine interaction tests, acid neutralization capacity (ANC) tests, up-flow percolation tests and sequential extraction tests were employed. The geochemical modeling software was applied to predict the formation of secondary mineral phases controlling the release of species in the fly ash-brine systems. Several analytical techniques such as x-ray diffraction (XRD), x-ray fluorescence (XRF), scanning electron microscopy-energy dispersion spectroscopy (SEM-EDS), inductively coupled plasma-mass spectroscopy (ICP-MS) and ion chromatography (IC) were applied to characterize the fresh fly ashes, solid residues recovered from the fly ash-brine interaction tests, the brine sample used in this study and the leachate samples in order to determine the chemical and mineralogical compositions and speciation of the waste materials.

The results of the XRD showed that the fresh fly ashes from Secunda and Tutuka predominantly contained some mineral phases such as quartz, mullite, calcite and lime. The XRF results showed that the fly ashes contained high concentrations of Al_2O_3, SiO_2, CaO and Fe_2O_3 as major oxides and trace elements such as Sr, Ba, Th, V, Ga, Cu, Y, Zr, Nb, La, Ce and Nd, Cr, Co, Ni, Zn, Pb, U and Cl. The IC and ICP-MS analysis carried out on the brine solution used in this study showed that the brine contained high concentrations of Ca, Na, Mg, K, Cl and SO_4 and trace amounts of As, Se, Cd, Cu, Cr, Fe, Mn and Co. The results of the batch reaction tests showed that species such as Na, Mg, Cl and SO_4 which constitute the major species of the brine solution were significantly removed from the brine with 30 minutes of interactions with the fly ashes. Minor elements such as As, Co, Cu, Pb, Ni and Zn were initially significantly removed from the brine after which some of these species were gradually released into the fly ash-brine batch systems over time. Despite the ability of the fly ashes to remove major and minor species from brine, some species such as Ca, Ba, Sr, K, Cr and Mo were significantly leached into the brine solution from the fly ashes thereby increasing their concentration in the leachates. PHREEQC modelling predicted the formation of mineral phases such as diaspore, gibbsite, barite, celestite, gypsum, anhydrite and brucite as a factor controlling the release of major species such as Al, Ba, Sr, Ca, SO_4 and Mg in the fly ash-brine systems. The minor species such as Fe, Mn, Cu, Ni and Zn among others were predicted to be controlled by the precipitation of mineral phases such as goethite, hematite, cupricferrite, $Ni(OH)_2$ and $Zn(OH)_2$. The results of the long-term fly ash brine interactions experiments, which was carried out at different contact times varying from 1 week to 12 months, showed that most of the major elements contained in the brine solution such Mg, Na, Cl, SO_4, As, B, Co, Cu, Mn, Ni, Pb, and Zn were significantly removed over time. The removal of Na, Cl, B, SO_4 and Mg from the brine during the long-term fly ash-brine interaction experiments was in the range of 1-34 %, 13-34 %, 39-100 %, 30-93 % and 98-100 % respectively. The percentage removal of Cu, Co and Zn from the brine solutions was found to range between 82 and 100 %, 61 and 100 %, and 5 and 80 % respectively. On the other hand, the concentrations of Al, K, Cr, Mo and Si increased in the excess brine decanted from the solid residues after the interactions experiments, which indicates that the species were leached from the fly ashes into the brine solution during the long-term interactions experiments. The ANC tests carried out on the solid residues generated from the long-term fly ash brine interactions experiments showed an increase in the mobility of most of the species captured by the fly ash as the pH of the systems decreased. The release of Na showed its independence on pH. Na concentration was higher at the natural pH and the high concentration continued throughout the ANC tests. This phenomenon showed that the Na-rich solid phase(s) formed during the long-term fly ash-brine interactions experiments are highly soluble and could re-dissolve when in contact with water irrespective of the pH of the solution. This gives clear evidence that the fly ashes cannot act as a long term sustainable salt sink. The results of the up-flow percolation tests showed that some species were removed from the brine solutions by both Secunda and Tutuka fly ashes at the beginning of the tests but later leached out after liquid/solid (L/S) 5. The calculated mass balance revealed that a significant percentage of species such as As (17.76-69 %), B (74.29-84.34 %), Co (27.45-100 %), Cu (21.65-86.33 %), Fe (59.11-99 %), K (3.56-4.4 %), Na (2.27 %), Ni (7.8-89.79 %), Pb (78.86-84.13 %), Si (51.6-81.55 %), Zn (45.46-95.04 %), Cl (8.52-30.34 %) and SO_4 (12.34-99.44 %) were transiently removed from the brine solution at some stage (L/S ratio) by Secunda fly ash while species such as Ba, Ca, Cr, Mo and Sr were leached from Secunda fly ash into the brine solution in significant quantities. In the case of Tutuka up-flow percolation systems, some species such as B (63.05-80.97 %), Co (15.93-80.69 %), Cu (44.66-74.01 %), Fe (18.9-72.22 %), K (5.33 %), Mg (46.36-99.93 %), Mn (13.85 %), Na (69.41 %), Ni (7.8-89.79 %), Pb (78.86-84.13 %), Si (51.6-81.55 %), Zn (45.46-95.04 %), Cl (8.52-30.34 %) and SO_4 (12.34-99.44 %) were observed to be removed significantly from the brine solution by the fly ash. The sequential chemical extraction tests showed that the concentration of Na was very high in the water soluble and exchangeable fractions, which is an indication that the mobility and availability of this species in the solid residues is high. Fe and Mn were predominant in the iron and manganese and residual fractions. The bulk of the Co, Cu, Ni, Pb and Zn are contained in the residual fraction. These species are not easily mobile under natural environmental conditions except when the pH is very low. This study demonstrates that when fly ash and brine are co-disposed in the real disposal scenario, the captured salt as well as toxic elements could leach and contaminate the environment. Despite several studies that have been carried out on fly ash, no study has been carried out on the interactions of fly ash and brine with the aim to determine the possibility of using fly ash as a sustainable salt sink. This study has been able to prove that fly ash, though could be used to remove some species from brine solution to certain extent, cannot be used as a sustainable salt sink.

Keywords

Fly ash, anti-scalants in brine, chemical interactions, leaching of contaminant, PHREEQC geochemical modeling, Mineral solubility, Sequential extraction, contaminant mobility

Declaration

I declare that ***Chemical interactions and mobility of species in fly ash-brine co-disposal systems*** is my own work, that it 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.

Ojo Olanrewaju Fatoba **November 2010**

Signed: ……………………………..

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Dedication

This project is dedicated to

The

Almighty God

For sparing my life and seeing me through this great journey

List of Abbreviation

ANC	Acid Neutralization Capacity
ASTM	American Society for Testing and Materials
SI	Saturation index
EC	Electrical Conductivity
TDS	Total Dissolved Solids
IC	Ion Chromatography
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
XRF	X-ray Fluorescence
XRD	X-ray Diffraction
SEM-EDS	Scanning Electron Microscopy-Energy Dispersive X-ray Spectroscopy
AMD	Acid Mine Drainage
SFA	Secunda Fly Ash
TFA	Tutuka Fly Ash
UB	Unreacted Brine
RO	Reverse Osmosis
ED	Electro Dialysis
EDR	Electro Dialysis Reversal
VC	Vapour Compression
IAWG	International Ash Working Group
TCLP	Toxicity Characteristic Leaching Procedure
SGLP	Synthetic Groundwater Leaching Procedure
MSW	Municipal Solid Waste
WHO	World Health Organization
COD	Chemical Oxygen Demand
MF	Micro-Filtration
UF	Ultra-Filtration
NF	Nano-Filtration
AAS	Atomic Absorption Spectrometry
GFAAS	Graphite Furnace Atomic Absorption Spectrometry

List of Abbreviation

SHMP	Sodium Hexametaphosphate
PPN	Polyphosphonate
PMA	Polymeleic Acid
ZLD	Zero Liquid Discharge

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Chapter 1

Introduction

1 Introduction

This chapter deals with the introduction to the study. The background of the study, the problem statement, aims and objectives, research questions and research approach are presented in this chapter.

1.1 Background

Fly ash, a non-volatile, incombustible, thermally altered mineral matter, is a waste product generated from the combustion of coal for power generation. South Africa is one of the countries that largely depend on combustion of coal to generate electricity, and this has resulted in the production of huge amounts of fly ash as waste product. For instance, ESKOM, South Africa's power utility produces approximately 40 Mt of fly ash annually (ESKOM report 2009) while SASOL Synfuels at Secunda produces 3 Mt fly ash and 7 Mt gasification ash annually. The large quantities of fly ash that are produced annually in some countries (including South Africa) as a result of an increase in coal combustion are disposed of in landfills, slurry pond or ash dumps. Only small amounts have been beneficially used (Iyer, 2002; McCarthy and Dhir, 1999; Iyer and Scott, 2001; Petrik *et al.,* 2005; ESKOM report, 2007). Fly ash generated from power stations contains some soluble oxides such as CaO and MgO, and the high pH values of the fly ash are attributed to these oxides (Choi *et al.,* 2002; Reardon *et al.,* 1995). The chemical composition of fly ash is typically made up of major elements such as Si, Ca, Al, Mg, Fe, Na and K, alongside various trace elements such as Co, Cd, As, Se, Zn, Mo, Mn, Pb, B, Cu and Ni (El-Mogazi *et al.,* 1988; Rubio *et al.,* 2008). The chemical composition of fly ash is said to be a function of the origin and type of feed coal, combustion sequence, method of collection, storage and climate (Adriano *et al.,* 1980; Steenari *et al.,* 1999).

The heat generated through combustion of coal in thermal power stations is used to heat up water in the pipes surrounding the boiler room in order to generate steam to rotate the turbines. The spent steam from the last stage of the turbine becomes concentrated with dissolved elements (salts) before it is condensed back into water as part of the generating process. The condensation is accomplished by circulating cooling water through the turbine condensers. Most power stations use raw water from rivers, underground water from coal mines which is highly concentrated with soluble salts, and treated sewage water as "make-up" water for the cooling water systems. The mine and river waters also introduce salts into the cooling water systems. These salts must be removed on a continuous basis in order to prevent accumulation of salts (Eskom Fact Sheet number CO 0001, 2008), to reduce the quantity of waste generated and to conserve water. The removal of the salts from the wastewaters is called desalination, which can be achieved by a process known as reverse osmosis or electro dialysis reversal. The conventional wastewaters treatment and desalination processes such as biological oxidation techniques (Gogate and Pandit, 2004a), reverse osmosis (RO), electro dialysis reversal (EDR), vapour compression (VC) (Slesarenko, 2003; Turek *et al.*, 2007), ultrafiltration and other membrane methods (Benítez *et al.,* 2008) are mostly employed to treat wastewaters for the purpose of producing much cleaner water for re-use. In addition to the production of cleaner water, these techniques also result in the production of streams of reject waters that are highly concentrated with soluble salts, and these effluents are referred to as brines.

Brines contain major species such as Na, K, Mg, Ca, Fe, Si, Se, Cl and SO_4 in high concentration and many other trace elements. According to Mooketsi *et al.* (2007), typical brines from Secunda power plant in South Africa contain major elements such as Na, Cl, Ca, SO_4, K, Mg, and trace elements such as Fe, Mn, Cr, V, Ti, P, Si, and Al. The composition of reject brine water from desalination plants in the Gulf region was reported in the study done by Ahmed *et al.* (2000). The pH values of the brines were reported to range between 6.7 and 8.2 while the electrical conductivity (EC) ranges between 11.33 and 79.6 mS/cm. The concentrations of the major species were high with Ca having values ranging between 173 and 1400 mg/L, Mg (282-7700 mg/L), Na (2315-18293 mg/L), SO_4 (1500-4800 mg/L) and Cl (4572-31905 mg/L). Brine contains different contaminants that must be removed before disposal in order to reduce its negative impact on the environment. The disposal of brine is costly because of its makeup and the large volumes that must be handled.

Despite the call for waste minimization/zero waste strategies in developing countries (Matete and Trois, 2008), which has led to the utilization of fly ash in a range of applications such as, a substitute for cement in concrete, as highway road basis, land remediation, synthesis of zeolites (Somerset *et al.,* 2005) and other beneficial uses, sufficiently large amounts of fly ash are not utilized. This has made the disposal and management of fly ash produced by coal-fired power plants a major problem in many parts of the world including South Africa. The disposal of fly ash constitutes a problem not only because of the large volumes generated (Iyer, 2002) but also because of the possibility of releasing toxic species to the environment (Baba and Kaya, 2004; El-Mogazi *et al.,* 1988; Travar *et al.,* 2009; Takeuchi *et al.,* 2009; Baba *et al.,* 2008). Due to the large quantity of ash generated and the need for its safe disposal, many countries have devised different methods of ash disposal. According to Sushil and Batra (2006) and Haynes, (2009), there are two different methods of fly ash disposal. These are wet and dry disposal techniques. Wet disposal technique is a process whereby the ash collected from the precipitators is mixed with water and pumped as slurry to an ash dump, while the dry disposal technique is the disposal of ash with little or no addition of water; in this case the ash is conveyed and stacked on surface. South African power stations employ two different methods of disposing fly ash; these are the dry and dense slurry disposal techniques. In Secunda (SASOL) power station for instance, the ash is added from the hoppers to a stirring tank with continuous addition of wastewaters/brines to form slurry with controlled density. This is then pumped continuously via pipes to the ash dam where the ash particles immediately settle out and the ash-water is either drained away via a penstock to the clear ash effluent dam, or percolates through the ash dam and is collected in a toe drain. The case of Tutuka (ESKOM) power station is different in that the fly ash from the precipitators is moistened with small amounts (about 16 %) of brine to suppress dust from the ash particles and is then taken to the ash dumps via conveyor belt for disposal. At the ash dump, the ash is irrigated with brine (generated from water treatment plants) to keep the ash moist for dust suppression and for the purpose of disposing brines.

The high pH and the high surface area of South African class F fly ash have been observed to contribute to the reactivity of fly ash species when in solution (Gitari *et al.,* 2009). Fly ash leachates, in most cases, are alkaline with pH ranging between 11 and 13. The dissolution and hydrolysis of oxide components such as CaO and MgO in fly ash contributes to its high pH value. The dissolution of soluble acidic oxides, such as B_2O_3; and salts containing hydrolysable constituents, such as $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ may contribute to lower pH values that are observed in some fly ashes (Reardon *et al.,* 1995). The reactivity of fly ash is determined by the particle size vis-à-vis the surface area. The smaller particle has a larger specific surface area, and the larger surface area is more susceptible to hydrolysis. According to several studies (Iyer, 2002; Yan, 1998; Choi *et al.,* 2002; Gitari *et al.,* 2009), about 1-3 % of the fly ash material is highly soluble in water with lignite fly ashes having a higher proportion of water soluble constituents. There are various interactions that occur when fly ash and water are in contact; these include precipitation/dissolution, complex formation, adsorption/desorption and redox reactions (Zhang *et al.,* 2008; Cornelis *et al.,* 2008). Various factors, including the above mentioned interactions, control the mobility of major and minor elements in the solution of fly ash (Gitari *et al.,* 2009). The concentration of elements in fly ash, the distribution of the elements in different mineral phases contained in the ash and the incorporation of the elements into secondary solid phases as a result of weathering reactions also determine the rates and amounts of elements released into solution during leaching (Ilic *et al.,* 2003). Studies on the behaviour of species in solution of fly ash and the reactions controlling the release of some elements into solution show that the concentration of most of the species in solution is controlled by the formation of secondary mineral phases at favourable conditions (Roy and Griffin, 1984; Fruchter *et al.,* 1990; Tiruta-Barna *et al.,* 2006; Eary *et al.,* 1990; Mattigod *et al.,* 1990; Gitari *et al.,* 2009). However, the long term stability of these secondary mineral phases is not understood. Due to the reactive nature of the species in fly ash, studies have been conducted on the reaction of fly ash with acid mine drainage (AMD) with the aim of using fly ash for the treatment and removal of major contaminants and trace metals from the AMD (Gitari *et al.,* 2006). Carbonation of municipal solid waste (MSW) (which has similar chemistry as fly ash) has been carried out with the aim of stabilizing the species in ash and to reduce the availability of species to the environment. These studies (Ecke, *et al.,* 2003; Li *et al.,* 2006; Meima *et al.,* 2002; Todorovic *et al.,* 2006) have detailed the effect of carbonation of MSW on the mobility of trace and major elements. According to the studies, the mobility of some species in the carbonated fly ash was found to decrease when factors such as partial pressure of CO_2, reaction time, temperature and pH were taken into consideration. The reactive behaviour of brine components under different physical and chemical conditions is largely unknown. Some studies (Kaszuba *et al.,* 2005; Soong *et al.,* 2006; Ramírez-Hernández and Garcia, 2004; Druckenmiller and Maroto-Valer, 2005) have been done on carbon sequestration using brine, which showed that brine can be used to trap CO_2. According to Soong *et al.,* (2006) and Druckenmiller and Maroto-Valer, (2005), the injection of CO_2 into saline aquifers could lead to storage of CO_2 by hydrodynamic and/or mineral trapping. In the mineral trapping, CO_2 was observed to be converted into carbonate minerals by a series of reactions with aqueous ions found in the saline aquifer. Despite these studies, no study has been reported on the reaction of brine with fly ash to actually understand the reactivity of brine components and to determine the impact of co-disposing brine and fly ash on the environment. It is expected that this study would contribute to a better understanding of the chemistry of the fly ash-brine interactions with a view to assessing its impact on the environment within a co-disposal system in South Africa.

1.2 Study area

Two South African coal-fired stations have been chosen as the study area for this research. These coal-fired stations are SASOL Synfuels at Secunda and ESKOM power station at Tutuka. These coal-fired stations were chosen not only because they co-disposed fly ash and brine but as a result of their different co-disposal techniques. SASOL Synfuels at Secunda practice wet disposal while ESKOM power station at Tutuka practice dry disposal. Fly ash is mixed with brine before being hydraulically transported and disposed in slurry form at the ash dumps in SASOL Synfuels (Secunda) at 70-80 % liquid/solid (L/S) ratio, while at ESKOM (Tutuka) power station, a small amount (about 16 %) of brine is added to moisten the fly ash before disposal to the dumps to aid dust suppression. At the ash dump in Tutuka, the disposed moistened ash is irrigated with brine. Fly ash samples from Secunda coal-fired station was taken directly from the precipitators while the fly ash samples collected from Tutuka coal-fired station had been contacted with some amount of brine before the collection. The brine sample used in this study was collected from the reverse osmosis (RO) desalination plant at ESKOM power station in Tutuka, South Africa. The brine sample was collected in plastic containers and stored in the refrigerator at 4 °C.

Secunda and Tutuka power stations were selected due to their different modes of ash disposal (wet and dry) and the fact that brine solutions are used to hydraulically transport fly ash and suppress dust respectively. Brine from Tutuka power station was used for consistency.

1.3 Problem statement

The focus on waste minimization and water conservation in recent years in the developing countries has resulted in the generation of concentrated or toxic residues as wastes from treatment technologies. It is of utmost important to dispose of both solid and liquid wastes in a sustainable manner in order to keep the environment safe in accordance with the environmental laws. The constraints and difficulties encountered in keeping the concentration of species in brine to a minimum level before disposal and the high cost of brine disposal has caused some power stations in South Africa to consider the option of co-disposing brine and fly ash. For instance, SASOL Synfuels at Secunda uses brine to slurry fly ash while ESKOM power station at Tutuka uses brine to moisten fly ash for dust suppression before disposal at the dump. Brine and fly ash contain toxic elements which may migrate to the soil and groundwater on disposal. The disposal of brine and fly ash may cause long-term health, environmental and land-use problem and thus prove to be unsustainable. This is due to weathering and leaching processes which may lead to the mobilization and release of high concentrations of major, minor and trace elements when brine impacted ash dumps are in contact with aqueous solutions such as infiltration by rainwater. Unfortunately, no study has been carried out to understand the leaching or stabilization of species when these South African fly ashes interact with brine solution in a co-disposal system.

1.4 Research questions

This study aims to address the following questions;

- How do the interactions of South African fly ash and brine affect the leachability of major and trace elements from the fly ash-brine systems?
- What are the geochemical factors that may influence the release of major and minor species from the fly ash-brine systems?
- What are the likely mineral phases that are likely to form as a result of fly ash-brine interactions?
- Do the secondary mineral phases formed disintegrate over time to release contaminants on continuous interactions with aqueous solutions?
- What is the effect of anti-scalants in brines on the interactions of species in the ash-brine systems?
- Can fly ash be used as sustainable salt sink for brine when the two waste materials are co-disposed?

1.5 Aims and objectives

The aims of this study are; 1) to provide a detailed insight into the leaching and removal of major and trace elements from fly ash-brine systems, 2) to assess the possibility of using South African fly ash as sustainable salt sink for brine, and 3) to understand the mobility of major and minor species when fly ash and brine are co-disposed.

The objectives of this study include the following;

- Understanding the interaction chemistry in fly ash-brine systems and the impact of the interactions on the release of species from the fly ash-brine systems.
- Understanding the trends of leaching of the major and minor species from fly ash-brine systems.
- Identifying mineral phases if any, that may form as a result of the interactions between fly ash and brine.

- Understanding the stability of the secondary mineral phases that may form during the fly ash-brine interactions.
- Understanding the influence of anti-scalant on the interactions and the release of species in the fly ash-brine systems.
- Understanding the mobility of major and minor species after the fly ash-brine interactions.

1.6 Research approach

The research approach used in this study in order to achieve the aims and objectives of the study are highlighted below.

1.6.1 Characterization of fresh fly ash and unreacted brine samples

XRF, XRD, SEM-EDS, ICP-MS and IC analyses were carried out on the fresh fly ash samples and the brine samples to determine the chemical and mineralogical compositions of the waste materials and to establish baseline data.

1.6.2 Batch reaction tests involving brine and fly ash

Different conditions such as brine concentration, contact time and liquid/solid (L/S) ratios of the fly ash-brine systems were considered. This was to understand the effect of these parameters on the release of major and minor species during the fly ash-brine interactions. ICP-MS and IC analyses were done on the leachates to determine the effect of the interactions on the brine quality. Mass balance calculation was done. PHREEQC geochemical modelling software was used to calculate the saturation indices using the data from the ICP-MS and IC in order to give an insight into solubility controlling the release of major and minor species in the fly ash-brine systems.

1.6.3 Long-term fly ash-brine interactions: Effect of leachant pH on the release of species.

Fresh fly ash was reacted with brine for some periods of time varying from 1 week to 12 months. This was done in a closed and static system to simulate the dry co-disposal scenario in Tutuka power station. The L/S ratio of the long-term fly ash-brine interaction systems is 1:1. The solid residues from the long-term fly ash-brine interactions were leached with solutions of different pH for a period of 48 hours. This was to understand the mobility of species in the solid residues when in contact with solutions of different pH values.

1.6.4 Up-flow percolation systems (column study)

The up-flow percolation test was carried out to simulate the co-disposal scenario at Secunda coal-fired station where fly ash and brine are co-disposed in slurry form. Fresh fly ash was packed in a column and brine was introduced in an up-flow direction for a period of 6 months. Samples were taken from the leachates at intervals to determine the species that were leached during the interaction of fly ash with brine over time.

Fresh fly ash was also packed in a column, and brine mixed with anti-scalants was introduced continuously into the fly ash in an up-flow direction for a period of 6 months. This was to determine the effect of anti-scalants on the degree of secondary mineralization and the release of species in the fly ash-brine systems.

ICP-MS and IC analyses of the leachates from the up-flow percolation tests were done to determine the concentrations of species released into solution during the percolation test. The sequential extraction test was carried out on the solid residues to determine the physicochemical forms and the mobility of the trapped species.

1.6.5 Analysis of the solid residues from the column study

XRF, XRD and SEM-EDS analyses of the solid residues were carried out. This was to determine the chemical compositions and the secondary mineral formation due to the fly ash-brine interactions.

1.7 Outline of the subsequent chapters

Apart from the chapter one which contains the introduction to this study, this thesis consists of six more chapters which are outlined below;

Chapter 2: A literature review

The chapter deals with the review of the literature. It reviews the morphology, mineralogical and chemical compositions of fly ash. Types of fly ash, ash-water interaction chemistry, disposal, environmental impacts and utilization of fly ash are also discussed in this chapter. The chapter also reviews literature on brine and its chemical composition, waste treatment processes, disposal of brine, scale formation, addition of antiscalants into brine and geochemical modeling.

Chapter 3: Sampling and Analytical Methods

The sampling, experimental and analytical methods used in this study are presented in chapter 3.

Chapter 4: Fly ash-brine interactions: characterization and batch reaction tests

Chapter 4 presents and discusses the results of the characterization carried out on the fresh fly ashes and the brine solution. The results of the batch reaction tests are discussed in this chapter. This chapter also discusses the geochemical modeling carried out to predict the solubility controlling the release of species from the fly ash-brine batch reaction systems.

Chapter 5: Long-term fly ash-brine interactions: A closed and static system

The results of the long-term fly ash-brine interaction experiments are discussed in chapter 5. The results of the characterization of the solid residues are presented and discussed. The results of the acid neutralization capacity (ANC) tests carried out to determine the mobility of species in the solid residues are presented and discussed in this chapter.

Chapter 6: Removal of major and minor species from fly ash-brine systems: Up-flow percolation test

The results of the up-flow percolation tests showing the release of major and minor species from the fly ash when brine was continuously introduced are presented and discussed in chapter 6. The results of the characterization of the solid residues are also discussed in this chapter.

Chapter 7: Conclusion and Recommendations

The summary and the conclusions of the study showing the overall effect of fly ash and brine co-disposal techniques on the release of species are contained in chapter 7. The recommendations for future work are made in this chapter.

Chapter 2

Literature Review

2 Introduction

This chapter deals with the review of literature on the generation of fly ash and brine, physical, chemical and mineralogical compositions; utilization, disposal and environmental impacts of fly ash and brine.

2.1 Fly ash

Fly ash is a by-product generated from coal combustion in power generation utilities. Fly ash was defined by South African Bureau of standards (SABS) (2002) as the powdery residue obtained by the separation of the solids from the flue gases during combustion of pulverized coal. Fly ash is a non-volatile, incombustible, thermally altered mineral matter comprising of the inorganic constituents that were initially contained in coal (Scheetz and Earl, 1998). Fly ash is the most abundant residue among other residues such as flue gas desulphurization (FGD) sludge, fluidized bed boiler (FBB) waste, slag and bottom ash (Adriano *et al.,* 1980) that are generated from the combustion of coal for power generation. It was observed that approximately about 80 % of the solid residue released from the combustion of coal is released as fly ash, while the rest consist of larger particles that are retained within the furnace as bottom ash (Jankowski *et al.,* 2006).

Fly ash is generated in large quantity in most countries of the world as a result of increase in the demand of electricity. Studies on coal consumption indicate that the combustion of coal to generate electricity will continue for the next several decades, which will eventually result in the generation of more fly ash. Several countries including South Africa generate huge amounts of fly ash annually. For instance, According to the American Coal Ash Association, (1998), USA generated 102 million tons (Mt) of coal combustion products in 1996, out of which fly ash was 59 million tons, but only 25 % of this fly ash was utilized (Duchesne *et al.,* 1999). In South

Africa, according to ESKOM report (2009), South Africa's largest power producing company, ESKOM, generates approximately 40 Mt of fly ash annually of which only 5 % is currently utilized, the rest being disposed of in the ash dams, landfills or ponds (Petrik *et al.,* 2005) while SASOL Synfuels at Secunda produces 3 Mt fly ash and 7 Mt gasification ash annually. The amount of fly ash generated in Korea was 4.43 Mt in 2000, out of which 54.62 % (2.42 Mt) was recycled and the rest was used in land filling (Korea Annual Report, 2001). Large quantities of fly ash produced annually by power stations in most countries including South Africa due to the increase in demand for electricity are disposed of in landfills, slurry pond or ash dumps, with only small amounts been productively used (Iyer, 2002; McCarthy and Dhir, 1999; Iyer and Scott, 2001; Petrik *et al.,* 2005; ESKOM report 2007).

2.2 Types of fly ash

Coal fly ashes are classified by American Society for Testing and Materials (ASTM) into class F or C by their aggregate alumina, silica, and ferric oxide contents. The distinction between Class F and Class C fly ash is based on the sum of the total silica, aluminium and iron oxides (SiO_2 + Al_2O_3 + Fe_2O_3) in the ash. When the sum is greater than 70 % an ash is classified as Class F. When the sum is between 50 % and 70 % the ash is classified as Class C (ASTM C 618, 1993).

Table 2.1 shows the ASTM standard classification of fly ash. Type C fly ash is produced by burning of lignite coal and contains more lime (18 %) (Iyer, 2002). Type C ashes are generally produced from the combustion of lower rank coals and contain more calcium in their bulk chemical compositions. Due to the higher calcium content in fly ash, the assemblage of the resulting mineralogical phase is quite different (Scheetz and Earl, 1998). Class C fly ash, in addition to having pozzolanic properties, also has some cementitious properties (ASTM C 618-1993).

Table 2.1: 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 burning of anthracite, bituminous or sub-bituminous coal produces type F fly ash. It has low lime content (<7 %) and more silica, alumina, and iron oxide (Iyer, 2002). Class F coal fly ashes are generated from the combustion of higher rank coals (coal which have lower calcium content). This fly ash (class F) possesses little or no cementitious value but in finely divided form and in the presence of moisture, will chemically react with calcium hydroxide at ordinary temperature to form cementitious compounds. The bulk chemical composition of class F ash dictates the mineralogical constituents of the ash. The most abundant phases in a class F fly ash are the glass that results from the melting of the clays and subsequent exsolution of mullite from the melt (Scheetz and Earl, 1998).

2.3 Physical characteristics of fly ash

Fly ash consists of very fine particles ranging in size from 0.01 to 100 µm, and these fine particles are spherical in shape. Fly ash particles are glassy and transparent due to the melting of the silicate materials during combustion (Young, 1993; Adriano *et al.,* 1980). The heating and cooling processes during coal combustion have a significant effect on the physical characteristics of fly ash. During combustion, at a very high temperature, the minerals in coal become fluid after which the minerals become cool rapidly at the post-combustion zone. The rapid cooling in the post-combustion zone therefore results in the formation of spherical and amorphous particles of fly ash (Kutchko and Kim, 2006). The fineness of fly ash particles was also reported by Campbell (1999) to be dependent on the combustion temperature and the size of pulverized coal introduced into burners while the spherical shape of fly ash is as a result of cooling and solidifying of molten droplets of inorganic coal residues after combustion. The spherical particles of fly ash could be hollow (cenospheres) or filled with smaller amorphous particles and crystals (plerospheres) (Adriano *et al.,* 1980). Apart from the spherical shape of the fly ash particles, fly ash has different colours ranging from water-white to yellow, orange to deep red, or brown to opaque. These colours, according to Adriano *et al*. (1980), could be influenced by the iron-rich fractions of fly ash. The colour of fly ash could also vary from tan to grey to black, depending on the amount of unburned carbon in the ash. The lighter the colour, the lower the carbon content of fly ash (Adriano *et al.,* 1980).

Fly ash in some cases has a smooth, hydrophilic surface and is extremely porous; some particles are edgy and rough on a micro scale while others may be partly covered with a powder condensed from a vapour phase after solidification (Campbell, 1999; Bosch, 1990; Iyer, 2002). The smooth and hydrophilic surface of fly ash particles has been reported to contain higher amounts of CaO which will easily dissolve into solution at a faster rate than the elements locked in the glass matrix (Mattigod *et al.,* 1990; Choi *et al.,* 2002; Reardon *et al.,* 1995). The morphology of fly ash can be related to the reactive properties of the fly ash. Particle morphology is one of the most important aspects of fly ash that has to be considered. The particle size distribution and the specific surface area provide quantitative information that is utilized in evaluating the interactions between fly ash and aqueous solution (Roy *et al.,* 1985). Studies by Iyer (2001) also indicated that fly ash particle size and the surface area are important characteristics in determining reactivity of fly ash. The smaller particle has a larger surface area, which makes available a large area for the adsorption of volatile elements during coal combustion. Hence, a large area is susceptible to hydrolysis when in contact with aqueous solution. In addition to the initial surface area of fly ash, changes in surface area as the reaction progresses are also important in a long term leaching process (Saikia *et al.,* 2006).

2.4 Chemical composition of fly ash

Fly ash is generated in huge amounts during combustion of coal for the production of electrical power in power generating stations, especially when low-grade coal is burnt like the case of South Africa where brown coal is burnt to generate electricity (Burgers, 2002; Bezuidenhout, 1995; Petrik *et al.,* 2003). The properties of the ash depend on physico-chemical properties of coal, coal burning process and other factors (Saikia *et al.,* 2006) which include source of coal. The chemical composition and the properties of fly ash are also a function of the origin and type of feed coal, combustion sequence and method of collection, storage and climate (Adriano *et al.,* 1980; Young, 1993; Steenari *et al.,* 1999). The chemical composition of fly ash is typically made up of elements such as silicon, calcium, aluminum, iron, magnesium, and sulphur oxides, along with carbon and various trace elements like Co, Cd, As, Se, Zn, Mo, Mn, Pb, B, Cu and Ni. These elements are found in the ash because of their high melting points and the short time the ash particles actually remain in the furnace during combustion. During the combustion process, because of the high temperature, the inorganic minerals melt and become fluid or volatile or react with oxygen, and on cooling, they form crystalline solids, spherical amorphous particles or condense as coating on the particles (Kutchko and Kim, 2006).

Many of the trace elements present in fly ash show a definite concentration trend with decreasing particle size. Elemental distribution in fly ash generally falls into three categories: (1) elements that are enriched in the fly ash, occurring at higher concentrations in smaller ash particles, (2) elements that are partitioned equally between bottom ash and fly ash, and show no concentration effect with particle size; and (3) elements that are intermediate between the first two categories. Those elements that are enriched in fly ash relative to bottom ash are primarily found in sulphide minerals that volatilize completely during combustion at furnace temperatures of between 1,300-1,600°C. As the flue gases progress farther up the stack, the temperature drops and these elements condense on particles composed of non-volatile ash components such as Si, Al and Fe. These non-volatile elements tend to be partitioned equally between fly ash and bottom ash and are generally found in silicate minerals (e.g. micas and feldspars), which have boiling points higher than furnace temperatures (Theis and Wirth, 1977).

Some of the mineral elements such as Na, Fe and Si in coal get volatilized due to the combustion temperature, and these elements are in higher concentrations relative to those found in the parent coal. Aluminium, calcium and iron occur in concentrations typical of soils. Sodium is present in concentrations generally exceeding those found in soil (Murarka *et al.,* 1991).

Fly ash is also enriched with sulphur when compared to soil. The sulphur content of the parent coal plays a role in the pH of fly ash which could range between 4.5 and 12 (Mattigod *et al.,* 1990). The increase in sulphur enrichment of fly ash could be due to the addition of conditioning agents such as sulphur trioxide, or sodium sulphate in order to improve the collection efficiency of electrostatic precipitators and this addition has the tendency to alter the ash chemical composition. Campbell (1999) reported that sulphur trioxide (SO_3) is the most popular additive used in South Africa to enhance collection of fly ash from electrostatic precipitator.

2.5 Mineralogical composition of fly ash

The mineralogy of fly ash refers to both amorphous and crystalline phases and other mineral fractions in the fly ash. Fly ash is a complex mixture of different minerals and high amounts of toxic elements are associated with these minerals (Saikia *et al.*, 2006). The major mineral phases that have been commonly identified in fly ash include: quartz (SiO_2); mullite, ($Al_6Si_2O_{13}$); tricalcium aluminate, $Ca_3Al_2O_6$; alite, (Ca_3SiO_5); belite (Ca_2SiO_3); magnetite, (Fe_3O_4); hematite, (Fe_2O_3); lime, (CaO); anhydrite, ($CaSO_4$); periclase, (MgO); melilite, ($Ca_2(Mg,Al)(Al,Si)_2O_7$); merwinite, ($Ca_3Mg(SiO_4)_2$, calcite ($CaCO_3$), pyrite (FeS_2) and thenardite, (Na_2SO_4) and a small portion of unburned carbon (Tishmack and Burns, 2004; Adriano *et al.,* 1980; Steenari *et al.,* 1999). Most of the quartz in fly ash originates from coal as silt and sand sized particles and it remains in the ash because it survived thermal transformation during combustion (Helmuth, 1987). Although bituminous coal ash may contain more than 50 wt% of SiO_2, only about 5-10 wt% is present as quartz (McCarthy *et al.,* 1990). Some Si is present in mullite but a greater portion of the Si is found in the amorphous glass phase (Tishmack and Burns, 2004). Mullite is the principal Al-bearing mineral in low-Ca bituminous coal. It originates from direct crystallization of clay minerals or by devitrification of glass on cooling (Hubbard *et al.,* 1984). South African coal ashes have high quantities of mullite because low-Ca bituminous coal which is rich in kaolinite is utilized during combustion. Fly ash with high Ca content contains lower amounts of mullite because of the presence of mica-illite or smectitic clays in their parent coal and also because some of the Al combines with Ca to form $Ca_3Al_2O_6$ (Tishmack and Burns, 2004). The principal Fe-oxides minerals in coal ash are magnetite (Fe_3O_4) and hematite (Fe_2O_3). Magnetite results mainly from the volatilization and oxidation of iron bearing minerals in coal, mainly pyrite (FeS_2). Hematite crystals survive the brief exposure to high temperature like quartz while pyrite is oxidized to magnetite with the release of SO_2. About a third to half of the Fe present in fly ash is in the form of magnetite and hematite, which are largely inert (McCarthy *et al.,* 1990). The rest is contained in the glass phase and becomes available when the glass dissolves (Helmuth, 1987). In addition to quartz, mullite and hematite, moderate to high Ca fly ashes contain other calcium bearing minerals which are reactive in the presence of water. The most common is $Ca_3Al_2O_6$ which occurs with Ca-aluminate-rich glass (Tishmack *et al.,* 1999). The principal Mg phase, periclase (MgO) is about half of the Mg present in sub-bituminous and lignite fly ashes. Magnesium is also found in melilite and merwinite, neither of which is known to significantly react with water (Tishmack and Burns, 2004). Most of the S in fly ash is in the form of anhydrite, which forms as a solid on the surface of the sub-bituminous and lignite fly ash particles (McCarthy *et al.,* 1989). Sulphur accumulates on the surface of fly ash particles from reactions between Ca, Na, O and SO_2 as the fly ash leave the hot part of the furnace and enter low temperature zones (Fishman *et al.,* 1999). Small amounts of anhydrite have been observed in fly ash with CaO content as low as 12 % (McCarthy *et al.,* 1989).

The most abundant phase in a class F ash is the glass that results from the melting of clays and subsequent exsolution of mullite from the melt. Major minerals in class F fly ash are quartz, the ferrite phase and mullite. Because of the higher calcium content of the class C ash, the mineral assemblage is quite different. Quartz, ferrite phase and mullite are present as in class F but the alteration of the clay content of the coal in the presence of calcium results in a suite of silicates, aluminosilicates and oxide phases instead of large amounts of glass. Only a minor amount of glass is formed which contains a rather high concentration of alumina. It is chemically, extremely reactive. Most notable among the mineral phases are lime, di-calcium silicate and tri-calcium silicate, periclase, gypsum/anhydrite can also be found (Scheetz, 2004). Studies have revealed that the mineralogical analysis of fly ash showed 70-90 % of the particles to be consisting of amorphous ferro-aluminosilicate glassy spheres (Solem and McCarthy, 1992;

Spears, 2000). The glass is generated from clay minerals such as feldspar, mica, chlorite and any other easily melted minerals (Hulett *et al.,* 1980; Spears, 2000). The crystalline phase present in fly ash consist of quartz (SiO_2), mica, chlorite, feldspars, mullite ($3Al_2O_3.2SiO_2$), spinel ($FeAl_2O_4$), haematite (Fe_2O_3) and magnetite (Fe_3O_4) depending on the mineralogy of the feed coal (Norton *et al.,* 1986; Vassilev and Vassileva, 1997; Vassileva *et al.,* 2005; Kutchko and Kim, 2006). Sakorafa et al, 1996 in the study carried out on the fly ash from Megalopolis lignite field, Peloponnese (Southern Greece) reported the main minerals present in the fly ash to be quartz, anhydrite, plagioclase, haematite, gehlenite and calcite. The presence of lime, alkali feldspars, bassanite, gypsum, mica and unburnt lignite are found in minor and trace amounts. Erol *et al.,* 2000, in their study on the fly ash obtained from çayirhan thermal power plant, Turkey, reported the presence of quartz, mullite, enstatite, anorthite and haematite as the major mineral phases present in the ash. Volatile elements released from the coal matrix during combustion enter into the vapour phase. As they cool, these gaseous compounds may condense into very small spherical particles and on the surface of other particles leading to surface enrichment of the species (Kim and Kazonich, 2004). In a previous study (Fatoba, 2008) carried out on some South African fly ashes (Secunda and Tutuka fly ashes), the major crystalline mineral phases in both Secunda and Tutuka fly ashes were found to be quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$). Lime and calcite phases were also identified but these phases were present in low amounts. The mineralogical compositions of the ashes from the two power stations are not different and showed a similar composition.

2.6 Utilization of fly ash

Fly ash generated from coal combustion is still under utilized for beneficial purposes despite the huge amounts of fly ash produced in different countries as a result of the increase in coal combustion. For instance, the US power plants which produced about 70 million tons of fly ash annually only utilized 45 % for beneficial purposes (ACAA, 2008). Utilization of fly ash has been investigated by many researchers in order to facilitate its disposal and minimize its negative environmental impacts by considering the chemical composition and leaching characteristics of the fly ash before utilization (Steenari *et al.,* 1999). Fly ash has been found to be useful in some areas despite the high concentration of trace elements and the increased mobility of these elements in weathering environments. Some of the processes and applications of fly ash include addition to cement and concrete products, structural fill and cover material, waste stabilization/solidification, roadway and pavement utilization, addition to construction materials as a light-weight aggregate, infiltration barrier and underground void filling, soil, water and environmental improvement. Some of these applications are discussed in the following sections.

2.6.1 Soils and wastelands amendment

The addition of fly ash to soils has been observed to increase its water-holding capacity and this has contributed to the increased utilization of fly ash. However, the increase in the water-holding capacity of the ash/soil mixtures did not increase the plant available water (Adriano *et al.,* 1980). The hydraulic conductivities of the soils were found to improve even at low rates of fly ash application and deteriorated when fly ash input exceeded 20 % by volume in calcareous soils and 10 % in acidic soils. The reduction of hydraulic conductivity at high application rates was thought to be caused by the pozzolanic reaction of fly ash which tends to cement soil particles when wetted.

The usefulness of fly ash in the stabilization of metal (Cu and Pb) contaminated soil has been investigated by Kumpiene *et al.,* (2007). An evaluation of the changes in Cu and Pb mobility and bioavailability in soils induced by the addition of coal fly ash revealed that the amounts of leached Cu decreased by 98.2 % and Pb by 99.9 %. Metal leaching from the treated soil was found to be lower by two order of magnitude compared to the untreated soil in the field lysimeters. They identified the formation of Cu- and Pb-bearing mineral phases as the factors controlling the mobility of these contaminants in the ash treated soil. They found during their investigation that there was low metal leaching, increased seed germination rate, reduced metal accumulation in plant shoots, and decreased toxicity to plants and bacterial.

Fly ash is also being used in soils management. In Australia (Yunusa *et al.,* 2006), agricultural soils had inherent limitations of a structural and nutritional nature which posed major constraints to crop productivity. Fly ash was applied to reduce the soil acidity and the pH of the soils was found to be raised. The overall effects of fly ash on soil structural and nutritional characteristics was assessed from plant growth, and lint produced by cotton was found to increase by 28 % with application of 3.5 t/ha of fly ash (Stevens and Dunn, 2004), and biomass produced by clovers (*Trifolium subterraneum)* increased almost 3-fold with application of fly ash to sandy loam soil (Summers *et al.,* 1998).

Fly ash application to areas that have been reduced to wastelands after the strip mining of coal has somewhat succeeded in reclaiming the land for agricultural purposes. The spoils are acidic and infertile as a result of the oxidation of the pyretic overburden, only sparse vegetation can be cultivated and as a result extensive erosion occurs. Fresh fly ash applied to these areas greatly improved the fertility and the yield of the crops cultivated (Adriano *et al.,* 1980). According to the study by Taylor and Schuman (1988), comparing the effectiveness of various levels of fly ash and lime in alleviating low pH of mine spoils showed that fly ash can be used as substitute for lime. This is because treatment of the spoils with both fly ash and lime successfully raised the pH and increased the elemental concentrations to the level not toxic to plants.

2.6.2 Additive to cement and concrete products

Fly ash, especially from South Africa, has been found to be a good additive to Portland cement and it has a number of positive effects on the resulting concrete which includes a decrease in the water demand of the concrete (Campbell, 1999; Foner *et al.,* 1999). The principal technical test (strength activity index (SAI)) of the suitability of fly ash for use as pozzolan, carried out on ordinary Portland cement (OPC) with 20 % of cement substituted by fly ash indicated that fly ash from South Africa gives SAI values greater than the minimum values required by ASTM standard (Foner *et al.,* 1999). Due to the smaller particle size of the fly ash particles in comparison to the aggregate, fly ash decreases the air entrainment in the concrete. Fly ash further increases resistance to corrosion and ingress of corrosive liquids by reacting with calcium hydroxide in the cement to form stable cementitious calcium silicate hydrate gel. The less soluble calcium silicate hydrate reduces the possibility of calcium hydroxide leaching from the concrete. The reaction products also lead to the filling of capillary voids in the concrete mixture, thereby reducing the permeability of the concrete (Halstead, 1986; Taylor, 1998). The fly ash spheres act as tiny ball bearings and improves the workability of the concrete. Addition of fly ash, when used in the correct proportions, ultimately results in a greater strength concrete than straight Portland cement (Halstead, 1986). Portland cement consists of four main compounds which react with water, to form products involved in cementation reactions. The four reactants are tricalcium silicate (alite, Ca_3SiO_5), dicalcium silicate (belite, Ca_2SiO_4), tricalcium aluminate ($Ca_3Al_2O_6$), and tetracalcium aluminoferrite ($Ca_4Al_2Fe_2O_{10}$). The hydration reactions of Portland cement generate portlandite according to the following reactions (Taylor, 1998):

$2Ca_3SiO_5 + 6H_2O \rightarrow Ca_3Si_2O_7.3H_2O + 3Ca(OH)_2$……………………................................*2.1*

$2Ca_2SiO_4 + 4H_2O \rightarrow Ca_3Si_2O_7.3H_2O + Ca(OH)_2$...*2.2*

It is this portlandite from reactions 2.1 and 2.2 that reacts with fly ash to produce more of calcium silicate hydrate, which adds more strength to the concrete. The use of fly ash brings about a savings on Portland cement material needed for concrete, resulting in a decrease in project cost. Also, blended cements and concretes containing large proportions of fly ash offer the benefit of CO_2 emissions avoidance by reducing the need for burning of lime.

2.6.3 Neutralization of Acid mine drainage (AMD)

Fly ash utilization in the neutralization of acid mine drainage (AMD) and in the treatment of wastewater has been investigated. According to Gitari (2006); Petrik *et al.* (2005); Klink (2003); Burgers (2002), fly ash can successfully be used to neutralize acid mine drainage (AMD) of pH ranging between 2-4 by reacting different amounts of fly ash with solutions of AMD in a batch set-up. The pH of the resulting solutions were found to be in the range of circum-neutral and alkaline pH values. Gitari (2006) extended the investigation to determine the capacity of the fly ash to remove the major inorganic contaminants with time by reacting acid mine drainage (AMD) with coal fly ash in a 24 hour equilibration time using different FA: AMD ratios to produce neutral and alkaline process waters. The efficiency of elements removal was directly linked to the amount of fly ash in the reaction mixture and to the final pH attained. Most elements were found to attain approximately 100 % removal only when the pH of minimum solubility of their hydroxides was achieved. Several other studies have investigated the potential of fly ash to neutralizing synthetic AMD. In the study undertaken by Klink, (2003), fly ash leachate from an ESKOM power station was used to neutralize synthetic AMD (SAMD). The study showed that the pH of the SAMD can be successfully increased by the addition of fly ash leachate. Fly ash leachates from Sasol and Arnot power stations were reacted with SAMD by O'Brien (2000). He observed changes in the pH of the solutions within a short period of the neutralization reaction.

South African coal-fired power utilities, SASOL-Secunda and ESKOM-Tutuka, are currently mixing brine with the fly ash generated during the combustion of coal with the aim of utilizing the fly ash to capture the 'salt' in the brine. This practice forms the basis for this study which aims to investigate the possibility and sustainability of using the fly ash to remove the major and minor species in brine as assumed by these power utilities.

2.7 Disposal of fly ash

The disposal of fly ash as a by-product of incineration of coal constitutes a greater problem than ash produced from burning of municipal solid wastes, rice husks and tea dusts because of its volume (Iyer, 2002). For instance, in India, Bhattacharjee and Kandpal (2002) reported that the major portion of fly ash produced is disposed in ash ponds and landfills and only 13 % (Iyer and Scott, 2001) is utilized. Due to the large quantity of ash generated and the need for its careful disposal because of its chemical compositions, many countries have devised different methods of ash disposal. According to Sushil and Batra (2006), there are two different methods of fly ash disposal operated by power stations in India. These are wet and dry disposal techniques. In the wet technique, the stacks are connected to the precipitators where the ash is collected before transported to the ash ponds as wet slurry. One of the power stations was reported to be using 100 % dry ash extraction system where the ash is stored in form of ash mounds after which it is sprayed with a polymer layer and vegetation is grown on top of it. South Africa also employs two different methods of disposing fly ash; they are dry and dense slurry disposal. In Secunda power station for instance, the ash is added from the hoppers to a stirring tank with continuous addition of brine to make a slurry with controlled density. This is then pumped continuously via pipes to the ash dam where the ash particles immediately settle out and the ash-water is either drained away via a penstock to the clear ash effluent dam, or percolates through the ash dam and is collected in a toe drain. The ash 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) and the waste product, brine (highly concentrated salt laden), from these treatment processes is again used for hydraulic transport of more ash from the hoppers. The case of Tutuka power station is different in that, the fly ash from the precipitators is moistened with low amounts (about 16 %) of brine and is taken to the ash dumps via conveyor belt for disposal. At the ash dump, the ash is irrigated with brine (generated from water treatment plants) to keep the ash moist.

Despite the different ways of utilizing fly ash and the significant quantities being used in the range of applications, such as a substitute for cement in concrete, as high way road basis, and other positive uses, sufficiently large amounts are not used, which makes the disposal and management of fly ash produced by coal-fired power plants a major problem in many parts of the world. For example, coal-fired plants in Bosnia and Herzegovina and Serbia (formerly Yugoslavia) produce approximately 5000 kt (5 Mt) of ash per year. 20 kt is used in cement industry and for production of paving slabs, building blocks and ready mixed concrete. The remaining ash is disposed of in ash depositories (Ilic *et al.,* 2003; Iyer, 2002). The large volume of unused fly ash is disposed in most cases to hold ponds, landfills and slag heaps (Iyer, 2002). According to Foner *et al.* (1999), Israel used to dispose fly ash generated from power stations by dumping at sea and stockpiled in embankments around the power stations but this could not continue due to legislation prohibiting the disposal.

The indiscriminate disposal of fly ash may cause long-term health, environmental and land-use problems (Ilic *et al.,* 2003; Baba and Kaya, 2004). This is due to the weathering and leaching processes ash undergoes which could lead to the release of high concentrations of trace elements and the increase in the mobility of these elements (Adriano *et al.,* 1980). However, leaching of elements from fly ash can be controlled to a certain extent by adequate waste disposal techniques. One of the ways to ameliorate the negative impact of disposal of fly ash is by rehabilitating ash-holding ponds or dams. This can be done by covering the ash dam with vegetation to prevent wind erosion of ash sediments (Burgers, 2002), as is being practiced in some power stations in South Africa and other countries.

2.8 Environmental effects of fly ash disposal

Fly ash has been considered hazardous to the environment because of the possible release of some toxic species contained in the ash due to weathering. The environmental impacts of fly ash when disposed have been found to include the following; loss of usable land and amenity, effects on plants, effects on soils and potential water pollution. The ash produced in thermal power plants can cause all the three environmental risks - air, surface water and groundwater pollution.

2.8.1 Effects on soils and plants

In South Africa, fly ash is being disposed of either by pumping in a slurry form into settling ponds or stockpiled on land. These disposal practices have resulted in the use of huge areas of land that were originally used for agricultural purposes. Fly ash, on disposal, has both advantages and disadvantages on soils and plants. The environmental effects of fly ash are best exemplified in its application in soils and its effects on plants. Field and greenhouse studies have indicated that many chemical constituents of fly ash may benefit plant growth and improve agronomic properties of the soil (Chang *et al.,* 1977). There are a number of problems associated with the growth of plants on ash deposits, both in relation to vegetation for aesthetic purposes and in terms of reclamation for agricultural purposes. These problems include the lack of essential nutrient such as phosphorous and nitrogen in ash, toxicity caused by high pH and soluble salt concentrations, high boron concentrations, and high concentrations of certain trace elements. The concentrations of S, Mo, and B in plant tissues have been shown to increase consistently with ash application to soil. Al, Se and Sr were also consistently increased (Adriano *et al.,* 1980). Application of fly ash on acidic strip mine soils has been reported to increase the yields of many crops. The increase in soil pH caused by ash application may lead to the deficiencies of Mn, Zn, Cu and Fe (Furr *et al.,* 1978) in crops.

2.8.2 Effects on groundwater

The primary area of concern of this study is the effects of the co-disposal of fly ash and brine on the environment and the potential for groundwater contamination due to leachate produced by weathering ash-brine deposits. The extent to which the disposal of ash actually affects the groundwater quality is largely dependent on the parent coal composition, which determines the ash composition, which in turn determines the concentration of leachable elements. Both the physical and chemical nature of fly ash in the ash dumps has environmental impacts relative to the water quality of the surface and groundwater of the surrounding area. The fine particle size, high pH, and initial highly saline leachate produced by ash deposits are potentially damaging to fauna and flora of the surface water bodies surrounding the ash dams (Smith and Harris, 1987). This concern is based on the elemental concentrations of leachate soluble salts and potentially toxic trace elements such as As, Ba, Cd, Cr, Pb, Hg and Se present in fly ash. According to Eary *et al.* (1990), the rates and amounts of minor elements released to solution during leaching of fossil fuel wastes are influenced by 1) the total concentration of the minor element in the wastes; 2) the distribution of those elements in the solid wastes; and 3) the incorporation of the minor elements into secondary solids formed as a result of weathering reactions. From the study done by Wasay (1992), on the release of toxic elements from fly ash at pH 7 when in contact with water, he found that 40 % of Cr, Hg, and As present in the fly ash was leachable and there is the possibility of these elements penetrating to the groundwater. Unweathered ash deposits have a much greater potential for groundwater contamination than weathered ash deposits. The reason according to Carlson and Adriano (1993) is that for an unweathered ash deposits there is generally a high initial release of soluble salts, followed by a more gradual decline in leachate soluble salt content. The studies carried out by the authors metioned above focused only on the interactions of fly ash with water, and this makes their studies different from this present study which focuses on the fly ash and brine interactions.

2.9 Fly ash-water interaction

The reactivity of fly ash is determined by the particle size. The smaller particle size has a larger specific surface area, and the large surface area is susceptible to hydrolysis. According to several studies (Iyer, 2002; Yan, 1998; Choi *et al.,* 2002), only about 1-3% of the fly ash material is highly soluble in water with lignite fly ashes having a higher proportion of water soluble constituents.

When fly ash is brought in contact with water, it passes through a variety of alteration pathways. The alteration pathway of fly ash and the composition of the water/fluid in contact are a function of the initial chemical and mineralogical compositions of the ash. Ash alteration may also depend on the mobility or retention of metals when constituents of the ash react with water (Fishman *et al.,* 1999; Saikia *et al.,* 2006). There are various interactions that occur when fly ash and water are in contact, which include precipitation/dissolution, complex formation, adsorption/desorption and redox reactions. Various factors, including these interactions, control the mobilization of major and minor elements in the solution. The concentration of elements in fly ash, the distribution of the elements and the incorporation of the elements into secondary solid phases as a result of weathering reactions also determine the rates and amounts of elements released into solution during leaching. Studies on the behaviour of species in solution of fly ash and the reactions controlling the release of some elements into solution have been carried out and many suggestions and predictions have been made. It was suggested by Roy and Griffin (1984) that the concentration of major elements like Al, Ca, Fe, Si in fly ash leachate was controlled by anhydrite, mullite, Al- and Fe-oxyhydroxides. It was affirmed by Roy and Griffin, (1984), Fruchter *et al.,* (1990), Garavaglia and Caramuscio, (1994) that the leaching of Al is controlled by amorphous $Al(OH)_3$ for a pH ranging between 6 and 9, and by gibbsite for pH higher than 9. The release of silicon is said to be governed by the solubility of quartz (SiO_2) at pH lower than 10 and by solubility of wairakite ($CaAl_2Si_4O_{12}.2H_2O$) at higher pH (Tiruta-Barna *et al.,* 2006).

The presence of a non porous continuous outer surface and a dense particle interior can restrict heavy metal leachability from residues. Leaching of trace elements from combustion residues is a very slow process and the solid and liquid phase equilibrium may not be attained even with long leaching times (Saikia *et al.,* 2006; Fishman *et al.,* 1999). The release of As, Mo, and V was observed to be controlled by adsorption/desorption reactions. Cr has been observed to be controlled by $BaCrO_4$ and $Ba(S,Cr)O_4$ while As is suggested to be controlled by $Ba_3(AsO_4)_2$ (Fruchter *et al.,* 1990).

Fly ash leachates, in most cases are alkaline with pH ranging between 11 and 13. The dissolution and hydrolysis of oxide components such as CaO and MgO in fly ash contributes to this high pH value. The dissolution of soluble acids, such as B_2O_3; and salts containing hydrolysable constituents, such as $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ may contribute to lower pH values (Reardon *et al.*, 1995).

In the column leaching carried out by Warren and Dudas (1984) to evaluate the relationship among leachate properties, weathering processes, and solid phase characteristics of alkaline fly ash, they were able to identify a number of solid phases that account for the characteristics of leachate during weathering. The first stages of leaching, characterized by the release of high concentrations of Ca, Na, and K and extreme solution alkalinity, is related to the hydrolysis of CaO and dissolution of highly soluble salts. This, in their conclusion, was responsible for the extreme alkalinity of the initial leachate. They also found that the leachate characteristics after moderate weathering of the ash were due to the release of relatively high levels of Si and Al from the glass phases.

The leaching characteristics of some South African fly ashes when in contact with water were investigated by Fatoba, 2008. The study considered the application of several leaching techniques such as Toxicity Characteristic Leaching Procedure (TCLP), DIN-S4, Acid Neutralization Capacity (ANC), Dissolution kinetic tests and Up-flow percolation tests to understand the leaching behaviour of major and minor species in the fly ash-water systems under different conditions. The study showed that significant concentrations of major and minor species of the fly ashes are easily soluble in aqueous solution. It was also found that at low pH, higher concentrations of major, minor and trace species are released into solutions of the fly ashes while the leaching of some species such as Na is independent of pH. The PHREEQC geochemical modeling data showed that the formation of secondary mineral phases could reduce the release of some elements in the fly ash-water systems. The re-dissolution of the secondary mineral phases formed during the fly ash-water interactions would require aggressive low pH leachants, high flow rate, high recharge and long-term leaching. It was concluded that despite the high concentrations of soluble species or leachable elements in the fly ashes, the leaching of major, minor and trace elements into the soils and the groundwater could be minimized if certain conditions such as avoiding acid rain that could reduce the pH of the ash system are adhered to. The interaction of the fly ash and brine has not been studied. The present study focuses on the interactions of fly ash and brine.

2.10 Leaching tests

Laboratory leaching tests are common tools designed to determine the parameters that control constituent release, evaluate leachability of hazardous constituents and allow the estimation of constituent release out of waste/solid materials. There are different types of leaching tests which usually give different results that reflect some aspects of the leaching behaviour. In the prediction of environmental impacts, the leaching characteristics of the fly ash in aqueous and weakly acidic solutions are most important although many leaching tests use more aggressive leaching media than those which occur in a natural environment. The leaching of combustion residues in an aqueous solution is similar to the situation during the early leaching stages of the waste. The weakly acidic solution is close to some natural leaching media, for example, acid rain. Because little information is available on field verifications of the leaching tests (van der Sloot *et al.,* 1997), most of the tests provide qualitative or semi-quantitative information relating to the relatively short-term leaching of combustion residues.

Leaching tests involve contacting the waste material with a liquid to determine which constituents will be leached by the liquid and released to the environment. Most of the leaching tests available include agitated extraction tests, serial batch tests, flow-through tests, flow-around tests, etc. These different tests are used to address different aspects of leaching such as the physical mechanisms involved, chemical interactions between the waste and the leaching fluid, the kinetics of leaching, leaching as a function of time, etc. (Sorini and Jackson, 1988).

2.10.1 Batch and column leaching tests

Several leaching methods have been applied to study the release of major and minor species from solid wastes, especially fly ash. The leaching tests are broadly divided into two groups; these are batch and column leaching tests.

2.10.1.1 Batch leaching tests

Batch leaching tests typically involve mechanical mixing of a unit volume of water, or an alternative solution, with a unit mass of hazardous waste with the intent to establish pseudo-equilibrium conditions. The goal of equilibrium batch testing is to represent constituent solubility and release over a range of conditions by varying a single parameter such as final extract pH, liquid-to-solid (L/S) ratio, contact time, etc. Once equilibrium is established, release is dependent on the geochemistry of the solid phase and chemistry of the liquid phase rather than on contact time (Lopez Meza *et al.,* 2008).

Extraction procedure (EP) is a batch test developed to classify a solid waste as hazardous, based on some specific organic and inorganic constituents designated in the US Federal Register (USEPA 1980). Toxicity Characteristic Leaching Procedure (TCLP) is another batch leaching test developed in 1984 under the Hazardous and Solid Waste Amendments for the Resource Conservation and Recovery Act (RCRA) (USEPA, 1990). The TCLP method is designed to simulate the leaching a waste will undergo if disposed in an unlined sanitary landfill. It is an agitated extraction test using a leaching fluid (either a sodium acetate buffer solution having a pH of 4.93 or an acetic acid solution with a pH of 2.88) that is a function of the alkalinity of the solid phase of the waste. This method is used by U.S. EPA regulators for the identification and classification of waste as hazardous or non hazardous based on their toxicity. The classification is based on an extensive list of organic and inorganic compounds and covers a wide range of waste types. TCLP is aggressive towards leaching of silver, arsenic, selenium and chromium (Sorini and Jackson, 1988). American Society for Testing and Materials (ASTM) Method D-3987 is an agitated extraction method that uses distilled water as the leaching fluid during 18 hours of contact time with the solid waste. The procedure is designed to rapidly generate a leachate from solid waste that can be used to estimate the mobility of inorganic constituents from the waste under the specified test conditions (ASTM 1995a). German Leach Test (DIN 38414 S4) (Institut fűr Normung, 1984) is an extraction test (batch test) that involves agitation of the ash sample with de-ionized water for a period of 24 hours at a liquid-to-solid ratio 10:1. This method is rapid, simple, reproducible, and applicable to solids, pastes, and sludge. This method is used to assess the readily soluble fractions of metals in the fly ash samples. This method has a number of shortcomings when the experimental conditions are compared with those occurring in nature under field situation. For instance, the liquid-solid ratio of the laboratory test is much higher than what will commonly be observed in field conditions (Ludwig *et al.,* 2005), and the rate of metal release can be highly influenced by shaking. This method is not suitable for the assessment of short-term and long-term effects of ash disposal on groundwater.

Synthetic Groundwater Leaching Procedure (SGLP) is a generic agitated extraction procedure that was developed to simulate natural groundwater conditions with respect to groundwater chemistry, to be site specific, and be directly comparable to the TCLP (Hassett, 1987). This method is similar to the TCLP except that synthetic groundwater is used in place of acetic acid solution or sodium acetate buffer solution. Acid Neutralization Capacity test (ANC) is a test involving reacting fly ash with acid solutions to attain different predetermined final pH. Leaching of trace elements from combustion residues is a very slow process and the solid and liquid phase equilibrium may not be attained even with long leaching times (Ugurlu, 2004). Since fly ash reacts with acidic solutions like acid rain, the buffering capacity of the residues is consumed by neutralizing reactions. An acidic leaching environment is therefore reasonable for some waste disposal conditions. Acid soluble fractions of fly ash also provide some information about the potential leachability of a given element under acidifying conditions. The difference between the acid soluble fraction and the initial, water-soluble fraction may therefore reflect the dissolution behaviours of various constituents in different leaching stages. Some of these batch leaching tests such as ANC will be used in monitoring the leaching of species from the brine/fly ash interaction in this study. Some modification will be done where necessary for the purpose of this study.

2.10.1.2 Columns tests

Column tests are designed to evaluate the release of constituents under either local equilibrium or advection conditions as a function of time. This method involves the flow of liquid through a fixed bed of solid material and the percolated liquid is collected as a function of L/S ratio, which is used as a surrogate for leaching time. When designing a column for leaching test, the flow rate of the liquid passing through the column is an important parameter that needs to be considered.

When the flow rate through the column is low, local equilibrium conditions are considered to control constituent release while at higher flow rates, the column testing could be aimed at determining the rates of constituent leaching during advective mass transport (Garrabrants and Kosson, 2005). Column procedures generally include a liquid to solid ratio which more closely represents a field situation. The mechanism of contacting a fixed body of waste with a transient liquid resembles the leaching mechanism imparted by gravity flow of liquid through a waste disposal site (Jackson *et al.,* 1984). Column tests can account for constituent wash out at lower L/S ratios, and the changes in solubility controlling phases that occur as a result (van der Sloot *et al.,* 2001; Dijkstra *et al.,* 2006). Column leaching testing can be considered a better basis for assessing field impact data than any other available batch test method because it provides a fundamental basis from which to estimate constituent release under a variety of field conditions. Leachate generated by the column method is reportedly more representative of leachate derived from a disposal site than is the leachate from the batch method.

Studies involving leaching of waste materials using both batch and columns have been investigated by several authors. Jackson *et al.* (1984) conducted a comparative study on both batch and column leaching tests by comparing the differences in the concentration of leachate constituents and experimental variation. The study was done to evaluate the advantages and the disadvantages of these test methods. They observed that using a column test for relatively impermeable wastes may be problematic and the results from this test could be highly variable. The batch extraction method offers an advantageous approach to extraction of waste constituents through its greater reproducibility and simplistic design. The batch method can be set up and used routinely by laboratory personnel more easily than the column method. Both batch and column extraction methods were considered effective in generating useful leachate profiles for evaluating potentially hazardous wastes. Although useful data can be produced by these methods, the relative accuracy of predicting levels of analytes leached from landfilled wastes remains uncertain based on these tests.

2.10.1.3 Advantages and disadvantages

Although batch or column testing can be used to evaluate equilibrium-controlled leaching, each of these testing approaches has advantages and disadvantages. Batch testing offers the advantage of simpler design, while column testing provides a closer approximation to leaching processes that occur under field conditions without compromising reproducibility of experiments (Jackson *et al.,* 1984; Caldwell *et al.,* 1990; Kjeldsen and Christensen, 1990; Sawhney and Frink, 1991; Wasay, 1992; van der Sloot *et al.,* 1996; Dijkstra *et al.,* 2006). Column tests are more suitable for prediction purposes, but they are often time consuming, ranging in duration from several weeks to years. Alternatively, batch tests can be carried out in shorter periods of time, varying from several hours to a few days. However, batch tests are often subjected to excessive mobilization of dissolved organic carbon (DOC) and/or colloids that are uncharacteristic for field scenarios (van der Sloot *et al.,* 2003).

2.10.2 Sequential extraction tests

Chemical speciation is the process of determining and identifying specific chemical species or their binding forms. Chemical speciation reveals the availability and mobility of metals in solid materials in order to understand their chemical behaviour and fate (Kalembkiewicz, *et al.,* 2008). It is widely recognized that the distribution, mobility and biological availability of trace metals in the solid phase depend not only on their total concentration but also on the physicochemical forms in which they occur (Nurmesniemi *et al.,* 2008; Filgueiras, *et al.,* 2002). Metal ions in solid materials are partitioned between the different phases in the materials such as organic matter, oxyhydroxides of iron, aluminium and manganese, phyllosilicate minerals, carbonates and sulfides. Metal ions also are retained on these solid phases by different mechanisms such as ion exchange, outer and inner-sphere surface complexation (adsorption), precipitation or co-precipitation (Rate, *et al.,* 2000; Filgueiras, *et al.,* 2002). To evaluate the availability and mobility of metals from solid materials such as fly ash and soil, some extraction tests have often been applied (Nurmesniemi *et al.,* 2008). Extraction tests are widely used as tools to estimate the release potential of constituents from waste materials over a range of possible waste management activities, including recycling or reuse, for assessing the efficacy of the waste treatment process, and after disposal (Kosson *et al.,* 2002; Daniels and Das, 2006; Nurmesniemi *et al.,* 2008). Among several extraction methods, the sequential extraction procedure has been widely used to evaluate the speciation of particulate metals, i.e., the partitioning among the various form in which the might exist (Tessier, *et al.,* 1979). The use of sequential extractions, although generally time consuming, provides detailed information about the origin, mode of occurrence, biological and physicochemical availability, mobilization and transport of trace metals. Sequential extraction experiments have been shown to provide a convenient means to determine the metals associated with the principal accumulative phases in sedimentary deposits. Fractionation is usually performed by a sequence of 'selective' chemical extraction techniques, which include the successive removal of these phases and their associated metals (Filgueiras *et al.,* 2002).

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According to Wan *et al.* (2006), a sequential chemical extraction procedure proposed by Tessier, *et al.* (1979) has been widely used to investigate the chemical phases of heavy metals in fly ash. In Tessier's extraction procedure, extraction of metals is divided into five different fractions based on the inorganic matrix in which the metal ions are likely to bind to. These fractions include; (1) Exchangeable fraction, which represents the most easily available metals; (2) Bound to carbonates, which represent acid-soluble fraction; (3) Bound to iron and manganese oxides, which represents the reducible fraction; (4) Bound to organic matter, which represents the oxidizable fraction; and (5) residual fraction, tightly bound to the silicate matrix of the sample (Tessier, *et al.,* (1979).

According to the International Ash Working Group (IAWG) (IAWG, 1997), the results of sequential extraction might not necessarily reflect the associations with the claimed phases, but rather represent the different leaching conditions within a landfill over time. The exchangeable phase is immediately available under neutral conditions; the carbonates phase is potentially available under neutral conditions; the phases of Fe–Mn oxides and organic matter are potentially available under reducing conditions; the residual phase is unavailable for leaching (Wan *et al.,* 2006).

Sequential extraction methods have been widely used to determine the chemical compositions and the partitioning of metals in waste materials such as fly ash (Chang *et al.,* 2009; Smeda and Zyrnicki, 2002; Bódog *et al.,* 1996; Smichowski *et al.,* 2008; Marrero *et al.,* 2007). Smeda and Zyrnicki, (2002), applied sequential extraction methods to study the partitioning of metals in fly ashes. The method initiated by Tessier, *et al.* (1979) was slightly modified by the introduction of leaching with deionized water as the first step. The sequential extraction procedure revealed much more information about the elements investigated than data obtained from measurements of their total concentrations. It was observed that the concentrations of some species vary at different extraction steps. For instance the concentrations of Ca and Mg in the water soluble fraction were lower than what was observed in the acid-soluble fraction. More than 60 % of the Ca and Mg were contained in the residue. Similar result was observed for Al and Fe with more than 98 % of their total concentrations found in the residual fraction. Chromium, boron and strontium were relatively easily extracted by deionized water as their concentrations in the water soluble fractions were significantly high. They recommended the inclusion of extraction using deionized water to determine the water soluble species as this could give very important information necessary to evaluate the risk of environmental pollution by fly ashes.

Bódog *et al.* (1996) reported a five-stage leaching procedure applied to fly ash samples collected at several emission sources in Europe. The analysis of the extracts by atomic absorption spectrometry (AAS) and graphite furnace atomic absorption spectrometry (GFAAS) showed different leachabilities and distribution patterns of Cd, Cr, Cu, Pb, V and Zn. They concluded that the difference in the partitioning of metals in the fly ashes depends considerably on the properties of the raw material and the operation conditions such as combustion temperature. As part of modification to Tessier, *et al.,* (1979) extraction method, Smichowski *et al.* (2008) applied a three-step metal fractionation scheme to study the distribution of species in fly ashes. This was done by combining the original five-step sequential extraction methods to three fractions i.e. (i) soluble and exchangeable fractions, (ii) carbonates, oxides and reducible fractions and (iii) residual fractions. The results of the fractionation procedure showed that majority of the elements in the fly ashes were found in the residual fraction, except Mo and S with percentages of 41 % and 18 %, respectively. Mo and S concentrations were higher in the soluble and exchangeable fraction. The high content of soluble S is consistent with the physicochemical characterization that reported that S was present as sulfate compounds such as $MgSO_4$ and $CaSO_4$-Gypsum (Smichowski *et al.,* 2008).

2.11 Brine

Brine, a hyper saline water solution, is a waste product generated in large quantity in the process of coal combustion for electricity in power stations. The boiling of water in the pipes surrounding the boiler at very high temperature in order to generate steam to rotate the turbine would result in water that is concentrated with dissolved elements over time. This highly concentrated salty water is referred to as brine. Apart from this source of brine generation in power utilities, the desalination of wastewaters or input waters which involves the removal of salt constituents from the wastewater to a usable level could lead to the generation of highly saline water called brine. The desalination processes involve three liquid streams; the saline feed water (brackish water or seawater), low-salinity product water, and very saline concentrate (brine or reject water). The feed water when treated by the desalination process is separated into two output streams: the low-salinity product water, and very saline concentrate streams (El-Manharawy and Hafezb, 2003). According to the World Health Organization (WHO), the permissible limit of salinity in water is 500 ppm and for special cases could be up to 1000 ppm. The treatment of wastewaters in power stations for water reuse using different desalination methods such as reverse osmosis (RO), electro dialysis reversal (EDR) and other membrane methods also results in production of brine.

Brines contain major species such as Na, K, Mg, Ca, Fe, Si, Se, Cl and SO_4 in high concentration and many other trace elements. According to Mooketsi *et al.* (2007), typical brines from Secunda power plant in South Africa contain major elements such as Na, Cl, Ca, SO_4, K, Mg, and trace elements such as Fe, Mn, Cr, V, Ti, P, Si, and Al. The composition of reject brine water from desalination plants in the Gulf region was reported in the study done by Ahmed *et al.* (2000). The pH values of the brines were reported to range between 6.7 and 8.2 while the electrical conductivity (EC) ranges between 11.33 and 79.6 mS/cm. The concentrations of the major species were high with Ca having values ranging between 173 and 1400 mg/L, Mg (282-7700 mg/L), Na (2315-18293 mg/L), SO_4 (1500-4800 mg/L) and Cl (4572-31905 mg/L). Brine contains different contaminants that must be removed before disposal in order to reduce its negative impact on the environment. The disposal of brine is costly because of its makeup and the large volumes that must be handled.

2.12 Wastewater Treatment Processes

The necessity to protect the natural environment from wastewater-related pollution due to the large amount of metals in wastewaters, and shortage of water for use domestically and in the industries has led to the treatment of wastewaters using different treatment techniques. Conventional water treatment methods such as chemical and biological treatments are common methods applied for the reclamation and reuse of wastewaters. In chemical oxidation procedures, ozone, hydrogen peroxide, UV radiation, and their combinations are the most frequent oxidants used to degrade organic compounds in wastewaters. Ozone is a powerful oxidant, which can be applied to wastewater treatment in order to achieve colour and chemical oxygen demand (COD) reduction, as well as an increase in the biodegradability of the remaining organic fraction for later biological treatments (Javier, *et al.*, 2008). Due to a rising demand for high quality water and increase in the industrial wastewaters, new alternatives treatment technologies were designed to provide low cost sanitation and environmental protection while providing additional benefits from the reuse of water. Apart from different techniques such as chemical precipitation, coagulation–flocculation, flotation and ion exchange, membrane technology such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), Electro Dialysis Reversal (EDR) and reverse osmosis (RO) are the alternative technologies which have been used recently in reclamation of both municipal and industrial wastewaters (Wintgens, *et al.*, 2005; Ahmad, *et al.*, 2005; Turek *et al.*, 2007). These treatment techniques have played a very important role in water purification because of their low costs and small environmental impacts.

2.12.1 Chemical precipitation

Chemical precipitation refers to the reactions involving dissolved metals in wastewater and additive chemical of some sort so that the metals to be removed are rendered insoluble, thereby separated from the water. Raising the pH of the water to a neutral or an alkaline level will precipitate most heavy metals as metal hydroxides. The chemical precipitation technique is widely used for heavy metal removal from inorganic effluent. After pH adjustment to the basic conditions (pH 11), the dissolved metal ions are converted to the insoluble solid phase via a chemical reaction with a precipitant agent such as lime (Wang *et al.,* 2004). pH adjustment to the basic conditions (pH 11) is the major parameter that significantly improves heavy metal removal by chemical precipitation. Lime or calcium hydroxide is the most commonly employed precipitant agent. Lime precipitation can be employed to effectively treat inorganic effluent with a metal concentration of higher than 1000 mg/L. Other advantages of using lime precipitation include the simplicity of the process, inexpensive equipment requirement, and convenient and safe operations, making it a popular method for metal removal from contaminated wastewater (Kurniawan *et al.,* 2006). Typically, the metal precipitated from the solution is in the form of hydroxide (Tünay 2003). The conceptual mechanism of heavy metal removal by chemical precipitation is presented in equation 2.3 (Wang *et al.*, 2004).

$$M^{2+} + 2(OH)^{-} \leftrightarrow M(OH)_2\downarrow \quad \text{……………………………………………………} \quad 2.3$$

Where M^{2+} and OH^{-} represent the dissolved metal ions and the precipitant, respectively, while $M(OH)_2$ is the insoluble metal hydroxide.

Chemical precipitation techniques has been observed to be a good technique for the treatment of wastewater having considered its advantages such as inexpensive equipment requirement and the readily availability of lime. Despite these advantages, chemical precipitation has its shortcomings which include the requirement of large amount of chemicals to be able to reduce the metals to an acceptable level for discharge (Jüttner *et al.,* 2000), its excessive sludge production that requires further treatment, the increasing cost of sludge disposal, slow metal precipitation, poor settling of the precipitated metals, the aggregation of metal precipitates, and the long-term environmental impacts of sludge disposal (Bose *et al.,* 2002; Yang *et al.,* 2001) .

Several researchers have investigated the effectiveness of chemical precipitation techniques in the treatment of wastewaters, and their findings were attractive. For instance, Charerntanyarak, (1999) in his study on heavy metals removal by chemical coagulation and precipitation, employed lime precipitation for the removal of heavy metals such as Zn(II), Cd(II) and Mn(II) cations with initial metal concentrations of 450, 150 and 1085 mg/L, respectively, in a batch continuous system. Despite the varying initial concentrations of the heavy metal, an almost complete removal from synthetic wastewater was achieved for all the metals at pH 11. The final concentration of Zn(II) and Mn(II) in the treated synthetic wastewater was less than 5 mg/L, the value which was a bit higher than the limit concentration set by the US EPA which is lower than 1 mg/L (US EPA, 1980).

The applicability of hydroxide precipitation in a closed system to treat synthetic wastewater containing Cd(II) and Cu(II) ions was investigated by Tünay and Kabdasli, (1994). They employed inorganic cations (Ca(II) and Na) as ligand-sharing agents for EDTA (ethylenediamine tetraacetic acid) and NTA (nitrilotriacetic acid). Ca(II) was observed to be the only cation that effectively bound both ligands to form the hydroxide precipitations of the complexed metals. At pH 11, EDTA was also found to be the major component that determined Cd(II) solubility (Tünay and Kabdasli, 1994). Papadopoulos *et al.* (2004) investigated the uptake of Ni from a wastewater stream with metal concentration of less than 100 mg/L. They observed about 71 % and 85 % of Ni(II) removal at pH 7.5 and 10.5, respectively when wastewater with an initial metal concentration of 51.6 mg/L was treated with chemical precipitation technique. The metal removal was attributed to the fact that a greater portion of the Ni(II) was precipitated and removed in the form of insoluble hydroxide compounds with the increasing pH.

2.12.2 Ion Exchange

Ion exchange is a process of removing ions that are detrimental from water and replacing them with less damaging ions. The chemical reactions that take place in ion exchange process involve exchanging ions from the solution for similar charged ions attached to immobile solid particles (Rengaraj *et al.,* 2001). In ion exchange process, cations such as nickel, copper, sodium etc. are exchanged with hydrogen ion while anion, as sulfates, chromates and chlorides etc. in the wastewater is exchanged with hydroxyl ion (Eom *et al.,* 2005). The solid ion exchange particles are either naturally occurring inorganic zeolites or synthesised organic resins. Resin beads are a polymer matrix containing many ion exchange sites both on the bead surface and within the matrix. Resins have to be charge specific, with some resins specifically designed for anion exchange, and other for cation exchange. Anion exchange resins have positively-charged sites with anions attached, and cation exchange resins have negatively-charged exchanged sites with cation attached. Ions exchange has proved to be suitable for chloride, calcium, magnesium, sodium and nitrates (Markhol, 1985).

Ion exchange has the advantage of treating a large volume of solution at once over other water treatment technologies, and it directly recycles the metals in a plating bath. This technology has been applied in the treatment of wastewaters in several feilds such as pharmaceutical purification, water softening processes, separation and purification in the food industry, catalyst and manufacture of ultra-pure water used in semiconductor processes. Several studies have been carried out on the application of ion exchange to remove metals from wastewaters. Eom *et al.* (2005) applied ion exchange to remove nickel ion from plating wastewater. In their study, a column packed with strongly acidic cation resin was used as the nickel recovery unit to separate nickel ion from the wastewater. The concentration of nickel in the treated modeled solution was originally 1.8 g-Ni/L, and this was allowed to flow through the resin as much as 20 times. The capacity of resin packed in the column was 1.7 meq/ml. It was observed that over 99 % nickel ions in the solution was removed.

The application of natural exchangers such as clinoptilolite and synthetic zeolite (NaPl) to purify synthetic wastewater containing Cr(III) was investigated by Álvarez-Ayuso *et al.* (2003). It was observed that synthetic zeolite demonstrated a sorption capacity of 43.58 mg/g (about 10 times) greater than that of clinoptilolite which was 4.10 mg/g, despite having a comparable surface area (20–28 m^2/g). This was attributed to the H^+ exchange capacity of zeolite and the strength of hydration shell cations that played major roles in the sorption capacities of both exchangers (Papadopoulos *et al.,* 2004). Rengaraj *et al.* (2001) investigated the removal performance of IRN77 and SKN1 resins in a synthetic solution containing Cr(III). They reported that a complete removal of Cr(III) with a higher metal concentration of 100 mg/L was achieved.

2.12.3 Electro dialysis (ED)

The electro dialysis technique is one of the techniques used in the treatment of wastewaters. This process allows water to flow between cation and anion permeable membranes that are placed alternately in an electro dialysis (ED) stack. This is connected to direct current (DC) which provides the motive force for the movement of the ions through the perm selective membranes. The process leads to the removal or concentration of ions in the direction opposite to the movement of the water sample (Bruggen and Vandecasteele, 2002). When a solution containing ionic species passes through the cell compartments, the anions migrate toward the anode and the cations toward the cathode, crossing the anion-exchange and cation-exchange membranes (Chen, 2004). Removal or separation of electrolytes can be achieved by electro-dialysis due to the ability of the membranes to selectively transport ions having positive or negative charge and reject ions of the opposite charge. Electro dialysis processes are unique compared to distillation techniques and other membrane-based processes (such as reverse osmosis) in that the dissolved species are moved away from the feed stream. Electro dialysis systems require feed pretreatment to remove species that could precipitate on the surface of the ion exchange membranes. This is necessary because the precipitate when formed on the membrane could decrease the efficiency of the electro dialysis system. The periodical cleaning of the membrane stack is therefore necessary to avoid blockage due to scaling and for good performance, and this can be done by disassembling the stack (Malleville, 1996).

There are several studies carried out to evaluate the efficiency of ED in the removal of metals from polluted or wastewaters. Marder *et al.* (2003) carried out a laboratory scale study on the removal of cadmium from synthetic plating wastewater using ED with two commercial cationic and anionic exchange membranes. They observed about 13 % Cd(II) removal within 120 min of the reaction with initial concentration of 2 g/L Cd. In another study carried out by Tzanetakis *et al.* (2003) on the performance of ion exchange membrane for the electro dialysis of nickel and cobalt ions from a synthetic solution, the investigation revealed that the removal efficiency of Co(II) and Ni(II) were 90 % and 69 %, with initial metal concentrations of 0.84 and 11.72 mg/L, respectively when perfluorosulfonic Nafion 117 membrane was used. The studies carried out by Marder *et al.* (2003) and Tzanetakis *et al.* (2003) indicate that ED cannot be effectively used for the treatment of inorganic effluent with a metal concentration higher than 1000 mg/L, thus suggesting that ED is more suitable for solutions of metal concentration less than 20 mg/L. Despite the limitation of ED, it is a good technique for the treatment of dilute wastewater containing heavy metals. It has the ability to produce a highly concentrated stream for recovery and the rejection of undesirable impurities from water (Kurniawan *et al.,* 2006).

2.12.4 Electro Dialysis Reversal (EDR)

The principle of operation of electro dialysis reversal (EDR) is the same as the standard principle of electro dialysis (ED). The polarity of the electrodes is automatically reversed about three to four times in an hour. The ions are transferred in opposite directions across the membranes by means of water operated valves. Saline feed water containing dissolved salts is separated into positively charged sodium and negatively charged chloride ions. These ions will move towards an oppositely charged electrode immersed in the solution i.e. cations move to the cathode while anions move to the anode (Shaffer *et al.,* 1980). A large number of alternating cation and anion membranes are stacked together, separated by plastic flow spacers that allow the passage of water. The streams of alternating flow spacers are a sequence of diluted and concentrated water which flow in parallel to each other. To prevent scaling, inverters are used which reverse the polarity of the electric field every 20 minutes (Safi *et al.,* 1999). Since energy requirements are proportional to the water's salinity, EDR is more feasible when the salinity of the feed water is not more than 6000 mg/L of total dissolved salts. Similarly, due to the low conductivity which increases the energy requirements of very pure water, the process is not suitable for water of less than about 400 mg/L dissolved salts (Bouchekima *et al.,* 2001).

2.12.5 Reverse Osmosis

Reverse osmosis (RO) is a pressure-driven membrane process developed for the production of portable water from saline water, and treatment of industrial wastewaters (Qdaisa and Moussab, 2004; Kurniawan *et al.,* 2006). A reverse osmosis system consists of four major components/processes: (1) pre-treatment, (2) pressurization, (3) membrane separation, and (4) post-treatment stabilization. In the RO process, water from a pressurized saline solution is separated from the dissolved salts by flowing through a water-permeable membrane. The permeate, which is the liquid flowing through the membrane, flows through the membrane by the pressure differential created between the pressurized feed water and the product water, which is at near-atmospheric pressure. The remaining feed water continues through the pressurized side of the reactor as brine. The permeable membranes inhibit the passage of dissolved salts while permitting the desalinated product water to pass through.

The use of reverse osmosis (RO) membranes is becoming an increasingly practical method of desalination, due to significant improvements in energy recovery systems and pre-treatment processes over the past couple of decades. One of the advantages of RO is that it does not only remove dissolved solids but bacteria, viruses, naturally occurring organics and other dissolved particulate matter are also removed by the membrane which serves as barrier between the feed water and the product water (Qdaisa and Moussab, 2004). Applying feed water (wastewater) to the membranes assembly of RO system would result in a freshwater product stream and a concentrated brine reject stream. Due to the imperfection of the membranes in their rejection of dissolved salts, a small percentage of salt may pass through the membranes and remains in the product water.

The brine (highly saline reject) generated from the RO desalination plant at Tutuka power station will be used for the purpose of this study. This reason for choosing this brine is not only because of the high concentration of the species such as Ca, Mg, Na, Cl and SO_4 in the brine but because the brine from the RO desalination plant is used in the Tutuka power station to moisten the Tutuka fly ash before disposal and to irrigate the ash dump in order to suppress dust.

2.13 Disposal of brine

Increase in water demand for use in the industries and for domestic purposes has drastically increased the desalination technologies such as RO and EDR which are used in the treatment of seawater and wastewaters. The efficiency of these desalination technologies used to treat wastewaters has improved over the last decade, but there are currently certain limitations that need to be addressed to make these technologies more cost effective (Sethi *et al.,* 2006). These limitations include low productivity or recovery that results in a large volume of concentrate, high-energy use, and relatively high treatment costs. The main challenge caused by the low productivity of the desalination technologies is the disposal of the large volume of concentrate (brine), in a cost-effective, environmentally sustainable manner. The disposal of brine poses significant environmental issues, due to the high concentrations of metals and salts. Hence, the need for safe disposal to reduce the adverse environmental effect it could have on the environment.

In recent times, brine has been conventionally disposed of by several means which include disposal to surface waters which include ocean or sewers, disposal via deep well injection, disposal in evaporation ponds, land application of brine and zero liquid discharge system (Jeppesen *et al.,* 2009; Sethi *et al.,* 2006; Mickley, 2004). A brief description of each disposal option is presented below.

2.13.1 Surface water or sewer disposal

Surface water and the sewer brine disposal method are simply processes of discharging brines into the ocean or an existing sewage collection system. These disposal methods are the most common disposal method practiced in the United States of America (USA) by approximately 80 percent of all desalination plants due to the low cost involved (Mickley, 2004; Mickley, 2001). Surface water or sewer disposal requires that the brine be transported via pipeline to the disposal site, where outfall structures (such as diffusers) are used to transfer the brine to the surface water body or the sewer. Design of appropriate outfall structures is necessary to ensure that the discharge is well mixed and will not cause damage to the receiving waters and environments (Jeppesen *et al.,* 2009). The design must consider factors such as ambient conditions (conditions of the receiving water including bathymetry, salinity, density, velocity, and temperature), and discharge conditions (conditions of the outfall structure including structure geometry, discharge rate and physical and chemical factors) (Mickley, 2004). For RO plants, the brine is highly saline and typically denser than the receiving water, so diffuser systems are typically employed to avoid spreading of the discharge over the sea floor and benthic communities, which are most affected by RO discharge (Lattemann and Höpner, 2008).

2.13.2 Deep well injection disposal

Deep well injection is the process of injecting brine into aquifers that are not used for drinking water. The depth of the injection well ranges from 0.2 miles to 1.6 miles below the earth surface (Younos, 2005). This method of brine disposal is not commonly used, as it is generally only economically viable for large desalination plants (Younos, 2005; Mickley, 2004). The geology and hydrogeology of the site design for deep well disposal must be taken into consideration in order to prevent the movement of brine constituents into potable groundwater (Jeppesen *et al.,* 2009).

2.13.3 Evaporation ponds disposal

Evaporation ponds are ponds constructed to evaporate water from the brine while the remaining salts accumulate in the base of the pond. Evaporation ponds were originally designed over the centuries to remove water from saline solution, but in the recent time, they have been considered as an effective method for brine disposal (Younos, 2005; Ahmed *et al.,* 2000). Evaporation ponds are frequently the least costly means of disposal, especially in areas with high evaporation rates and low land costs (Mickley *et al.,* 1993). This disposal method is commonly used due to its several advantages which include easy construction, low maintenance and little operator attention. This method requires little mechanical equipment except for the pump that conveys the wastewater to the pond (Ahmed *et al.,* 2000). This method is only economical for small volume plants, and can cause contamination of underground aquifers if not properly designed or constructed. This can be prevented to some extent if the ponds are lined (Mohamed *et al.,* 2005; Younos, 2005).

2.13.4 Land application

Land application such as spray irrigation and percolation pond is another method used to dispose brine generated from desalination plants. This method provides an opportunity for a beneficial use of brine, which can be used to irrigate salt-tolerant crops or grasses such as those used on golf courses (Younos, 2005). This disposal system can pose serious risk to groundwater and surface water resources if it is not properly designed (Jeppesen *et al.,* 2009). This method of disposal is being practiced at Tutuka power station as a way of disposing the brine generated from the RO desalination plant.

2.13.5 Zero liquid discharge system

Zero liquid discharge (ZLD) system is a process which involves converting liquid brine into a dry solid before dispose to landfill or use in other ways. This is essentially thermal method such as thermal evaporators, crystallizers and spray dryer that can reduce the brine to a solid product. One of the advantages of this disposal method is that it reduces the discharge of brine to surface or groundwater (Mickley, 2004). The solid waste generated from ZLD process can pose an environmental risk when disposed to landfill due to chemical leaching of the species from the solid brine into the groundwater. This contamination can also be reduced if the landfill is designed appropriately. Another barrier to using ZLD processes is the high cost due to high energy required (Younos, 2005), possibility of corrosion and subsequent leakage in the well casing, seismic activity which could cause damage to the well and subsequently result in ground water contamination as well as the uncertainty in the estimation of the well's half life (Ahmed *et al.,* 2001).

2.14 Scale formation and control

The accumulation and deposition of undesired materials on the solid surfaces, most often in an aquatic environment is called fouling. Build-up of fouling film leads to an increase in resistance and deteriorates the performance of process equipment such as membranes and heat exchangers (Al-Anezi and Hilal, 2007). One of the major fouling phenomena encountered in the aqueous systems is scale formation, which is due to the precipitation of salts present in seawater or brine. The formation of scale on the surface of the water treatment membrane is a function of the nature of the feed water to the membrane (Al-Shammiri *et al.,* 2000). However, water-formed scales that deposit in evaporators, water-cooling towers and heat exchangers can be classified based on their chemical compositions. For instance, alkaline scales consist of calcium carbonate, magnesium hydroxide, and admixtures of both compounds (Gryta, 2008; Helalizadeh *et al.,* 2000; Al-Anezi and Hilal, 2007), and its formation is inherent to the chemistry of brine which contains significant amounts of bicarbonate, calcium and magnesium ions. Formation of alkaline scales is strongly dependent on temperature, pH, and the rate of release of CO_2 as well as the concentrations of HCO_3^-, CO_3^{2-}, Ca^{2+}, and Mg^{2+} ions in the water (Quteishat *et al.,* 2003 and Al-Sofi, 1999). Alkaline scale formation in brine occurs as a result of thermal decomposition of the bicarbonate ion (HCO_3^-), which disintegrates to CO_3^{2-} and leads to loss of carbon dioxide (equation 2.4). This reaction causes the precipitation of $CaCO_3$ once the solubility limit is reached (equation 2.5). At higher temperature, CO_3^{2-} hydrolyses to OH^-, which can lead to the formation of $Mg(OH)_{2(s)}$ in the presence of Mg ions in the brine (equations 2.6 and 2.7) (Shams El Din *et al.,* 2002).

$2HCO_3^- \longrightarrow CO_3^{2-} + CO_2 + H_2O$……………………………………………*2.4*
$CO_3^{2-} + Ca^{2+} \longrightarrow CaCO_{3(s)}$……………………………………………………*2.5*
$CO_3^{2-} + H_2O \longrightarrow 2OH^- + CO_2$………………………………………………*2.6*
$2OH^- + Mg^{2+} \longrightarrow Mg(OH)_{2(s)}$…………………………………………………*2.7*

The overall reaction describing the crystallization of $CaCO_3$ scale is represented by:

$Ca^{2+} + 2HCO_3^- \rightarrow CaCO_3\downarrow + CO_2\uparrow + H_2O$……………………………………………*2.8*

Scaling is a major engineering problem in process industries, since deposits on heat transfer surfaces create a barrier to heat transfer, increase pressure drop and promote corrosion of tube material. Scaling can disturb the brine flow through the flash chamber of multi-stage flash (MSF) distiller thereby deteriorating the performance and efficiency of the whole desalination plant, and hence cause a cost increase in most commercial units. Due to the effect of scaling on the MSF, various techniques have been proposed to retard scale formation in desalination plants (Shams El Din *et al.,* 2002). These include; the controlled acidification of brine to around pH 4.0 in order to affect the decomposition of the bicarbonate; the use of sponge ball cleaning (Tapproge system) – the process which mechanically wipe the condenser tubes and prevent the adherence of solid scales (Al Bakri and El Hares, 1993); acid cleaning of the distiller, which is carried out by circulation of seawater/brine acidified to pH ≈2.0 through the condenser to dissolve the accumulated scales (Shams El Din *et al.,* 2002); ion exchange softening, this involves exchanging sodium for magnesium and calcium ions that are concentrated in the seawater or brine (http://www.lenntech.com/antiscalants.htm); and the use of anti-scale agents which have the ability to be absorbed on the surface of the formed crystallites thereby preventing their adhesion and growth into compact layers. The later preventive measure is an area of interest in this study due to the fact that the desalination plants in South African power stations under study add anti-scalants in order to prevent scale formation in their system.

2.15 Anti-scalants and addition of anti-scalants

Anti-scalants are polymeric inorganic and organic substances having the ability to be absorbed on the surface of the formed crystallites, preventing their adhesion and growth into compact layers. Anti-scalants are surface active materials that interfere with precipitation reactions in three primary ways: (1) Threshold inhibition - the ability of an anti-sclant to keep supersaturated solutions of springly soluble salts, (2) Crystal modification - the ability of anti-scalant to distort crystal shapes, resulting in soft non adherent scale. As a crystal begin to form at the submicroscopic level, negative groups located on the anti-scalant molecule attack the positive charges on scale nuclei interrupting the electronic balance necessary to propagate the crystal growth. Crystal modifier types of anti-scalant make the scale crystals appear distorted, oval in shape, and less compact, and (3) Dispersion - the ability of some anti-scalants to adsorb on crystals or colloidal particles and impart a high anionic charge, which tends to keep the crystals separated (http://www.lenntech.com/antiscalants.htm).

The addition of anti-scalants to seawater or brine is a common phenomenon employed in multistage flash (MSF) desalination plants to combat the formation of alkaline scales on the process equipment. The dosage rates of the antiscalants vary from one plant to another depending on the concentrations of scale-forming species in the seawater or brine. There are several antiscalants that are commonly used to control scaling, these include; mineral acids and scale control additives (SCAs) such as polyphosphonate based (PPN) and polymeleic acid based (PMA) (Dalvi *et al.,* 2000). The types of anti-scalants used in water treatment plants depend mainly on the types of scales that could possibly dominate the brine or seawater. For instance, calcium carbonate scaling can be controlled by the addition of acid such as sulphuric acid

(H_2SO_4) while sodium hexametaphosphate (SHMP) can be used to inhibit calcium sulphate ($CaSO_4$) scale (Al-Shammiri *et al.,* 2000).

Apart from acting as scale retardant, anti-scalants has been studied to be good inhibitors to the thermal decomposition of HCO_3^-. In the study carried out by Shams El Din *et al.* (2002), on the effects of polymaleates (anti-scalants) as inhibitors on thermal decomposition of HCO_3^-, three different anti-scalants of different concentrations were added to the simulated seawater, and the reaction was monitored at intervals. They observed that the addition of polymaleate compounds lowered the rate of the thermal decomposition of HCO_3^- when compared with the rate of decomposition of HCO_3^- in anti-scalant-free seawater. It was also observed that an increase in the concentrations of the anti-scalants reduced the rate of HCO_3^- decomposition.

The effectiveness of antiscalants could be influenced by the chemical nature of the antiscalant, the plant configuration and design, heat transfer rate and the antiscalant reaction with brine constituents. As anti-scalants play the role of inhibiting the formation of scales in brine, some constituents of brine may interact with the anti-scalants thereby negatively affecting the performance of the anti-scalants in water treatment plants. In seawater some transition ions are present in trace concentrations which can preferentially coordinate with anti-scalants thus reducing their efficiencies (Dalvi *et al.,* 1999; Dalvi *et al.,* 2000). The generation of oxides of iron, copper and nickel due to corrosion is unavoidable. The ferrous and ferric ions such as Fe^{2+} and Fe^{3+} may readily complex with the anti-scalants thereby reducing the availability of antiscalant for scale control reaction. Fe_2O_2 and $Fe(OH)_3$ may also form a good suspension in brine, providing nucleation sites for alkaline scale formation thereby accelerating the rate of scaling. In the study by Dalvi *et al.,* (1999) on the effect of various forms of iron in recycle brine on the performance of anti-scalants in MSF desalination plants, it was observed that various forms of iron such as Fe^{2+}, Fe^{3+}, Fe_2O_2, $Fe(OH)_3$ at 2 ppm concentration and at 95 °C showed detrimental effect on the efficiency of the anti-scalants (PPN and PMA). It was discovered that among all the various forms of iron, $Fe(OH)_3$ reduced the efficiency of the anti-scalants by a maximum of 40 %. It was concluded that iron species may affect the efficiency of an anti-scalant agent due to their characteristic complexing and coagulant abilities.

Anti-scalants are considered efficient when the percentage of precipitated $CaSO_4$ or $CaCO_3$ did not exceed 10 % of the total $CaSO_4$ or $CaCO_3$ available in solution. However, evaluation of the effectiveness and performance of different anti-scalants on laboratory bench-scale before being used in the real plant has been considered necessary by Al-Shammiri *et al.* (2000). The screen tests carried out by Al-Shammiri *et al.,* (2000) on several commercial chemicals as scale inhibitors for calcium sulphate and carbonate scales at the Doha research plant (DRP) in Kuwait revealed that "Flocon 100" one of the anti-scalants, with the lowest dosing rate (4 mg/L), had the greatest effectiveness in controlling sulphate scaling, and the "POC" (anti-scalant) was observed to completely inhibit carbonate precipitation at a 6 mg/L dosage. They concluded that the effectiveness of these anti-scalants was specific to certain waters under certain conditions. Apart from the evaluation of the anti-scalant performance, the dosing rate is an important parameter to be considered when adding anti-scalants to the water treatment process (Al-Rammah, 2003). Due to the inability to easily confirm the presence of anti-scalants in the water system unlike acid dosing which can be monitored by pH, optimization of the dosage rate of the anti-scalant before the application is necessary to prevent overdosing (Kelle Zeiher *et al.,* 2003).

2.16 Geochemical modeling

The environmental assessment of the utilization and disposal of solid waste materials such as fly ash is necessary in order to understand the weathering processes and their effect on trace elements leaching. Considering waste materials as mineral assemblages, the use of geochemical knowledge has been considered to be an appropriate method of characterizing the waste and understanding the mobility of species from the solid wastes. Geochemical models are constructed to simulate the chemical processes that take place in the earth's natural environment. Therefore, modeling forms a valuable instrument that contributes to the identification of the dominant processes that control the behaviour of components and contaminants in solid waste materials or soils (Dijkstra, 2007). Several studies have applied geochemical modeling to predict the factors controlling the leaching of species from waste materials. These studies have shown that dissolution/precipitation reactions control the release of major, minor and trace elements from waste materials such as fly ash (Rai *et al.,* 1987; Mattigod *et al.,* 1990; Fruchter *et al.,* 1990) and municipal solid waste incineration (MSWI) bottom ash (Kirby and Rimstidt, 1994;

Comans and Meima, 1994; Zevenbergen and Comans, 1994). Leaching of major elements such as Ca and SO_4 has been often shown to be controlled by the dissolution of mineral phases, but in weathered materials, heavy metals such as Cd and Pb are presumably controlled by sorption to neoformed iron and aluminium (hydr)oxides (Meima and Comans, 1998; 1999; Dijkstra, 2007). The distribution of contaminants in the field is a function of the controlling geochemical processes and the physical transport processes (Dijkstra, 2007). Therefore the application of reactive transport modeling to waste environment can be a valuable instrument in assessing the time dependent leaching potential of waste materials as well as the fate of the contaminants in the environment after leaching. This study shall apply the geochemical modeling to investigate the secondary mineral phases influencing the release of major, minor and trace elements from fly ash-brine interactions.

Mineral dissolution, solution speciation and sorption modeling are often carried out by using several geochemical and hydrogeochemical computer software such as PHREEQC (different version), Visual MINTEQ and MINTEQA2. Visual MINTEQ is a geochemical thermodynamic equilibrium model capable of calculating equilibrium aqueous speciation, adsorption, gas-phase partitioning, solid-phase saturation states, and precipitation/dissolution of metals (Gustafsson, 2006; Zhang, *et al.* 2008). Meima and Comans (1998); Astrup, (2006) and Eighmy (1995) employed Visual MINTEQ in their research to describe heavy metal speciation and leaching behavior from incineration residues. This geochemical modeling code has proved to be able to provide useful insights into the leaching characteristics of heavy metals. The model employs a predefined set of components that includes free ions such as Ca^{2+} and neutral and charged complexes (e.g., H_4SiO_4 and $Cr(OH)^{2+}$). The ion speciation, solubility and precipitated solid of the reacting system can be calculated based on the equilibrium constants K from the database of the software. Zhang, *et al.* (2008) in their study on the leaching of heavy metals from municipal solid waste incineration bottom ash and its geochemical modeling employed visual MINTEQ to determine the solid phase dissolution behaviour as a function of pH. The model was run in two different modes, predicting the pH dependent leaching behaviour in the absence and presence of surface complexation reactions. The pH-dependent leaching behaviour predicted was in agreement with analytical values over a large pH range. The findings from the models revealed that the main equilibrium reactions that controlled the leaching of heavy metals from the bottom ash were precipitation/dissolution and adsorption reactions.

2.17 Conclusion

The generation of fly ash by coal-fired power stations is on the increase due to the increase in the demand for electricity in the world. Fly ash contains some major and minor species such as Al, Si, Fe, Ca, K, Fe, Mn, As, Mo, Cr, Se etc. The disposal of fly ash is of major environmental concern due the dissolution of soluble salts on interaction with water during transport and after disposal. Leaching of this highly metal laden leachate to the groundwater is of major concern.

The generation of brine in the coal-fired power stations is also on the increase due to the need for process water for steam generation which requires treatment for reuse. The disposal of brine, which contains major elements such as Na, Ca, Mg, Cl and SO_4, is a major problem encountered by the power stations due to the possible release of contaminants into the environment. As a result of the law regulating the indiscriminate disposal of brine and due to the large quantity produced and the cost of safe disposal the co-disposal of fly ash and brine has been practiced by some power utilities such as SASOL Synfuels in Secunda and ESKOM power stations in Tutuka, South Africa. This was done by these power utilities with the aim of utilizing fly ash to capture the salt contained in the brine solution. It is therefore very important to understand the chemical interaction in the fly ash-brine systems so as to determine the possible usefulness of fly ash as a sustainable salt sink. Several studies (Kirby and Rimstidt, 1994; Comans and Meima, 1994; Warren and Dudas, 1984; Reardon *et al.,* 1995; Tiruta-Barna *et al.,* 2006; Saikia *et al.,* 2006; Fishman *et al.,* 1999; Iyer, 2002; Yan, 1998; Choi *et al.,* 2002 Garavaglia and Caramuscio, 1994) have been carried out to understand the release of major and minor species from fly ash when in contact with aqueous solution. Despite several studies on the fly ash, the chemical interaction when fly ash and brine are co-disposed has not been studied. No study has been done on the release of species from fly ash and the removal of species from brine solution when fly ash and brine are in contact. Moreover, the capacity of fly ash to act as sustainable salt sink to brine has not been studied. Therefore, the main aim of this study as stated in section 1.5 is to assess the possibility of using South African fly ashes as sustainable salt sink, and to understand the effect of fly ash-brine interactions on the quality of brine solution.

Several methods including the batch reaction test, long-term fly ash-brine interaction experiment, the acid neutralization capacity test, sequential extraction test and the up-flow percolation test (which will be discussed in detail in the subsequent chapters), will be employed to determine the chemical interactions and the release of major and minor species in fly ash-brine systems. The secondary mineral formation controlling the release of species from fly ash will be predicted by the use of PHREEQC geochemical modeling software. The up-flow percolation test was used in this study instead of a column test using gravitational flow, in order to prevent preferential path-flow of the leachant which could occur as a result of secondary mineral formation in the column or due to the pozzolanic property of fly ash.

The next chapter (chapter three) gives detailed principles of the sampling procedures and the analytical techniques used in this study.

Chapter 3

Sampling, Experimental and Analytical techniques

3 Introduction

The previous chapter of this study (chapter 2) focused on the review of literature. This chapter describes the chemical, sampling, experimental and analytical methods used in this study. The description of the chemicals used and their preparation are presented in section 3.1 while the sampling details of the samples used are presented in section 3.2. Sections 3.3 and 3.4 present the standard experimental procedures and the analytical techniques used respectively.

3.1 Materials

3.1.1 Chemicals used in the study

A list of chemicals used in this study is given in Table 3.1 below.

Table 3.1: List of chemicals used in the study

Chemical	Supplier	Purity
Hydrofluoric acid	Merck	Min 48 %
Nitric acid	Merck	Min 55 %
Hydrochloric acid	Merck	Min 32 %
Boric acid	Kimix	99%
Ammonium acetate	Kimix	98.5%
Acetic acid	Merck	30%
Hydroxylamine hydrochloride	Kimix	99%

3.1.2 Preparation of reagents

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

2 M Nitric acid (HNO_3)

171 cm^3 of concentrated HNO_3 was accurately measured and added into 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 1 L mark with ultrapure water and mixed.

0.025 M Nitric acid (HNO_3)

2.1 cm^3 of concentrated HNO_3 was accurately measured and added into 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 1 L mark with ultrapure water and mixed.

0.1 M Hydrochloric acid (HCl)

9.8 cm^3 of concentrated HCl was accurately measured and added into 1 L volumetric flask containing ultrapure water. More ultrapure water was added to the diluted HCl and the diluted acid was shaken and made up to 1 L mark with ultrapure water and mixed.

1 M Ammonium acetate (NH_4AC)

77.09 g of ammonium acetate 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.

1 M Acetic acid (CH_3COOH)

57.47 cm^3 of acetic acid was measured into 1 L volumetric flask containing ultrapure water. More ultrapure water was added and the diluted acid was shaken and made up to 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 Sampling

The description of the samples (fly ash and brine used in this study is described below

3.2.1 Fly ash

Fresh fly ash samples from coal-fired power utilities operated by ESKOM (Tutuka) and SASOL (Secunda) in South Africa were used in this study. The fly ash from SASOL (Secunda) was collected directly from the hoppers while the fly ash from ESKOM (Tutuka) was collected from the conveyor belt taking the ash to the ash dump. The Tutuka fly ash used in this study was preconditioned with about 16 % brine solution to suppress dust before the ash was sampled. There was no access to the fresh fly ash directly from the hopper because of the regulations of the power station. The ash samples were kept in plastic containers which were tightly closed to prevent ingress of air, and stored at room temperature.

3.2.2 Brine and brine-antiscalant

The brine sample used in this study was collected from the highly saline retentate stream of the reverse osmosis (RO) desalination plant at ESKOM power station in Tutuka, South Africa. Tutuka brine was chosen for this study because of the high concentrations of the major species such as Na, Cl and SO_4, and in order to avoid inconsistency. The brine sample was collected in plastic containers and stored in a refrigerator at 4 °C. The brine sample used for this study was sampled at once because of the large variability found over time. The chemical composition (Table 3.2) of the brine used in this study was analyzed using ICP-MS and IC for cation and anion respectively.

According to Al-Shammiri *et al.,* (2000), sodium hexametaphosphate (SHMP) can be used to inhibit the formation of calcium sulphate ($CaSO_4$) scale in brine containing significant concentrations of Ca and SO_4. Because the type of antiscalants used by Secunda and Tutuka power utilities was not disclosed to the author, sodium hexametaphosphate (SHMP) was used as the antiscalant in this study because of the significant concentrations of Ca and SO_4 in the brine solution (Table 3.2).

0.05 g of the antiscalant was weighed accurately and dissolved in 1000 mL of brine solution in order to give 50 ppm brine-antiscalant stock solutions. This indicates that 50 mg of the antiscalant was dissolved in 1L brine solution.

Table 3.2: Composition of the Tutuka RO brine (A) and brine-antiscalant mixture (B) used in the up-flow percolation tests (concentration in m/L except pH and EC (mS/cm))

Major elements	A	B	Minor elements	A	B
B	2 ± 0.1	2.2 ± 0.2	Al	0.01 ± 0	0.06 ± 0.03
Ca	91 ± 0.7	90.8 ± 1.2	As	0.007 ± 0	0.007 ± 0
K	106.2 ± 3.8	116.7 ± 5.2	Ba	0.06 ± 0	0.06 ± 0
Mg	147.5 ± 10.6	157.3 ± 13.7	Cd	BDL	0.0001 ± 0
Na	4323.2 ± 44.8	4327.7 ± 33.8	Co	0.01 ± 0	0.01 ± 0
Si	11.1 ± 0.03	11.1 ± 1.2	Cr	0.02 ± 0	0.02 ± 0
Sr	2.6 ± 0	2.6 ± 0.05	Cu	0.2 ± 0	0.2 ± 0.02
Cl	2424 ± 17	2436 ± 16.9	Fe	0.1 ± 0	0.1 ± 0
SO_4	8858 ± 86	8858 ± 86.3	Mn	0.002 ± 0	0.002 ± 0
pH	7.89	7.92	Mo	0.04 ± 0	0.04 ± 0
EC (mS/cm)	14.63	14.72	Ni	0.1 ± 0	0.1 ± 0
			Pb	0.007 ± 0	0.003 ± 0
			Se	0.007 ± 0	0.004 ± 0
			Ti	0.001 ± 0	0.003 ± 0
			V	0.02 ± 0	0.02 ± 0
			Zn	0.1 ± 0	0.1 ± 0

3.2.3 Storage of samples

The fly ash samples were stored in sealed plastic containers. The plastic bags were stored in a dark cool cupboard far away from source of heat, out of direct sunlight and away from fluctuating temperatures.

The brine sample was collected in plastic containers and stored in the refrigerator at 4 °C.

3.2.4 Storage of leachates for analysis

The aliquot samples from the leachates of the fly ash-brine interaction tests were taken after being filtered through a 0.45 μm membrane filter. The aliquot samples for cation analysis were acidified with dilute HNO_3 to pH ± 2 and kept in the refrigerator at 4 °C while aliquot samples for anion analysis were kept in the refrigerator at 4 °C without adding dilute HNO_3. The samples were analysed for anions and cations using IC and ICP-MS respectively.

3.3 Standard experimental methods

There are several standard experimental methods employed in this study. These methods include; Total acid digestion test; Batch reaction tests; Long-term fly ash-brine interaction tests; Acid neutralization capacity (ANC) tests; Up-flow percolation tests; and sequential extraction tests.

3.3.1 Total acid digestion

This test involves contacting fly ash with concentrated acid to determine the total concentrations of species in the sample. This test was carried out according to Jackson and Miller (1998). 2 ml of concentrated hydrofluoric acid (HF) and 5 ml aqua regia were reacted with 0.25 g of fly ash in a digestion vessel (Parr bomb) at 200 °C for 2 h. The sample was allowed to cool after which the excess HF in the digestate was neutralized by the addition of 25 ml of saturated H_3BO_3 solution. The digestate was filtered through 0.45 μm membrane filter and the solution was diluted to 50 ml with de-mineralized water.

3.3.2 Batch reaction tests

The batch reaction tests were carried out on Secunda and Tutuka fly ash samples (see section 3.2) to evaluate the interaction chemistry of the fly ash-brine system at different liquid/solid (L/S) ratio and at different contact time. These tests were aimed at simulating the aggressive mixture of fly ash and brine (practiced by Secunda coal-fired power utility) before transported in slurry form to the ash dump. The batch reaction tests were carried out according to the German leach test (DIN 38414 S4) (Institut fur Normung, 1984) but with slight modification such as varying the contact times of the fly ash-brine systems.

3.3.2.1 Preliminary batch reaction tests

The preliminary batch reaction tests were carried out to determine the effect of some parameters such as the brine concentration, contact time, L/S ratio on the pH and EC of the fly ash-brine systems. The effect of these parameters on the pH and EC of the systems will form the basis for choosing the parameters for the main batch reaction tests.

Concentrated brine (undiluted) (CUB) and brine diluted with ultrapure water (ratio 1:1) (DUB) were used for the preliminary batch reaction tests. 50 g of fly ash was reacted with varying concentrations and volumes of brine at various L/S ratios (1:1, 2:1 and 3:1). The fly ash-brine mixtures were agitated on a mechanical shaker at different contact times varying from 30-240 minutes at room temperature. The pH and EC of the supernatants were measured before filtration using a Hanna HI 991301 pH meter with portable pH/EC/TDS/Temperature probe. The supernatants were filtered using a 0.45 µm membrane filter after which the filtrates were prepared for anion and cation analysis (see details in section 3.2.4). The filtrates were stored at 4 °C before the analysis. Experiments were done in triplicate over a period of different contact times varying from 30-240 minutes. Table 3.3 shows the experimental parameters considered in the preliminary batch reaction tests.

Table 3.3: The experimental protocol showing the L/S ratio and the contact time of the preliminary batch reaction tests

	Concentrated brine (CUB)		Diluted brine (DUB)	
L/S ratio	Secunda	Tutuka	Secunda	Tutuka
1:1	30 min	30 min	30 min	30 min
	60 min	60 min	60 min	60 min
	120 min	120 min	120 min	120 min
	240 min	240 min	240 min	240 min
2:1	30 min	30 min	30 min	30 min
	60 min	60 min	60 min	60 min
	120 min	120 min	120 min	120 min
	240 min	240 min	240 min	240 min
3:1	30 min	30 min	30 min	30 min
	60 min	60 min	60 min	60 min
	120 min	120 min	120 min	120 min
	240 min	240 min	240 min	240 min

3.3.2.2 Main batch reaction tests

50 g of fly ash was reacted with varying volumes of brine (see section 3.2) which resulted in L/S 1:1, 1.5:1 and 5:1. The fly ash-brine mixtures were agitated on a mechanical shaker for extended contact times varying from 5-1440 minutes at room temperature. The pH and EC of the supernatants were measured before filtration using a Hanna HI 991301 pH meter with portable pH/EC/TDS/Temperature probe. The supernatants were filtered using a 0.45 µm membrane filter after which the filtrates were prepared for anion and cation analysis. The filtrates were stored at 4 °C before the analysis. Experiments were done in triplicate.

The major, minor and trace elements in the unreacted brine (UB) sample obtained from Tutuka RO desalination plant (section 3.2.2) and in the supernatants recovered from the fly ash-brine batch reaction tests were determined using inductively coupled plasma mass spectrometry (ICP-MS). The anions were determined by the use of Ion Chromatography (IC).

3.3.3 Long-term fly ash-brine interactions experiment

The long-term fly ash-brine interaction experiment was carried out by weighing 600 g of each of the fresh fly ash (Secunda and Tutuka) respectively into 1L plastic container. 600 mL of the brine solution from Tutuka RO plant was accurately measured and mixed with the fly ash in the plastic container. After the mixing of the fly ash and the brine solution in the plastic container, the container was closed. The mixture of fly ash and brine (1:1 wt/v) in the container was allowed to stand for different periods ranging from 1 week to 12 months. After each predetermined interactions period, the excess brine on the fly ash was decanted, filtered and stored in the refrigerator at 4 °C for ICP and IC analysis. The fly ash-brine solid residues were oven-dried at 50 °C. The oven-dried residues were crushed, milled, homogenized and stored in tightly-closed plastic containers at room temperature for further experiments and analysis. The long-term fly ash-brine interactions experiments were carried out in duplicate. Tables 3.4 and 3.5 below give the description of the materials used in the long-term fly ash-brine interaction experiments.

For easy identification, the residues from the fly ash-brine interaction experiments were labelled as; SAC, SBC, SCC and SDC for residues of Secunda fly ash-brine interactions experiments at 1 week, 1 month, 6 months and 12 months respectively, and TAC, TBC, TCC and TDC for residues of Tutuka fly ash-brine interactions experiments at 1 week, 1 month, 6 months and 12 months respectively. Secunda and Tutuka fresh fly ashes were labelled SFA and TFA respectively.

Table 3.4: The description of the long-term Secunda fly ash-brine interaction set-up

Sample label	Weight of fly ash (g)	Volume of brine (mL)	Contact time
SAC	600	600	1 week
SBC	600	600	1 month
SCC	600	600	6 months
SDC	600	600	12 months

Table 3.5: The description of the long-term Tutuka fly ash-brine interaction set-up

Sample label	Weight of fly ash (g)	Volume of brine (mL)	Contact time
TAC	600	600	1 week
TBC	600	600	1 month
TCC	600	600	6 months
TDC	600	600	12 months

3.3.4 Acid Neutralization Capacity experiment (ANC)

The acid neutralization capacity (ANC) test was carried out on the solid residues from the long-term fly ash-brine interactions tests based on the methodology of the European standard prEN14429. The method is divided into two stages which are; the preliminary test to determine the acid consumption of the fly ash-brine interactions residues; followed by the determination of acid neutralization capacity of the fly ash-brine residues.

3.3.4.1 Stage 1: Determination of acid consumption

According to prEN14429 (2003), preliminary determination of the acid consumption of the solid residues must be done to determine the volume and the concentration of acid needed to attain eight (8) different final pH values between the natural pH of the fly ash and pH 4. The preliminary determination can be done by two different methods which are; i) by titration and ii) by arbitrary division of the maximum acid consumption for the extreme pH values. The titration procedure was considered in this research for the preliminary determination of acid consumption. Approximately 15 g of each of the fly ash-brine long-term interactions residues was weighed into a rinsed bottle. 135 ml of de-mineralized water was added to each fly ash-brine residue in a bottle, which was equivalent to a liquid/solid ratio (L/S) 9:1 (this was done in order to attain a liquid/solid ratio ranging from 10:1 to 11:1 after the addition of the acid solution). The mixture was agitated for 1hour. The natural pH value of the eluate was determined after leaving the mixture to settle down for 10 minutes. In order to determine the amount of acid required by the fly ash-brine residue to attain different predetermined pH, different amounts of 2M HNO_3

solution were added to each of the different bottles containing the fly ash-brine residues as specified and the pH value was determined for each sample after 30 minutes of agitation. This process continued for 24 hours until the different predetermined pH values ranging from the natural pH to pH 4 were obtained. The amount of the 2M HNO_3 required to attain each of the different pH values were recorded and used for the main acid neutralization capacity (ANC) test.

3.3.4.2 Stage 2: Main ANC experiment

The main ANC experiment was carried out using the results of the preliminary acid consumption test. Different leachants were prepared by adding different amounts of 2M HNO_3 to each of the bottles containing de-mineralized water (based on the amounts of 2M HNO_3 required to attain the predetermined pH as calculated from the preliminary test) and made up to 150 ml. Each of these leachant solutions containing different amounts of HNO_3 was divided into three equal parts. 15 g of each of the fly ash-brine residues were placed in 250 ml bottles and the divided leachants were added at three different times (according to prEN14429 2003). The bottles were closed and the suspensions agitated each time a portion of the leachant was added, and the pH value was also measured and recorded after each leachant addition. After the addition of the last portion of the leachants to each of the fly ash-brine residue solutions, the each of the suspensions was agitated until $t = t_0 + 48$ hours. The pH, EC and TDS was measured before the solid residue was separated from the leachates after 48 hours by filtration using a membrane filter of 0.45µm. The leachates were preserved in a refrigerator at 4 °C before the analysis using IC and ICP-MS for anions and cations respectively.

3.3.5 Up-flow percolation tests

The test was carried out according to European standard method prEN14405 (prEN14405, 2003). This method involves packing the material to be tested (fly ash) in a column in a standardized manner (as described in section 3.3.5.2), and the brine is percolated in an up-flow direction through the column at a specified flow-rate to attain a fixed liquid/solid (L/S) ratios. This method was used to determine the release of constituents from fly ash packed in a column after a specific volume of brine had percolated through it. A continuous vertical up-flow was used in this study so that the column would be properly saturated with the brine and preferential percolation of the leachant would also be avoided. The method is designed to give insight into the release or removal of species from the fly ash-brine systems when brine solution is introduced continuously at controlled flow rate.

3.3.5.1 Sample preparation for the up-flow percolation test

The fly ash from Secunda being a dry and powdery material was humidified by adding small amounts of brine in order to allow easy packing of the material into the columns. The fly ash from Tutuka has been conditioned with brine before the sample was taken from the ash dump and there was no need to add more brine solution. The actual moisture contents of the moist fly ashes were determined before the samples were packed.

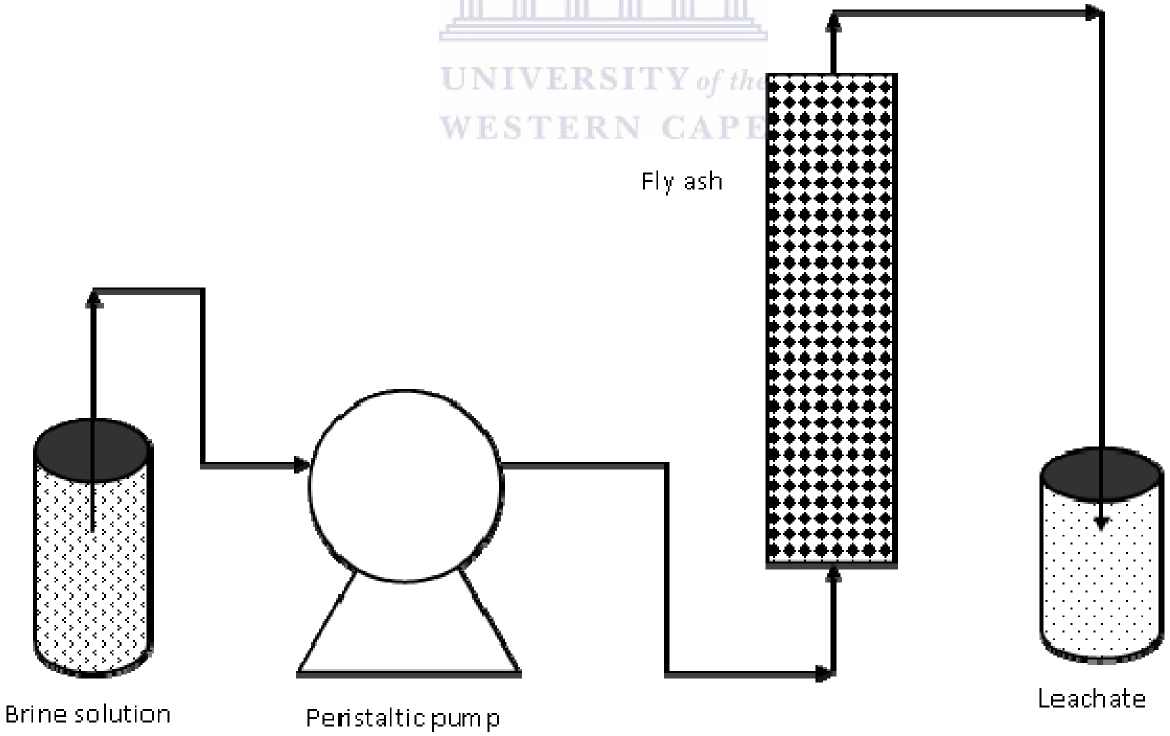

Figure 3.1: Schematic diagram of up-flow percolation test

3.3.5.2 Packing of the column

The column of height 30 cm and internal diameter 5 cm was designed for the up-flow percolation test. The column, including top and bottom sections, and filters were rinsed with 1M nitric acid (preparation of the acid in section 3.1) and de-mineralized water consecutively. After drying, the empty column was weighed (including top and bottom sections, filters and filter plates) to an accuracy of 1 g. The bottom section, equipped with filter plate and filter, was fitted to the column (photo shown in Figure 3.2). The fly ash sample (described in 3.3.5.1 above) was introduced into the column in five consecutive layers with each layer being introduced in three sub-layers. Each layer was compacted by dropping a rammer of weight 125 g, three times on the fly ash sample. The column was packed with the fly ash sample to the height of 25±5 cm. The top section of the column equipped with filter plate and filter was fitted firmly to the column so that brine flowing through the column could not bypass the filter. No open space was allowed above the packed material. The column filled with the packed fly ash was then weighed to determine the dry mass of the test portion in the column.

Table 3.6: Description and the total mass (g, dry weight basis) of fly ash in the columns

Column code	Column description	Weight of dry fly ash (g)	Weight of brine saturated ash (g)	Saturated pore volume (mL)
CL1	Secunda fresh ash + brine	615.07	894.18	279.21
CL2	Secunda fresh ash + brine	615.07	894.18	279.11
CL3	Tutuka fresh ash + brine	514.89	829.46	314.57
CL4	Tutuka fresh ash + brine	514.89	829.46	315.07
CLA1	Secunda fresh ash + brine-antiscalant	611.36	900.85	290.11
CLA2	Secunda fresh ash + brine-antiscalant	611.36	900.85	289.49
CLA3	Tutuka fresh ash + brine-antiscalant	514.75	830.79	316.04
CLA4	Tutuka fresh ash + brine-antiscalant	514.75	830.79	316.24

3.3.5.3 Start-up of the test

The inlet and outlet hoses were fitted on the inlet and outlet of the column respectively as shown in Figures 3.1 and 3.2. The column was saturated with brine or brine-antiscalant (as the case may be) using a peristaltic pump. The saturated fly ash was left standing for a period of three days in order to equilibrate the systems. After the equilibration period, brine or brine-antiscalant was pumped into the column using a peristaltic pump pumping at a flow rate of 12 mL/h. The outlet hose was connected to the collection bottle and samples were taken at different times for analyses over a period of time until a cumulative L/S 80 was attained. At each leachate collection, time and volume of the eluate fraction was recorded in order to calculate the liquid/solid ratio and other necessary calculations at the end of the experiment. The pH, EC and alkalinity (details in section 3.4.1) of the eluate were measured immediately after the eluates were taken. Samples were thereafter preserved with HNO_3 for analysis of metals by inductively coupled-mass spectrometry (ICP-MS) for major elements and un-acidified samples diluted accordingly for SO_4^{2-} and Cl^- analysis by ion chromatography (IC). Samples were refrigerated at 4^oC until analysis.

The up-flow percolation tests were carried out in duplicate.

Table 3.7: Characteristics of the up-flow percolation tests

Column height = 30 cm

Column internal diameter = 5 cm

Flow rate = 12 mL/h

Filling height = 25±5 cm

Equilibration time = 3 days

Initial L/S ratio = 15

Fraction number	Cummulative L/S ratio	Time	Volume of brine added (mL)				Volume of brine-antiscalant added (mL)			
			CL1	CL2	CL3	CL4	CLA1	CLA2	CLA3	CLA4
1	0.1	5 h	62	62	52	52	61	61	52	52
2	0.2	10 h	124	124	104	104	244	244	104	104
3	0.5	25 h	309	309	259	259	550	550	259	259
4	1	2.5 d	617	617	516	516	1161	1161	516	516
5	2	5 d	1232	1232	1031	1031	2995	2995	1031	1031
6	5	11 d	3077	3077	2576	2576	6052	6052	2576	2576
7	10	23 d	6152	6152	5151	5151	9109	9109	5151	5151
8	20	44 d	12303	12303	10300	10300	15223	15223	10300	10300
9	35	76 d	21529	21529	18023	18023	24393	24393	18023	18023
10	55	120 d	33830	33830	28322	28322	36620	36620	28322	28322
11	80	173 d	49207	49207	41194	41194	51904	51904	41194	41194

Figure 3.2: A photo of column set-up for the up-flow percolation experiment

3.3.6 Preparation of the up-flow percolation solid residues for analyses

After the up-flow percolation tests, the columns were turned upside down so that the bottom portion where the brine was continuously introduced represented the top section of the column. Each of the columns was divided into four (4) different sections representing the depth of the columns. Solid residue samples were taken at 1 cm (top), 10 cm, 20 cm and 30 cm (bottom) depths from each of the columns. The samples at these different depths were oven-dried at 50°C. After cooling, each of the solid residue samples from different depths were separately crushed, milled and homogenized before a representative sample was taken for different analyses and test(s).

3.3.7 The pH and EC of the solid residues

The pH and EC of the solid residues was determined using 1:1 solid residue: water ratio by following the method of Eckert (1988). 20 g of each of the solid residues extracted from the columns at different depths (1 cm, 10 cm, 20 cm and 30 cm) (see section 3.3.6) were weighed into in a beaker and an equal amount (20 ml) of ultrapure water was added. The mixture was then stirred thoroughly for 5 minutes, allowed to settle for 15 minutes and the pH and EC of the supernatant recorded. The procedure was duplicated.

3.3.8 Sequential chemical extraction

The sequential extractions were carried out by agitating the solid residue samples recovered from the up-flow percolation tests (described in section 3.3.6) on a mechanical shaker. After each extraction, samples were centrifuged at 3000 rpm for 20 minutes and the supernatants were filtered through a 0.45 µm membrane filter. The extraction experiments were done in triplicate. Multi-elemental analysis was done using the ICP-AES (major elements) and ICP-MS (trace elements). The extraction procedures were divided into five different fractions as described below. The detailed description on the preparation of the chemicals used for the sequential extraction tests was presented in section 3.3.8.

Water soluble fraction (Step 1): 1g of the solid residue was weighed into 50 ml centrifuge tubes and 45 mL of de-ionized water added. The sample was shaken on a mechanical shaker at room temperature for 1 hour. The solution was centrifuged at 3000 rpm for 20 minutes. 20 mL of the supernatant was measured into a 200 mL volumetric flask and the solution was made up to the mark with de-ionized water. Samples were taken for the elemental analysis. The diluted supernatant samples were acidified with drops of HNO_3 to prevent precipitation of species, and stored in the refrigerator at 4 °C.

Exchangeable fraction (Step 2): 45 mL of 1 M ammonium acetate buffer solution (pH 7) was added to the residue recovered quantitatively from step 1. The solution was shaken on a mechanical shaker for 1 hour at room temperature. The solution was centrifuged at 3000 rpm for 20 minutes. 20 mL of the supernatant was measured into a 200 mL volumetric flask and the solution was made up to the mark with de-ionized water. The diluted supernatant samples were taken for the elemental analysis and stored in the refrigerator at 4 °C.

Carbonate fraction (Step 3): 45 mL of solution containing the mixture of 1M acetic acid (CH_3COOH) and 1M ammonium acetate buffer (pH 5) was added to the residue recovered quantitatively from Step 2. The solution was shaken on a mechanical shaker for 1 hour at room temperature. The solution was centrifuged at 3000 rpm for 20 minutes. 20 mL of the supernatant was measured into a 200 mL volumetric flask and the solution was made up to the mark with de-ionized water. Diluted supernatant samples were taken for the elemental analysis and stored in the refrigerator at 4 °C.

Iron and manganese fraction (Step 4): 45 mL of 0.25M hydroxylamine hydrochloride (NH_2OHCl) prepared in 0.025M nitric acid (HNO_3) was added to the residue recovered quantitatively from Step 3. The solution was shaken on a mechanical shaker for 1 hour at room temperature. The solution was centrifuged at 3000 rpm for 20 minutes. 20 mL of the supernatant was measured into a 200 mL volumetric flask and the solution was made up to the mark with de-ionized water. Diluted supernatant samples were taken for the elemental analysis and stored in the refrigerator at 4 °C.

Residual fraction (Step 5): Solid residue from step 4 was rinsed with de-ionized water and completely transferred to a crucible and oven dried. The dried sample was transferred into a Teflon vessel and put into a Parr bomb. 14 mL of solution containing concentrated hydrofluoric acid (HF), concentrated nitric acid (HNO_3) and concentrated hydrochloric acid (HCl) (mixed in the ratio of 2:1:1 respectively) was added. The residue was digested in a Parr bomb at 200 °C for 3 hours. After cooling, excess HF in the digestate was neutralized by adding 25 mL of saturated H_3BO_3 solution. The solution was filtered using 0.45 µm membrane filter and the filtrate was diluted and made up to 100 mL in a volumetric flask.

3.4 Analytical Methods

This section describes the analytical techniques used in this study and the principles involved.

3.4.1 pH measurements

One of the most common measurements carried out on any liquid sample including natural waters and wastewater is the pH. This analysis is based on electrical measurement involving electrodes. A pH electrode consists of two half-cells; an indicating electrode and a reference electrode. Most applications today use a combination electrode with both half cells in one body. The pH of a solution is a measure of the hydrogen ion $[H^+]$ concentration in solution.

Mathematically, $pH = -\log [H^+]$ ….. *3.1*

pH measurement involves comparing the potential of solutions with unknown hydrogen ion $[H^+]$ to a known reference potential. 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 a 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.

3.4.1.1 Procedure

The pH of all the brine and the leachate samples in this study was measured by using a Hanna HI 991301 pH meter with portable pH/EC/TDS/Temperature probe. The pH meter was calibrated before use with buffer solution of pH 4.01 and 7.01. Duplicate sample measurements were done at room temperature.

3.4.2 Electrical Conductivity (EC)

Electrical conductivity (EC) is related to the concentration of ionized substances in water sample, and is a measure of the ability of a water sample to convey an electrical current. 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. H^+, Na^+, K^+, Mg^{2+}, Ca^{2+}, Cl^-, SO_4^{2-} and HCO_3^- ions have a major influence on water conductivity while ions such as Fe^{2+}, Fe^{3+}, Mn^{2+}, Al^{3+}, NO_3^-, HPO_4^{2-}, $H_2PO_4^-$ and dissolved gases have a minor influence on the conductivity. Organic compounds have poor conductivity. Water conductivity increases with temperature due to a decrease in viscosity and an increase in dissociation. EC is normally measured in mS/cm or µS/cm, or in µmhos/cm (1 mS/cm=1000 µmhos/cm).

3.4.2.1 Procedure

The electrical conductivity (EC) measurements of the samples were determined using a Hanna HI 991301 pH meter with portable pH/EC/TDS/Temperature probe. The meter was calibrated before use by using a standard of 12.88 mS/cm at room temperature. Duplicate sample measurements were taken at room temperature.

3.4.3 Total Dissolved Solids (TDS)

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 sol) suspended form. Generally the operational definition is that the solids must be small enough to survive filtration through a sieve size of two micrometres. The two principal methods of measuring total dissolved solids are gravimetry and electrical conductivity. Gravimetric methods (Radojević and Bashkin, 1998) are the most accurate and involve evaporating the liquid solvent to leave a residue which can subsequently be weighed with a precision analytical balance (normally capable of 0.0001g accuracy). This method is generally the best, although it is time consuming and leads to inaccuracies if a high proportion of the TDS consists of low boiling point organic chemicals, which will evaporate along with the water. In the most common circumstances inorganic salts comprise the great majority of TDS, and gravimetric methods are appropriate. 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. When correlated with laboratory TDS measurements, electrical conductivity provides an approximate value for the TDS concentration, usually to within ten percent accuracy (Azzie, 2002).

3.4.3.1 Procedure

The total dissolved solids (TDS) of the leachate samples in this study were estimated via EC using a Hanna HI 991301 pH meter with portable pH/EC/TDS/Temperature probe. The pH meter was calibrated and duplicate sample measurements were taken at room temperature.

The total dissolved solid (TDS) of the brine sample was determined gravimetrically by weighing known amounts of brine into an evaporating dish and then oven-dried at 105 °C until a constant weight was achieved. The weight of the dry solid residue was used to calculate the total dissolved solids of the brine solution.

3.4.4 Alkalinity

Alkalinity is the measure of a solution’s capacity to react with a strong acid to a predetermined pH. The alkalinity of a solution is usually made up of carbonate, bicarbonate, and hydroxides. Similar to acidity, the higher the alkalinity, the more neutralizing agent is needed to counteract it. Water samples with pH between 4.5 and about 8.5 will most likely have only bicarbonate alkalinity.

3.4.4.1 Procedure

Alkalinity of the samples was determined by titration with an acid using a standard method 2320B described by Eaton *et al.* (1995). The method involved titrating 20 ml of the sample solution with 0.1 M HCl to an end point of pH 4.0. The alkalinity was then calculated using the formula shown below (equation 3.2) and reported in mg/L $CaCO_3$.

$$\text{Alkalinity (mg CaCO}_3\text{/L)} = [A \times N \times 50 \times 1000] / \text{Vol. of sample} \quad \ldots\ldots 3.2$$

Where:

A = volume (ml) of standard acid used

N = normality/molarity of acid used.

The alkalinity reported as mg /L $CaCO_3$ was recalculated to mg/L HCO_3^- (equation 3.3) and the data was used for input during solution modeling by PHREEQC software.

$$\text{mg HCO}_3^-\text{/L} = \text{mol HCO}_3^-\text{/L} \times 61.0171 \times 1000 \quad \ldots\ldots 3.3$$

Where

$$\text{mol HCO3}^-/\text{L} = \frac{\text{mg CaCO3/L}}{50\ 000} \quad \ldots\ldots 3.4$$

3.4.5 Ion Chromatography (IC)

Ion chromatography (IC) 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. Ion chromatography is used for analysis of aqueous samples in parts-per-million (ppm) quantities of common anions (such as fluoride, chloride, nitrite, nitrate, and sulphate and common cations such as lithium, sodium, ammonium, and potassium) using conductivity detectors. The chromatograph also has the capability to analyze aqueous samples in parts-per-billion (ppb) quantities. Ion chromatography is a form of liquid chromatography where retention is predominantly controlled by ionic interactions between the ions of the solute and counter ions that are situated in, or on, the stationary phase. For example, to separate organic acids, it is the negatively charged acid ions that need to be selectively retained. It follows that the stationary phase must contain immobilized positively charged cations as counter ions to interact with the acid ions to retain them. Conversely, to separate cations, the stationary phase must contain immobilized anions as counter ions with which the cations can interact. Ion exchange stationary phases are available in mainly two forms. One form (probably the most popular) consists of cross-linked polystyrene polymer beads of an appropriate size which have been suitably treated to link ionic groups to the surface.

The other form is obtained by chemically bonding ionic groups to silica gel by a process similar to that used to produce bonded phases. These materials are called ion exchange media, a term which has given rise to the term “ion exchange chromatography” as an alternative to ion chromatography. Ionic substances can also be adsorbed on the surface of a reverse phase media and act as an adsorbed ion exchanger. The mobile phase is made to contain a small percentage of a soluble organic ionic material (e.g. tetrabutyl ammonium dihydrogen phosphate or n-octyl sulphonate). These substances are adsorbed onto the surface by dispersive interactions between the alkyl groups of the agent and those of the bonded phase and act as counter ions. In general ion chromatography is one of the more difficult types of liquid chromatography to exploit and is most often used for analysis of anions for which there are no other rapid analytical methods (Dionex, 1998).

3.4.5.1 Procedure

The leachates collected after each fly ash-brine interaction tests 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 Dionex DX-120 ion chromatograph with an Ion Pac AS14A column and AG14-4 mm guard column.

3.4.6 Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

The Inductively Coupled Plasma (ICP) coupled with a mass spectrometer (MS) gives very high sensitivity for the determination of elements and even isotopes in solution. This technique has the ability to detect very low levels (parts per billion) of most elements in an aqueous sample. The dynamic range is typically ten orders of magnitude and data reduction is relatively simple. Rapid data acquisition and data reduction enable the measurement of large numbers of samples in a short period of time. ICP-MS is the technique of choice for trace element analysis of natural waters, and can be used in analysing minerals and rocks after digestion. In ICP-MS, a plasma or gas consisting of ions, electrons and neutral particles is formed from Argon gas. The plasma is a very aggressive ion source, and virtually all molecules in a sample are broken up into their component atoms because of the high temperature (7000 K) at which the ion source operates. To create the inductively-coupled plasma (ICP), a radio frequency signal is fed into a tightly wound, water-cooled coil where it generates an intense magnetic field. In the centre of this coil is a specially made glass or quartz plasma torch where the plasma is formed. The plasma is generated in the argon gas by "seeding" the argon with a spark from a Tesla unit (similar to that used on a car spark plug). When the spark passes through the argon gas, some of the argon atoms are ionized and the resultant cations and electrons are accelerated toward the magnetic field of the radio frequency coil. Through a series of inelastic collisions between the charged particles (Ar^+ and electrons) and neutral argon atoms, stable high temperature plasma is generated. The plasma is used to atomize and ionize the elements in a sample. When the sample aerosol passes through the plasma, it collides with free electrons, argon cations and neutral argon atoms. The result is that any molecules initially present in the aerosol are quickly and completely broken down to charged atoms. The resulting ions are then passed through a series of apertures (cones) into the high vacuum mass analyzer. The isotopes of the elements are identified by their mass-to-charge ratio (*m/e*) and the intensity of a specific peak in the mass spectrum is proportional to the amount of that isotope (element) in the original sample (Jarvis *et al.*, 1992).

3.4.6.1 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 µS/cm. Major, minor and trace elements were analysed using ICP-AES (Varian Liberty II) and ICP-MS (Agilent 7500ce).

3.4.7 X-ray diffraction (XRD)

X-ray diffraction is an analytical technique which uses the diffraction pattern produced by bombarding a single crystal with X-rays to determine the crystal structure. The diffraction pattern is recorded and then analyzed or "solved" to reveal the nature of the crystal. 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 spacing in the crystal lattice can be determined using Bragg's law ($n\lambda = 2d\sin\theta$)**.** 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.

3.4.7.1 Procedure

The mineralogical compositions of the fresh fly ashes and the solid residues were determined using X-ray diffraction (XRD) and a Philips PANalytical instrument with a PW3830 X-ray generator operated at 40 kV and 25 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 samples were step-scanned at intervals of 0.02° 2theta from 5° to 85° and counted for 0.5 seconds per step.

3.4.8 X-ray Fluorescence (XRF)

XRF spectroscopy is widely used for the qualitative and quantitative elemental analysis of solid environmental, geological, biological, industrial and other samples. Compared to other competitive techniques, such as Atomic Absorption Spectroscopy (AAS), Inductively Coupled Plasma Spectroscopy (ICPS) and Neutron Activation Analysis (NAA), XRF has the advantage of being non-destructive, multi-elemental, fast and cost-effective. Furthermore, it provides a fairly 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 (ppm). Its main disadvantage is that analyses are generally restricted to elements heavier than fluorine and that a large sample is required (Kalnicky and Singhvi 2001).

3.4.8.1 Sample preparation and procedure

Procedures for sample preparation vary considerably in the cases of in situ or intrusive measurements. Solid samples such as rock minerals must be polished to assure surface homogeneity, while powders are usually pressed into pellets. In all cases, x-ray transparent supporting media should be used (polyethylene, Kapton, Mylar, etc.).

Fresh fly ash and the solid residues generated from the fly ash-brine interaction tests were analysed for elemental composition using X-ray fluorescence (XRF), and a Philips 1404 Wavelength Dispersive Spectrometer fitted with a Rh tube was used. The samples were oven-dried at 50 °C for 12 hours to remove the water content prior to analysis. The XRF technique reports in % oxides for major elements and ppm for minor elements. The elements reported as % oxides (in the case of batch reaction tests' solid residues) were converted to ppm elements using element conversion software assessed at http://www.marscigrp.org/oxtoel.html.

3.4.9 Scanning Electron Microscopy-Energy Dispersion Spectroscopy (SEM-EDS)

3.4.9.1 Scanning Electron Microscopy

The scanning electron microscope (SEM) is a type of electron microscope capable of producing high-resolution images of a sample surface. 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 of the sample. 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. 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. Specimen preparation includes drying the sample in an oven at 100 °C and making it conductive to electricity by sputter coating with carbon or gold, if it is not already. Micrographs 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.

3.4.9.2 Detection of secondary electrons

The most common imaging mode in SEM 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.

3.4.9.3 Energy Dispersive Spectroscopy (EDS)

EDS, also called Energy Dispersive X-ray Spectroscopy (EDX), is a technique based on the collection and energy dispersion of X-rays created when high energy electrons bombard a sample. The EDS is attached to the Scanning Electron Microscope (SEM) and the two techniques are often used together. The X-rays have energies that are characteristic of the elements in the sample. The instrument's electronics process the signals to give histograms of energy vs. signal strength, the latter being related to relative elemental concentration. EDS can also provide elemental maps of the composition of sample that can be compared to the electron micrographs. The method detects all elements from boron to uranium and is usually non-destructive. Detection limits range from 0.05-2 % for high to low Z elements, respectively. EDS is particularly good for relating elemental composition to topographical features but it is only qualitative and should be supported by other techniques such as XRF for quantitative elemental composition.

When an element is bombarded with a particle beam and an electron beam, the specimen will release some of the absorbed energy as X-rays. Much of the time, the energy is the result of changes in the speed of an electron, which is random; however, when this interaction removes an electron from a specimen's atom, frequently an electron from an outer shell (or orbital) occupies the vacancy. When an outer electron occupies a vacancy, it must lose a specific amount of energy to occupy the closer shell. This amount is readily predicted by the laws of quantum mechanics and usually much of the energy is emitted in the form of X-rays. Two methods are used to determine the x-rays that are produced: (1) energy-dispersive analysis separates and detects X-rays of specific energy and displays them as histograms, whereas (2) wavelength-dispersive analysis uses the reflection of X-rays off of a crystal at a characteristic angle to detect x-rays of specific wavelength.

3.4.9.4 Procedure

The fresh fly ash samples from the two coal-fired stations and the solid residues generated from the fly ash-brine interaction tests were oven-dried at 105 °C for 12 hours in preparation for the SEM-EDS analysis. The dried samples were sprinkled on special glue mixed with carbon graphite and mounted on aluminium stubs. The morphology of the samples was established by secondary electron mode. The "photo" imaging was used to identify regions of relative homogeneity and thereafter EDS analysis was done on some spots for qualitative elemental composition.

3.4.10 Geochemical modeling of the fly ash-brine interactions

Geochemical modeling is a powerful tool for evaluating geochemical processes. When properly applied modeling can provide valuable insights into processes controlling the release, transport and fate of contaminants in surface water environments. Several computer codes are available for modeling, these include WATEQ4F (Ball and Nordstrom, 1991), MINTEQA2 (Allison *et al.*, 1991) and PHREEQC (Parkhurst, 1995). All these computer codes perform the following type of calculations using chemical analysis of aqueous samples as input, temperature and pH:

1) corrects all equilibrium constants to the temperature of the sample using either the Van't Hoff equation or an empirical polynomial.

2) calculates speciation, for each element by solving a matrix of equations consisting of a stability constant for each complex and a conservation of mass equation for each element.

3) calculates activity coefficients by either the Debye-Hückel equation or the Davies equation.

4) calculates the state of saturation of the solution with respect to all the solids in its database that contain the elements in the input analysis.

5) performs calculations related to oxidation-reduction processes.

PHREEQC performs other calculations such as reaction-path and advective transport calculations involving specified irreversible reactions, mixing of solutions, mineral and gas equilibria, surface complexation reactions and ion exchange reactions and inverse modeling which finds sets of mineral and gas mole transfers that account for composition differences between waters, within specified compositional uncertainties (Parkhurst, 1995). PHREEQC is designed to perform low temperature aqueous geochemical calculations. PHREEQC simulates chemical reactions and transport processes in natural as well as polluted waters. The MINTEQ.V4 database supplied with the PHREEQC computer code was used for the calculations in this work.

3.4.10.1 Geochemical modeling

Precipitation of solid phases may be the most important chemical process influencing on the fate of major (SO_4^{2-}, Fe Al, Mn, Ca, Na, Cl) and minor elements (Zn, Cu, Mo, Ni, B, Sr) in the fly ash-brine leachates. Activities of aqueous species and mineral saturation indices of selected mineral phases were calculated using PHREEQC software (Parkhurst, 1995) and the MINTEQ.V4 database. Analysis data of the leachates were input and used to estimate the activities of the various species. The activities of the dissolved species were calculated with Davies equation (Davies, 1962). The data used for the ion activity calculations were pH, solute concentrations for Al, Ca, Cu, Fe, Zn, SO_4^{2-}, Na, K, Si, Mn, Pb, B, Sr, Ba, and Mo. Saturation index (SI) is used when large deviations from equilibrium are observed. For SI = 0, there is equilibrium between the mineral and the solution; SI <0 reflects sub-saturation, and SI >0 super-saturation. For a state of sub-saturation dissolution of the solid phase is expected and super saturation suggests precipitation.

3.4.11 Quality control during aqueous sample analysis

The quality control of the data generated was assured through several techniques which include analysis of certified reference materials (CRM) (Tables 3.8 and 3.9), spiking with standard solution and determining recoveries (Table 3.10).

Table 3.8: Comparison of experimental mean with certified reference material (CRM) (NIST1643e), n=3

					calc	DF=2
	CRM	mean (n=3)	SD	% RSD	t-values	$t_{crit;95\ \%}$
Li	17	21.387	2.338	25.804	3.25	4.3
Be	13.64	12.08	0.52	11.437	5.196	
B	154	168.8	9.667	9.61	2.652	
Al	138.33	122.8	25	11.227	1.076	
Si		140.998	131.503			
P		30.177	2.924			
Ti		75.113	0.558			
V	36.93	36.8	0.473	0.352	0.476	
Cr	19.9	19.977	0.336	0.385	0.396	
Mn	38.02	38.26	1.56	0.631	0.266	
Fe	95.7	103.513	3.391	8.164	3.991	
Co	26.4	26.347	0.138	0.202	0.67	
Ni	60.89	60.08	0.193	1.33	7.256	
Cu	22.2	22.27	0.4	0.315	0.303	
Zn	76.5	76.057	1.062	0.58	0.723	
As	58.98	59.683	0.062	1.192	19.578	
Se	11.68	11.41	0.533	2.312	0.877	
Sr	315	305.8	1.867	2.982	8.722	
Mo	118.5	144.367	3.222	21.828	13.904	
Cd	6.408	6.11	0.118	4.656	4.371	
Ba	531	537.6	0.4	1.243	28.578	
Hg		0.296	0.03			
Pb	19.15	18.397	0.402	3.934	3.244	

Table 3.9: ICP-MS results (ppb) and the % recovery when spiked with standard solutions

	Unspiked	+ 115.6ppb	% Recovery	+ 99ppb P + 98.4ppb MBH	% Recovery
Li	1913				
Be	0.1				
B	5	145	121		
Al	56.7	170.6	98.5		
Si	421				
P	22.2			125.7	104.5
Ti	173			252.9	80.7
V	0.4			91.33	91.8
Cr	13.5	132	102.5		
Mn	0.3	114.8	99.1		
Fe	32.5	148.5	100.3		
Co	0.1	119.5	103.3		
Ni	1.1	116.3	99.6		
Cu	49.5	162.4	97.6		
Zn	40.8	148.6	93.2		
As	0.4				
Se	1.1				
Sr	76960				
Mo	6.8			106.2	100.4
Cd	0	113.6	98.3		
Ba	8869				
Hg	0.1				
Pb	10.3	121.3	96		

Table 3.10: ICP-AES results (ppm) and % recovery when spiked with standard solutions

	0.92 ppm QC		9.18 ppm QC	
	Analysed	% RSD	Analysed	% RSD
Ca	1.01	9.6	9.18	0.1
K	0.92	0.2	9.47	3.1
Mg	0.93	1	9.33	1.7
Na	0.98	6.1	9.4	2.4
Sr	0.97	5.4	9.26	0.9

	Spike Recovery		
	unspiked	+ 4.9ppm	% Recovery
Ca	1.55	6.46	100.9
K	0.07	5.4	109.6
Mg	0.03	4.91	100.5
Na	0.26	5.21	102
Sr	0.01	4.82	98.8

The accuracy of the analysis was validated by the t-test which compares the experimental mean with a known true value (μ). In the case of this study, a certified reference material (CRM) NIST-1643e traceable to National Institute of Standards and Technology, Boulder, Colorado USA was used (Rossouw, 2008) (Table 3.8). Species not covered by the NIST CRM, accuracy was validated by the use of a multi-element plasma calibration standard traceable to NIST (bought from MBH Analytical, Holland House, Barnet, England) and Quality control (QC) for AES purchased from MERCK Chemical, South Africa and traceable to NIST. From the calculated t values Be, Ni, Sr, As, Mo, and Ba $t_{calc}>t_{crit}$ and hence random errors alone could not explain the deviations. The ICP-MS analysis seems to work adequately for Li, B, Al, V, Cr, Mn, Co, Cu, Zn, Se, Pb but poor for Be, Ni, Sr, As, Mo, and Cd. With the spiking technique, adequate recovery was obtained for Al, Ti, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Pb and Mo but poor for B and P (Tables 3.8 and 3.9). With ICP-AES, adequate recovery (98.8-100.9) was obtained for Ca, K, Mg, Na and Sr (Table 3.10). Hence analysis of Ca, K, Mg, Na and Sr with ICP-AES is accurate.

The next chapter (chapter 4) will present and discuss the results of the characterization of the fresh fly ash and brine samples. The result of the batch reaction tests carried out on the fly ashes from Secunda and Tutuka and brine solution will also be presented and discussed.

Chapter 4

Fly ash-brine interactions: characterization and batch reaction tests

4 Introduction

This chapter presents and discusses the results of the physical and chemical characterization of fresh fly ash samples from Secunda and Tutuka, and the brine solution (as the case may be) used in this study. Different analytical techniques such as XRD, XRF, SEM-EDS and total acid-digestion tests were utilized to characterize Secunda and Tutuka fresh fly ashes, while IC and ICP-MS was employed to determine the chemical composition of the brine solution (analytical and experimental procedures in chapter 3). This chapter also presents and discusses the results of the batch reaction tests (experimental details in section 3.3.2) involving the interactions of the fly ashes and brine solution. A preliminary test was carried out to determine the effects of the brine concentrations, contact time and L/S ratio on the release and removal of species from the brine solution. Thereafter, based on the results of the preliminary batch reaction tests, the batch reaction tests were carried out with extended contact times and different L/S ratios. The batch reaction tests tend to models the aggressive fly ash-brine interactions scenario in Secunda power utility where the fly ash from the hoppers is aggressively mixed directly with brine solution before transported to the ash dump in a slurry form. The batch reaction tests were carried out to understand the effect of L/S ratio and contact times on the leaching and removal of species, and to understand the effect of the aggressive fly ash-brine interactions during mixing on the brine quality. Apart from the results of the characterization of the fly ash and brine solution, and the results of the batch reaction tests, this chapter also presents and discusses the results of the geochemical modeling carried out using the data from the batch reaction tests. The saturation indices (SI) of different mineral phases were calculated using PHREEQC geochemical modeling software in order to determine the solubility controlling the release and removal of species from the fly ash-brine systems.

The results and discussion of this chapter is divided into four (4) sections (4.3.1, 4.3.2, 4.3.3 and 4.3.4). Section 4.3.1 presents and discusses the results of the physical and chemical characterization of fresh fly ash samples and the brine solution. Section 4.3.2 deals with the results and discussion of the preliminary batch reaction tests carried out to determine the effects of L/S ratio, brine concentrations and contact times on the release and removal of species from the brine solution. Section 4.3.3 presents and discusses the results of the batch leaching tests involving the fly ashes and brine solution at extended contact times and at different L/S ratios. Section 4.3.3 deals with the geochemical modeling of the data from the batch reaction test.

4.1 Overview

Fly ash generated as a result of coal combustion in order to generate electricity has been considered to be a significant source of potential toxic elements that can be released to the environment (Marrero *et al.,* 2007). The release of the species contained in fly ash is dependent on the characteristic of the types of coal burnt, the combustion conditions and the handling of the residue. Fly ash is being disposed of in landfills, and used in some beneficial ways which include additives to cement and soil amendment. According to the American Coal Ash Association (1998), USA generated 102 million tons (Mt) of coal combustion products in 1996, out of which fly ash was 59 million tons, but only 25 % of this fly ash was utilized (Duchesne and Reardon, 1999). In South Africa, according to the ESKOM report (Eskom report, 2009), ESKOM generates approximately 40 Mt of fly ash annually of which only 5 % is currently beneficially utilized, the rest being disposed of in ash dams, landfills or ponds (Petrik *et al.,* 2005) while SASOL Synfuels at Secunda produces 3 Mt fly ash and 7 Mt gasification ash annually. Brine is also a waste material generated in power utilities as a result water re-use. Brine contains major and minor species in significant quantities (Turek, 2004; Mooketsi *et al.,* 2007) which makes its disposal problematic. In the search for ways to reduce the disposal problems of brine and fly ash, some coal-fired power generating utilities in South Africa use brine streams to hydraulically transport fly ash to ash dumps while others use brine for dust suppression in ash dumps. For instance, in SASOL-Secunda, the fly ash is mixed with about 60 % brine solution to form slurry before it is transported hydraulically to the ash dumps. At ESKOM-Tutuka, the fly ash is conditioned with about 16 % brine for dust suppression before conveying the ash to the dump for disposal where it is further conditioned with brine. Despite the co-disposal of fly ash with brine, the interaction chemistry of the species in the system is yet to be understood. The interactions of some species in the fly ash and brine could result in precipitation of salts due to super-saturation or adsorption. It is necessary to study the chemical interactions in fly ash-brine systems. This will give an insight into the effect of the interaction on the brine quality as well as the sustainability of the co-disposal scenario over time when fly ash and brine are co-disposed.

The understanding of the physical and chemical compositions of waste materials is necessary to determine the impact of disposal on the environment. Several analytical and instrumental techniques such as x-ray diffraction (XRD), x-ray fluorescence (XRF), scanning electron microscopy-energy dispersion spectroscopy (SEM-EDS), inductively coupled plasma-mass spectroscopy (ICP-MS) and ion chromatograph (IC) have been used to determine the physical, chemical and mineral compositions of fly ash (Das *et al.,* 2001; Spears & Martínez-Tarrazona, 2004; Pires & Querol, 2004; Aubert *et al.,* 2006; Li *et al.,* 2004; Marrero *et al.,* 2007). The characterization of the fly ashes and the brine solution used in this study is expected to give an insight into the chemical compositions of these waste materials and assess the impacts of their disposal on the environment.

The objectives of this chapter are; (1) to determine the physical, chemical and mineralogical compositions of the fly ash, and the chemical composition of the brine solution, (2) to evaluate the effects of L/S ratio and contact times on the leaching and removal of species during the batch reaction tests, (3) to evaluate the effects of the chemical interactions of fly ash and brine components on the brine quality, and (4) to determine the possible mineral phases controlling the release of species in the batch reaction systems.

4.2 Materials and methods

The detailed descriptions of the fly ash and brine samples used in the section of the study are presented in chapter 3 sections 3.2.1 and 3.2.2. The analytical procedures such as XRD, XRF and SEM-EDS are presented in section 3.4.7, 3.4.8 and 3.4.9 respectively while the experimental procedures of the total dissolved solids (TDS) and batch reaction tests are presented in sections 3.4.3 and 3.3.2 respectively. The anion and cation analysis of the leachates from the batch reaction tests were done using IC and ICP-MS respectively (see sections 3.4.5 and 3.4.6 respectively).

4.3 Results and discussion

The results and discussion presented in this chapter of the thesis are in the following sequence; Section 4.3.1 presents and discusses the characterization of fresh fly ash samples and the brine solution while section 4.3.2 deals with the results and discussion of the preliminary batch reaction tests. Section 4.3.3 presents and discusses the results of the main batch reaction tests while the geochemical modeling of the data from the batch reaction tests will be presented in section 4.3.3. The experimental details are in chapter 3 as stated in section 4.2 above.

4.3.1 Characterization of fly ash and brine

The characterization of the feedstock materials (fresh fly ash and brine) used for further experiments are presented in this section 4.3.1. The main reason for the characterization of the fresh fly ashes and the brine used in this study is to control the input parameters and to be able to do mass balances in a controlled environment. The objective of this section is to understand the physical, chemical and mineralogical compositions of the fresh fly ash, and the chemical composition of the brine solution. Several analytical and instrumental techniques such as x-ray diffraction (XRD), x-ray fluorescence (XRF) and scanning electron microscopy-energy dispersion spectroscopy (SEM-EDS) were used to characterize the fresh fly ashes while inductively coupled plasma-mass spectroscopy (ICP-MS) and ion chromatograph (IC) were employed for the analysis of the brine. The characterization of the fly ashes and the brine solution used in this study is expected to give an insight into the chemical compositions of the waste materials.

4.3.1.1 Physical composition of fresh fly ashes: (SEM-EDS)

The morphology of the fresh fly ashes is shown in Figure 4.1 below while Table 4.1 shows the elements present in the area analyzed (determined by EDS) on each sample.

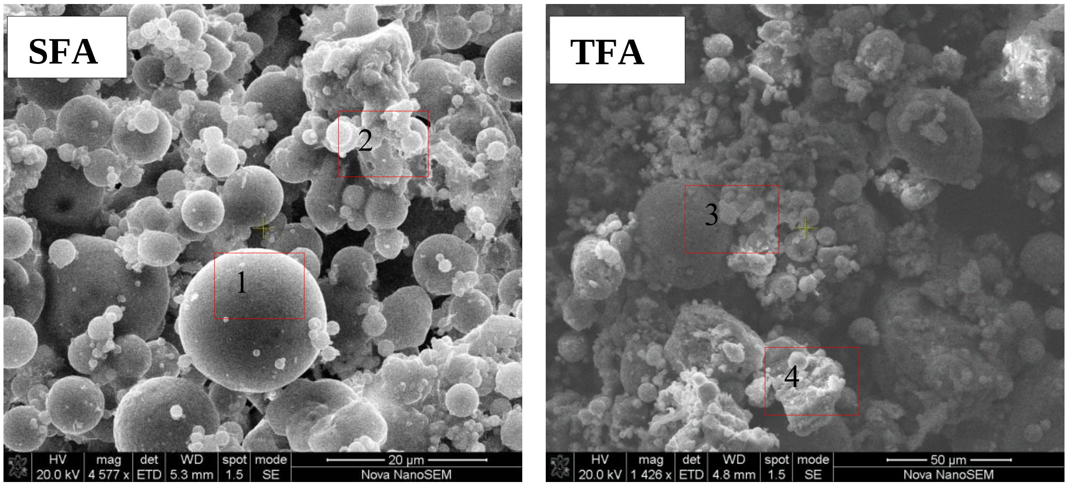

Figure 4.1: SEM-EDS micrograph of Secunda fresh ash (SFA) and Tutuka fresh ash (TFA) showing the area chosen for EDS analysis.

Table 4.1: EDS analysis of the chosen areas (weight %) of Secunda and Tutuka fresh fly ashes (SFA and TFA respectively)

Element	1	2	3	4
O	45.67	37.18	53.05	47.56
Mg	1.59	ND	ND	ND
Al	17.43	21.68	10.04	16.55
Si	25.48	30.76	33.59	22.89
S	ND	1.06	ND	ND
K	1.49	1.14	ND	ND
Ca	8.34	7.2	3.32	13

1 and 2 = Secunda fresh ash; 3 and 4 = Tutuka fresh ash

The surface morphology of Secunda fresh fly ash (SFA) and Tutuka fresh fly ash (TFA) are shown in Figure 4.1 while Table 4.1 showed the EDS analysis of selected area of the SEM micrographs. The micrographs from the SEM show that the particles of the fly ashes, especially Secunda fresh fly ash (SFA), are spherical in shape. The spherical shape of the fly ash particles has been attributed to the conditions of combustion and the high temperature during coal combustion (Gitari *et al.,* 2009; Saikia *et al.,* 2006). The spherical shape of fly ash particles are formed as a result of relatively sudden cooling during combustion processes (Li *et al.,* 2003).

The EDS analysis of selected areas in the fresh fly ashes showed that the fly ash samples are rich in oxygen, aluminum and silicon (Table 4.1). Ca was observed to be present in a significant percentage in the fly ashes. Apart from the aluminosilicate content, the analyzed area in Secunda fresh fly ash (SFA) showed the presence of Mg and K while these elements were not observed in the analyzed area of Tutuka fresh ash (TFA). SEM-EDS analysis has been observed not to be a suitable quantitative method of analysis for the determination of chemical composition of fly ash but could be used to qualitatively establish the presence of various elements in fly ash (Fatoba, 2008).

4.3.1.2 Mineralogical composition of fly ash: (XRD analysis)

The XRD patterns of fresh Secunda and Tutuka fly ashes used in this study are shown in Figure 4.2.

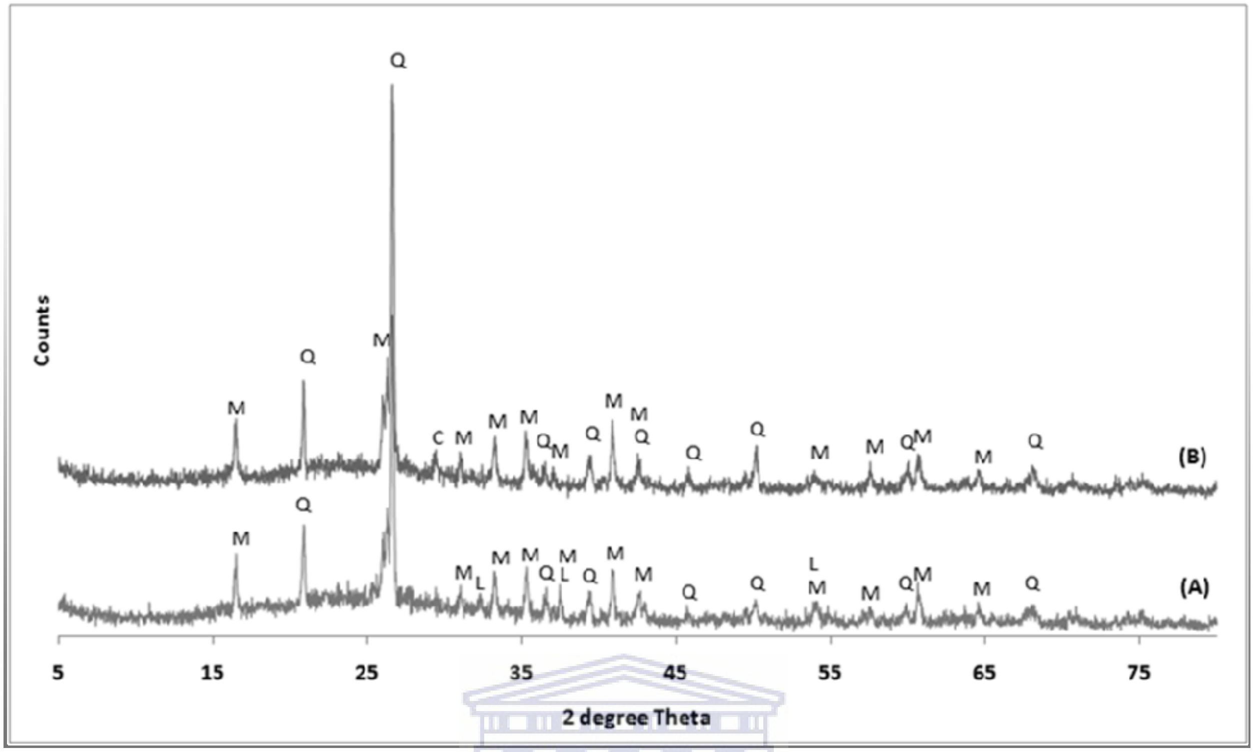

Figure 4.2: XRD spectra of Secunda (A) and Tutuka (B) fresh fly ash; M = Mullite, Q = quartz, C = Calcium Magnesium Aluminum Silicate Chloride, L = CaO

It was observed (Figure 4.2) that the major crystalline mineral phases of the two fly ashes are quartz (SiO_2) and mullite ($3Al_2O_3.2SiO_2$). The mineralogical compositions of Secunda and Tutuka fly ashes are similar except for the identification of CaO in Secunda and Calcium Magnesium Aluminum Silicate Chloride $[(Ca_{19}.44Mg_{2.56})(Si.75Al._{25})_8O36Cl_2]$ in Tutuka fly ash. The peak intensity of CaO observed in Secunda fly ash was very low when compared to the intensity of other peaks (Figure 4.2) which could indicate that the amount of CaO in the fly ash is low. The non-appearance of the CaO peak in Tutuka fly ash (Figure 4.2) could indicate that its concentration in fly ash sample is too low to be identified by XRD. The Calcium Magnesium Aluminum Silicate Chloride $[(Ca_{19}.44Mg_{2.56})(Si.75Al._{25})_8O36Cl_2]$ identified in Tutuka fly ash could be attributed to the preconditioning of Tutuka fly ash with brine before disposal. The Tutuka fly ash was moistened with brine in order to suppress dust before disposal and irrigated with brine after disposal at the dump. This treatment could have lead to the interactions between the various elements contained in brine and fly ash before the sample was taken.

4.3.1.3 Chemical composition of fly ash

The chemical composition of fresh fly ash from Secunda and Tutuka power utilities as presented in Table 4.2 below was determined using XRF (see section 3.4).

Table 4.2: The chemical composition (major elements as oxides in % w/w and trace elements in ppm) of Secunda and Tutuka fly ash samples (n=3)

Secunda fly ash				Tutuka fly ash			
Major elements (%w/w)		Trace elements (ppm)		Major elements (%w/w)		Trace elements (ppm)	
Al_2O_3	26.03	V	219.7	Al_2O_3	24.5	V	204.0
CaO	9.30	Cr	129.8	CaO	5.9	Cr	145.3
Cr_2O_3	0.02	Co	10.5	Cr_2O_3	0.0	Co	21.0
Fe_2O_3	2.36	Ni	58.5	Fe_2O_3	5.4	Ni	62.2
K_2O	0.81	Cu	37.0	K_2O	0.8	Cu	32.8
MgO	2.25	Zn	32.1	MgO	1.4	Zn	48.5
MnO	0.05	Ga	40.8	MnO	0.1	Ga	33.6
Na_2O	0.61	Rb	33.8	Na_2O	0.3	Rb	42.2
P_2O_5	0.89	Sr	3268.1	P_2O_5	0.5	Sr	1164.4
SiO_2	49.58	Y	81.9	SiO_2	51.8	Y	74.4
TiO_2	1.58	Zr	419.2	TiO_2	1.5	Zr	382.8
LOI	4.35	Nb	35.8	LOI	8.0	Nb	33.7
sum	97.82	Ba	2292.0	sum	100.1	Ba	983.7
		La	119.8			La	108.3
		Ce	259.4			Ce	199.7
		Nd	86.9			Nd	67.9
		Pb	41.0			Pb	50.3
		Th	47.6			Th	39.5
		U	2.0			U	8.9
		Cl	73.9			Cl	730.3

The fly fresh ashes from Secunda and Tutuka power stations (Table 4.2) were mainly composed of Al_2O_3, SiO_2, CaO and Fe_2O_3 as major elements. According to the American Society for Testing and Materials (ASTM, 1988), which classified fly ashes based on the percentage composition of Al_2O_3, SiO_2 and Fe_2O_3 in the ash, fly ashes from Secunda and Tutuka can be classified as class F fly ashes ($SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70$ %). The concentrations of the major elements (as oxides) (determined by XRF as specified in section 3.4.8) in the two fly ashes vary. For example, the CaO, Al_2O_3 and MgO concentrations in Secunda fly ash was higher than the concentrations of these oxides found in Tutuka fly ash. On the other hand, the concentrations of SiO_2 and Fe_2O_3 in Tutuka fly ash were higher than what was detected in fly ash from Secunda. The variation in the concentrations of these oxides in the two different fly ashes could be due to the different types of coal burnt at each power station or as a result of the preconditioning treatment of the Tutuka fly ash with brine before the sample was taken (see section 3.2.1). The dissolution of these oxides has a significant effect on the pH of the fly ash solution. CaO (9.3 %) and MgO (2.25 %), which concentrations are higher in Secunda fly ash, are basic oxides and when dissolved in aqueous solution could lead to an increase in the pH of the fly ash solution, while the Fe_2O_3 (2.36 %) which is an acidic oxide, could decrease the pH of the fly ash solution when dissolved in aqueous solution. It was observed that the concentration of various trace elements in Tutuka fly ash was slightly higher than their concentrations in Secunda fly ash. For instance, except for elements such as Sr, Ba, Th, V, Ga, Cu, Y, Zr, Nb, La, Ce and Nd, the concentrations of other trace elements such as Cr, Co, Ni, Zn, Pb and U were found to be higher in Tutuka fly ash with concentrations of 145.33 ppm, 21 ppm, 62.22 pm, 48.53 ppm, 50.33 ppm and 8.91 ppm respectively. Generally, the concentrations of some elements such as Sr, Ba, V, Zr and Ce present in the two fly ashes were higher and ranged between 1164 and 3268 ppm, 983 and 2292 ppm, 203 and 220 ppm, 382 and 419 ppm and 199 and 259 ppm respectively when compared to the concentrations of trace elements such as Cr, Co, Ni, Cu and Pb among others (Table 4.2). The chloride content of Tutuka fly ash was observed to be higher than that of Secunda fly ash. The significant difference in the concentration of Cl (730 ppm) in Tutuka fly ash when compared to the concentration in Secunda fly ash could be as a result of preconditioning the Tutuka fly ash with brine solution, which is high in Cl (Table 4.3), before the sample was collected.

4.3.1.4 Chemical composition of brine

The chemical composition of the brine solution (see section 3.2.2 for the sampling and analysis details) collected from the RO desalination plant at Tutuka power station, South Africa and used in this study is presented in Table 4.3 below.

Table 4.3: Chemical compositions (concentration in mg/L except pH and EC (mS/cm)) of unreacted brine (UB) solution from Tutuka power station (n=3).

Major elements (mg/L)		Minor elements (mg/L)	
B	2.24 ± 0.024	Al	0.045 ± 0.0063
Ca	106.99 ± 1.69	As	0.0068 ± 0.000053
K	106.2 ± 0.85	Ba	0.057 ± 0.0019
Mg	163.36 ± 0.85	Cd	0.00017 ± 0.000012
Na	4804.88 ± 2.72	Co	0.014 ± 0.00037
Si	13.11 ± 0.075	Cr	0.014 ± 0.0014
Cl	2424 ± 16.97	Cu	0.26 ± 0.087
SO_4	8858 ± 86.27	Fe	0.24 ± 0.2
pH	7.75 ± 0.031	Mn	0.0017 ± 0.000089
EC (mS/cm)	16.69 ± 0.50	Mo	0.039 ± 0.0011
TDS	15400 ± 282.84	Ni	0.12 ± 0.00071
		P	0.82 ± 0.025
		Pb	0.0039 ± 0.0036
		Se	0.0049 ± 0
		Sr	3.055 ± 0.0098
		Ti	0.00069 ± 0.00055
		V	0.019 ± 0.000035
		Zn	0.13 ± 0.014

The chemical composition (major, minor and trace species) of brine used in this study was determined using ICP-MS and IC analytical techniques and the results are presented in Table 4.3. It was observed that the concentrations of major species such as Ca, Na, Mg, K, Cl and SO_4 were high in the brine solution. The concentrations of Na (4804.88 mg/L), Cl (2424 mg/L) and SO_4 (8858 mg/L) in the brine were significantly higher than other major species. The concentrations of trace elements such as As, Se, Cd, Cu, Cr, Fe, Mn, Co, etc were very low in the brine solution. The pH of the brine solution is near neutral (7.75) while the electrical conductivity (EC) and total dissolved solids (TDS) values were found to be 16.69 mS/cm and 15400 mg/L respectively. The measured pH (7.75) indicates that the brine solution is not acidic in nature while the high EC and TDS values (16.69 mS/cm and 15400 mg/L respectively) indicate the presence of ionic species and a high amount of dissolved salts in the solution.

4.3.1.5 Summary

The characterization of the fly ashes used in this study by XRD, XRF and SEM-EDS revealed the physical, chemical and mineralogical composition of the fly ashes. The SEM micrographs showed that the fly ashes particles were smooth and spherical in shape. The EDS of the chosen areas in the fresh fly ashes showed the abundance of oxygen, aluminium and silicon with lesser amounts of Ca and K in the fly ash samples. The identification of new mineral phase (Calcium Magnesium Aluminum Silicate Chloride) $[(Ca_{19}.44Mg_{2.56})(Si.75Al._{25})_8O36Cl_2]$ by the XRD in Tutuka fly ash as well as the expected quartz and mullite phases was attributed to the preconditioning of Tutuka ash with brine before disposal because this phase was not identified in the fresh fly ash from Secunda which did not have contact with brine before it was sampled. The XRF analysis carried out on the fresh fly ashes revealed that most of the major oxides in Secunda fly ash were higher that what was observed in Tutuka ash. This could be the effects of the preconditioning of Tutuka fly ash with brine before disposal, which may have led to the slight dissolution of these oxides. The effect of moistening of Tutuka fly ash with brine before disposal was shown on the concentration of Cl which was in ten order of magnitude higher than the concentration of Cl in Secunda fly ash. The XRF analysis showed that the fly ashes from Secunda and Tutuka power stations could be 'class F' type of fly ash based on the summation of the percentage compositions of Al_2O_3, SiO_2, and Fe_2O_3 in the fly ashes which was found to be greater than 70.

The chemical composition (as determined using ICP-MS and IC) of the brine solution showed that the brine used in this study contained very high concentrations of Ca, Mg, K, Na, Cl and SO_4. The concentrations of trace elements such as As, Se, Cd, Cu, Cr, Fe, Mn and Co in the brine solution were very low. Even though the pH of the brine solution was near neutral (7.75), the very high total dissolved solids (TDS) (15400 mg/L), which indicates that the brine contains high amounts of dissolved elements, forbids the indiscriminate disposal of the brine solution.

Having determined and understood the chemical compositions of the fly ashes and the brine used in this study using different characterization techniques, the possible release of the elements from the fly ashes when in contact with brine, and the possible removal of species from the brine solution when in contact with fly ashes will be considered in the next section (4.3.2). The results of the preliminary batch reaction tests carried out to determine the effect of brine concentrations, contact times and the L/S ratios will be discussed in the next section.

4.3.2 Preliminary studies on fly ash-brine interactions: effects of brine concentration, L/S ratio and contact time.

The preliminary batch reaction tests on the fly ash-brine interactions was carried out to investigate the effect of liquid/solid (L/S) ratio, contact time and concentration of the brine on the pH and EC of the fly ash-brine systems (see section 3.3.2.1 for the experimental details). The aim of this preliminary study was to gain an insight into the effects of diluting the brine solution, the L/S ratio and the contact time on the pH and EC of the fly ash-brine leachates. The findings of the preliminary tests were used as the basis for choosing the parameters applied in the main batch reaction tests involving fly ash and brine. The study was carried out by reacting concentrated (undiluted) (CUB) and diluted (1:1) brine (DUB) (details in section 3.3.2.1) with the fly ashes from Secunda and Tutuka at different brine: fly ash ratio (L/S 1:1, 2:1 and 3:1), and sampling the pH and EC at different contact times (30 -240 min).

4.3.2.1 pH and Electrical Conductivity (EC)

The pH and EC of the preliminary batch reaction tests are shown in Figures 4.3 and 4.4. The preliminary batch reaction experiments involving fly ash and brine solutions of different concentrations were carried out at L/S 1:1, 2:1 and 3:1 at maximum contact time of 240 minutes.

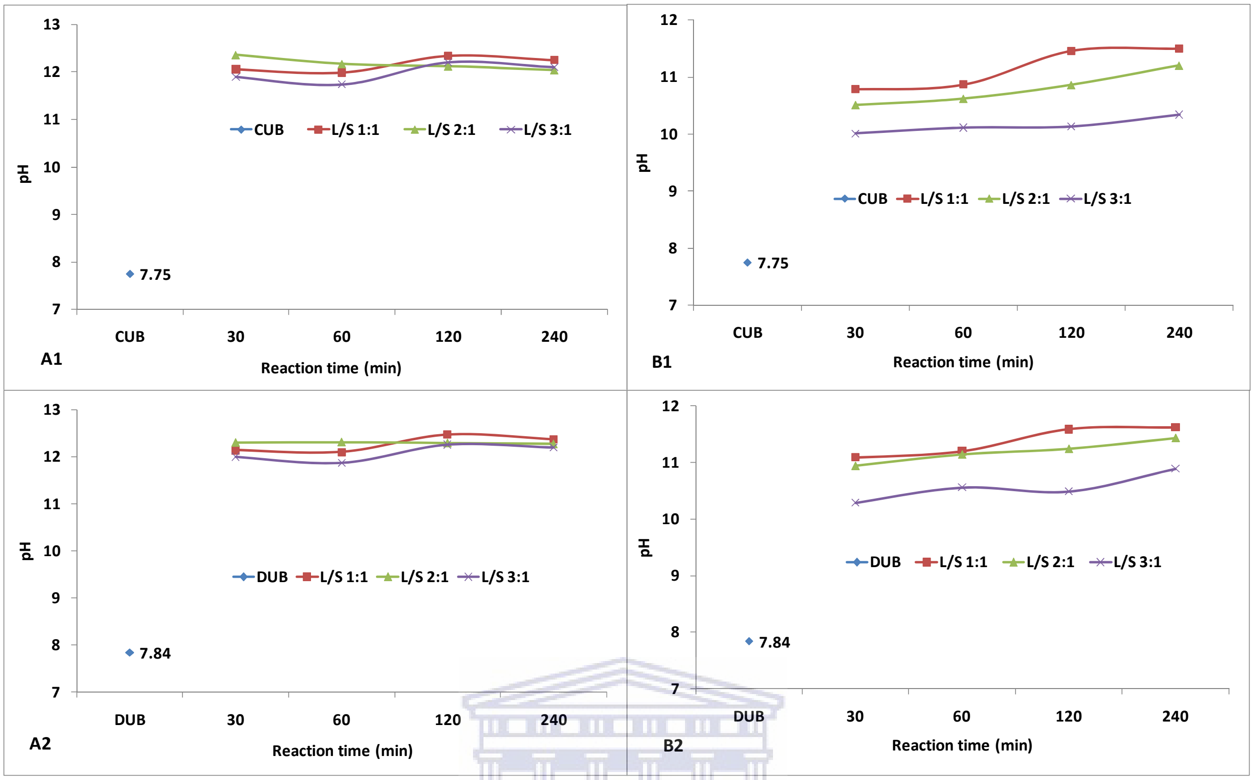

Figure 4.3: pH trends of Secunda (A1 and A2) and Tutuka (B1 and B2) fly ash-brine interactions at L/S 1:1, 2:1 and 3:1 as a function of contact time; CUB = concentrated unreacted brine, DUB = diluted unreacted brine

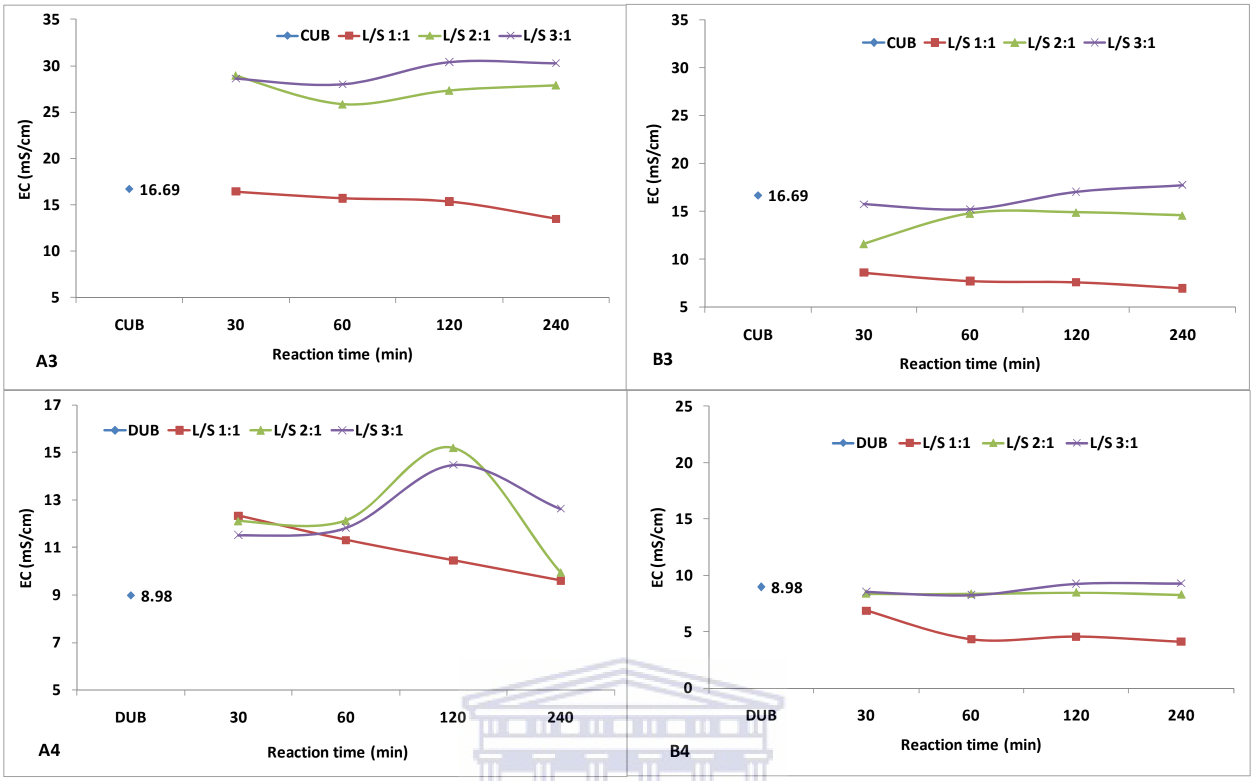

Figure 4.4: EC trends of Secunda (A1 and A2) and Tutuka (B1 and B2) fly ash-brine interactions at L/S 1:1, 2:1 and 3:1 as a function of contact time; CUB = concentrated unreacted brine, DUB = diluted unreacted brine.

The pH of the unreacted brine was found to be 7.75 and 7.84 for concentrated brine (CUB) and diluted brine (DUB) respectively. These values indicate that the unreacted brine solution was not acidic but slightly alkaline, and that the dilution of the brine solution with ultrapure water had no significant effect on the pH of the brine. After the fly ash-brine batch reaction experiments at different contact times, the pH of Secunda and Tutuka fly ash-brine solutions increased irrespective of the L/S ratio or dilution of the systems. The pH of Secunda fly ash-brine batch systems ranged between 11.9 and 12.36 at L/S ratios 1:1, 2:1 and 3:1 for the systems containing concentrated brine [Figure 4.3 (A1)] while in the case of Secunda fly ash-brine batch systems containing diluted brine [Figure 4.3 (A2)], the pH was found to be in the range of 12 and 12.3 for the three L/S ratios irrespective of the contact time. The pH values, after the initial increase, were almost stable throughout the batch reaction test. The trends of pH observed in Tutuka fly ash-brine batch systems were similar to that of Secunda fly ash-brine batch systems in that the pH values increased slightly and gradually with an increase in the contact time. The pH of Tutuka fly ash-brine systems after 30 minutes contact time increased and ranged between 10.01 and 10.79 at L/S ratios 1:1, 2:1 and 3:1 for the systems containing concentrated brine [Figure 4.3 (B1)] while the pH of the systems containing diluted brine [Figure 4.3 (B2)] ranged between 10.29 and 11.09 at the three L/S ratios.

The effect of dilution was more evident in the changes in EC values of the concentrated (CUB) compared to diluted (DUB) brine solutions (Figure 4.4). The EC of the concentrated and the diluted unreacted brine was found to be 16.69 and 8.98 mS/cm respectively. The halving of the EC value of DUB showed that the dilution of the brine solution has a significant implication on the species availability. The EC values of Secunda fly ash-concentrated brine and Secunda fly ash-diluted brine systems increased significantly from 16.69 and 8.98 mS/cm respectively at the beginning of the fly ash-brine batch reaction tests to about 29 and 12.5 mS/cm respectively after 30 minutes.The EC values of Secunda CUB and DUB at all the L/S ratio were higher except at L/S 1:1 [Figure 4.4 (A3)] where a gradual decrease in the EC was observed over time. At 120 minutes, the EC of Secunda systems at L/S 2:1 and 3:1 was high which could be attributed to the dissolution of some species from the fly ash into the systems. The EC trends of Tutuka fly ash-concentrated brine and Tutuka fly ash-diluted brine systems were different. The EC values of Tutuka systems at the three L/S ratios were found to decrease gradually when comparing the CUB and DUB values. The decrease in the EC values of Tutuka fly ash-brine batch systems was prominent in the systems at L/S 1:1 while the decrease observed at L/S 2:1 and 3:1 was insignificant. Thus, significant differences were observed between the EC trends of Secunda fly ash-brine systems compared to Tutuka fly ash-brine systems. This difference could be attributed to the different compositions of the fly ashes (especially the easily soluble oxides such as CaO) (Table 4.2) and the different treatment of the fly ashes before the samples were taken for this study. A detailed discussion of the chemistry of the leachates with respect to the pH and EC values after the batch reaction tests is presented in section 4.3.3.

4.3.2.2 Effect of brine concentration, L/S ratio and contact time on pH and EC

When considering the effect of brine concentrations on the pH and the EC values of the fly ash-brine solutions, it was noticeable that the dilution of the brine solution did not have a significant effect on the pH of the leachates (Figure 4.3). The pH of the Secunda and Tutuka fly ash-brine systems was respectively similar when the fly ash-concentrated brine systems were compared with the fly ash-diluted brine systems. Despite the dilution of the brine solution, the pH of the fly ash-diluted brine systems was almost the same with the pH of fly ash-concentrated brine systems.

The effect of the brine concentration was observed in the change in the EC values of the fly ash-brine systems (Figure 4.4). Considering the fact that the EC of diluted unreacted brine (DUB) was half of the EC value of the concentrated unreacted brine (CUB), it is apparent that after their contact with the fly ashes, the EC values of the leachates from the fly ash-diluted unreacted brine systems was almost half of that of fly ash-concentrated brine systems. The EC of Secunda and Tutuka fly ash-diluted brine systems was almost half of the EC of Secunda and Tutuka fly ash-concentrated brine systems respectively. The observed EC trends gave an insight to the possible effect of dilution of brine by rain water infiltration on the release or removal of species from the brine solutions by fly ash.

The effect of L/S ratio on the pH was not significant the pH of the systems stayed almost the same except for the pH at L/S 3:1 in Tutuka system which was slightly lower. This indicates that the L/S ratio had little or no influence on the pH of the systems. The trends of the EC in the systems give an insight to the effect of L/S ratio on the leaching or removal of species from the systems. Doubling or tripling (L/S 1:1, 2:1 and 3:1) the volume of brine relative to the mass of fly ash in the respective fly ash-brine systems did not result in a consistent increase in the EC values of the systems after the preliminary batch reaction tests. Apart from the fact that this development gives an insight into the possible solubility controls in the systems (Reardon *et al.* 1995), it also revealed that the L/S ratio of the fly ash-brine systems could have an effect on the leaching of species from fly ash or removal of species from the brine solutions.

The effect of contact time was not evident in the observed pH and EC trends of the fly ash-brine systems. The effect of contact time could be best noticed when the elemental results are presented (section 4.3.3). A previous study (Fatoba, 2008), involving the interactions of fly ash and water, revealed the effect of contact times on the leaching or removal of species from fly ash systems.

4.3.2.3 Summary

The aim of the preliminary study on the fly ash-brine interactions was to gain an insight into the effect of changing variables such as brine concentration, L/S ratio and contact time on the leaching from fly ash or possible removal of contaminant species from brine when in contact with fly ash. This study was also carried out to optimize the L/S ratio at which the possible removal of species from brine could be prominent.

The preliminary study showed that the dilution of the brine solution did not significantly affect the pH of the systems. This could also indicate that the dilution of the brine solution may not significantly affect the release or removal of major and minor species from the brine solution. The insignificant effect of the dilution of brine on the pH of the systems could indicate that the dilution of the brine solution may likely not influence the removal of major and minor species from the brine solution by the fly ashes. The effect of the L/S ratio was shown on the EC of systems, which could also indicate that the L/S ratio may affect the release or removal of species from the brine solution during the fly ash-brine interactions tests. The preliminary study showed that the EC of the systems was lower at L/S 1:1. This gave an insight that the optimum L/S ratio where the removal of species from the brine solution is likely to prominent could be at 1:1. The effect of the contact time was not significantly revealed in the pH and EC of the systems, which could indicate that the contact time was too short to observe a significant effect in the pH and EC of the systems. Therefore, a longer contact time is may be necessary.

Having gained an insight into the effect of the brine concentration, L/S ratio and contact time on the EC of the preliminary batch reaction tests, the batch reaction tests were repeated with increased contact time (5 to 1440 minutes). L/S 1.5:1 and 5:1 was included with the existing L/S

1:1 which gave the lowest EC values. Using brine solutions of different concentrations was discarded in the repeated batch reaction tests due to the insignificant effect of brine concentrations on the EC of the fly ash-brine systems during the preliminary tests. The results and discussion of the extended batch reaction tests are presented in the next section (section 4.3.3).

4.3.3 Removal of major and trace elements from brine: A batch reaction test

This section presents and discusses the results of the main batch reaction tests (see section 3.3.2.2 for experimental details) involving Secunda and Tutuka fly ashes and brine solution. As stated earlier, the purpose of the batch reaction tests was to simulate the aggressive fly ash-brine interactions scenario in Secunda power utility where the fly ash directly from the hoppers is aggressively mixed with brine solution before being transported to the ash dump as a slurry. The preliminary batch reaction tests presented in the previous section (4.3.2) gave an insight into the effect of the brine concentration, the L/S ration and the contact time on the pH and EC of the fly ash-brine systems. The pH and EC profiles clearly showed the effect of these parameters on the pH and EC of the systems thereby giving a clear indication that chemical interaction takes place when fly ash and brine interact.

Having determined the effects of the brine concentration, L/S ratio and the contact time on the pH and EC of the fly ash-brine systems during the preliminary batch reaction tests, the main batch reaction tests were carried out for extended contact times of 5 to 1440 minutes at L/S 1:1, 1.5:1 and 5:1. The main batch reaction tests were carried out as described in section 3.3.2.2. This section evaluates the effects of L/S ratio and contact times on the leaching or removal of species during the batch reaction tests and evaluates the effects of the chemical interactions of fly ash and brine components on the brine quality. In this section, the variation in major, minor and trace species over time at different L/S ratio in the batch reaction tests will be discussed. Thereafter, the geochemical modeling predicting the mineral phases controlling the release of species in the batch reaction systems will be presented and discussed in section 4.3.4.

4.3.3.1 pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS)

The pH and TDS profiles of the main batch reaction tests involving fly ash and brine at extended contact times (5-1440 minutes) and different L/S ratio (1:1, 1.5:1 and 5:1) are presented in Figure 4.5 below. The main batch reaction experiment was carried out at different liquid/solid ratios (L/S 1:1, 1.5:1 and 5:1) and at different contact times ranging from 5 to 1440 minutes in order to determine the effect of the L/S ratio and the contact time on the release of species from fly ash into the brine, or the removal of species from the brine solution.

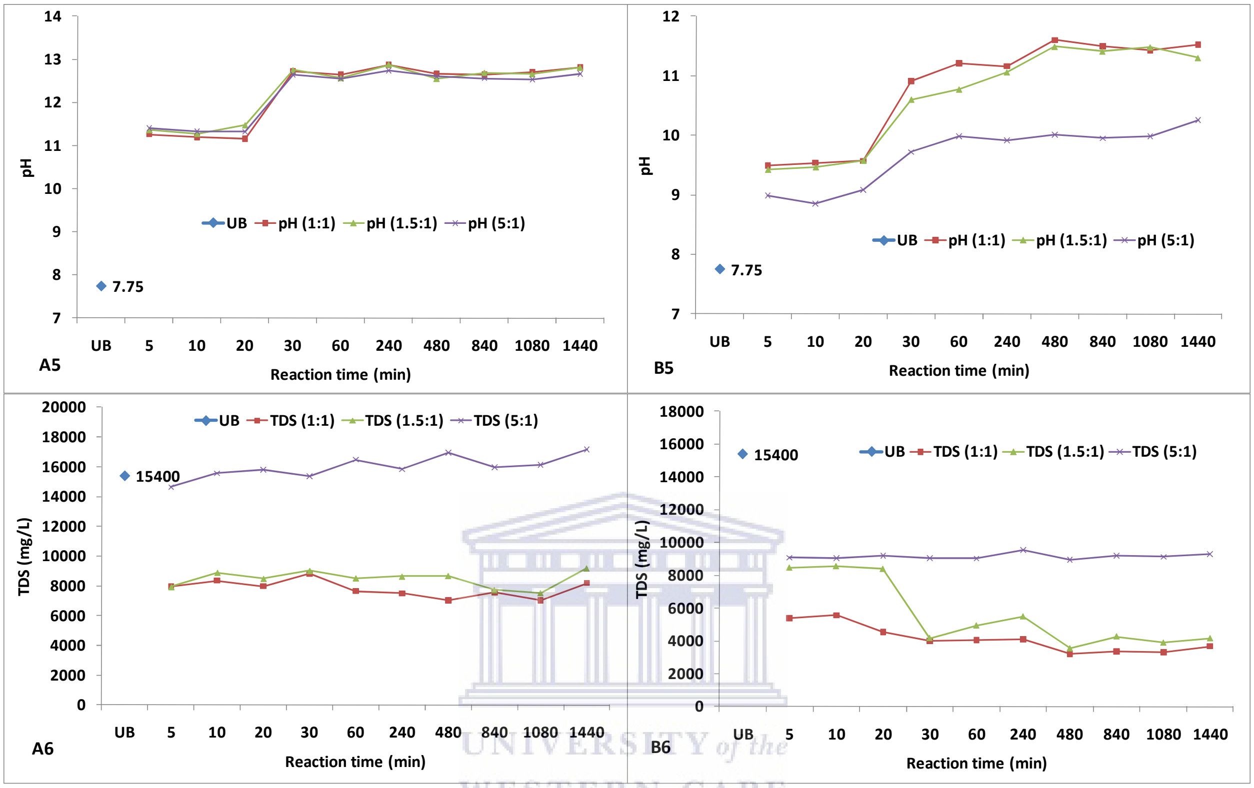

Figure 4.5: pH and TDS of Secunda (A5-A6) and Tutuka (B5-B6) fly ash-brine batch reaction at L/S 1:1, 1.5:1 and 5:1 as a function of reaction time. (UB = unreacted brine)

Figure 4.5 shows the pH and TDS profiles of Secunda (A5-A6) and Tutuka (B5-B6) fly ash-brine batch reaction tests. The pH of the brine solutions after contact with the fly ashes increased abruptly from 7.75 (for UB) to 11.26 for Secunda ash-brine systems and to ≈9 for Tutuka ash-brine systems after 5 minutes contact time (Figure 4.5). These pH values were then stable irrespective of the applied L/S ratio of the solutions until 30 minutes contact time whereafter a further significant increase was observed in the pH values of the solutions of the fly ashes. Thereafter, the pH was stable at levels above pH 12 in the case of Secunda fly ash-brine solutions but the pH of Tutuka fly ash-brine solutions stabilized between pH 11-12 until the end of the batch reaction experiments. The observed increase in the pH of the brine solutions to alkaline values after contacting with the fly ashes could be due to the dissolution and hydrolysis of some basic oxides such as CaO and MgO which are present in significant quantities in the fly ashes (Table 4.2). The pH value of Secunda fly ash-brine solution was found to be consistently higher than that of Tutuka fly ash-brine solution (Figure A5 and B5) at the same contact time. This could be attributed to the variation observed in the concentrations of the alkaline-contributing oxides (CaO and MgO) in the fly ashes. The concentrations of basic oxides (CaO and MgO) were higher in Secunda fly ash (9.3 % CaO and 2.25 % MgO) than in Tutuka fly ash (5.89 % CaO and 1.36 % MgO) (Table 4.2). The pH of fly ash solutions has been observed to depend on the relative quantities of the soluble basic or acidic oxides in the fly ash (Fatoba, 2008; Gitari *et al.,* 2009). In their studies, Choi *et al.,* (2002) and Reardon *et al.,* (1995) attributed the high pH value of fly ash solutions to the dissolution and hydrolysis of basic oxides such as calcium and magnesium oxides while the low pH value observed in their studies was attributed to the dissolution of soluble acids such as B_2O_3, and the salts containing hydrolysable constituents, such as $Fe_2(SO_4)_3$ and $Al_2(SO_4)_3$ in the fly ash. There was no significant difference observed in the pH values of the fly ash-brine solutions with respect to the different L/S ratios in the case of Secunda but a significant difference was observed in Tutuka especially at L/S 5:1. The difference observed in the pH of Tutuka fly ash-brine system at L/S 5:1 could be attributed to the higher brine: fly ash ratio. In this case, (at L/S 5:1), more species contained in the brine solution may interact with the hydroxyl ions (OH^-) released from the dissolution of oxides such as CaO in the fly ash, thereby reducing the amounts of the hydroxyl ions in the Tutuka fly ash-brine system at L/S 5:1.

The TDS values of the brine solutions (determined gravimetrically, see section 3.4.3) after contact with the fly ashes at different L/S ratios (Figure 4.5 (A6 and B6) were observed to decrease significantly when compared to the TDS value of the unreacted brine (UB) except at L/S 5:1 for Secunda fly ash-brine systems. The decrease in the TDS values of the fly ash-brine solutions was maintained from the beginning of the batch reaction tests (5 minutes) to the end (1440 minutes) for most of the L/S ratios (Figure 4.5 (A6 and B6). At L/S 5:1 for Secunda fly ash-brine solution, the TDS was observed to fluctuate slightly for the entire period of the batch reaction test. The TDS values of both Secunda and Tutuka fly ash-brine solutions were found to be lower at L/S 1:1 than the values at other L/S ratios (L/S 1.5:1 and 5:1). The decrease observed in the TDS after the batch reactions at different L/S ratios indicates that some of the major cations and anions such as Na, SO_4 and Cl in the unreacted brine solution may have been removed by the fly ashes either by adsorption or precipitation as a result of super-saturation occurring in solution due to dissolution of fly ash components. The reduction in the TDS of the fly ash-brine solutions was more prominent in Tutuka fly ash-brine solution where the minimum value of 3200 mg/L (79.22 % reduction) (Table 4.5) was observed at 1080 minutes for the solution at L/S 1:1. The fluctuation observed at L/S 5:1 for Secunda fly ash-brine solution could be an indication that there was no precipitation occurring due to under-saturation of the species in the fly ash-brine systems as a result of the high L/S ratio employed. Instead of precipitation, more soluble species may have been released into the brine solution from fly ash.

The electrical conductivity (EC) (graphs not shown, see Table 4.5) of the Tutuka fly ash-brine solutions decreased rapidly (10.55 mS/cm) by 5 minutes contact time when compared with the EC of UB (16.69 mS/cm). The EC of the Tutuka fly ash-brine solutions thereafter decreased gradually for the remaining period of the reaction test. The EC of the Secunda fly ash-brine solutions was found to decrease gradually with an increase in the contact time until at 1440 minutes where a slight increase in the EC was observed (Table 4.4). The EC of Tutuka fly ash-brine solution decreased faster with an increase in the contact time than that of Secunda fly ash-brine solution. This indicates that more ions were removed from the brine solution by Tutuka fly ash. It was reported by Wong *et al.* (1997) that precipitation of soluble salts could cause a decrease in the EC of the fly ash solution. The decrease observed in the EC of the fly ash-brine solutions could indicate the precipitation of soluble salts from the fly ash-brine solution in the form of transient mineral phases.

4.3.3.2 Sodium (Na) and Chloride (Cl)

The concentrations of Na and Cl in the leachates of the fly ash-brine batch reaction tests at different contact times and L/S ratios are shown in Figure 4.6.

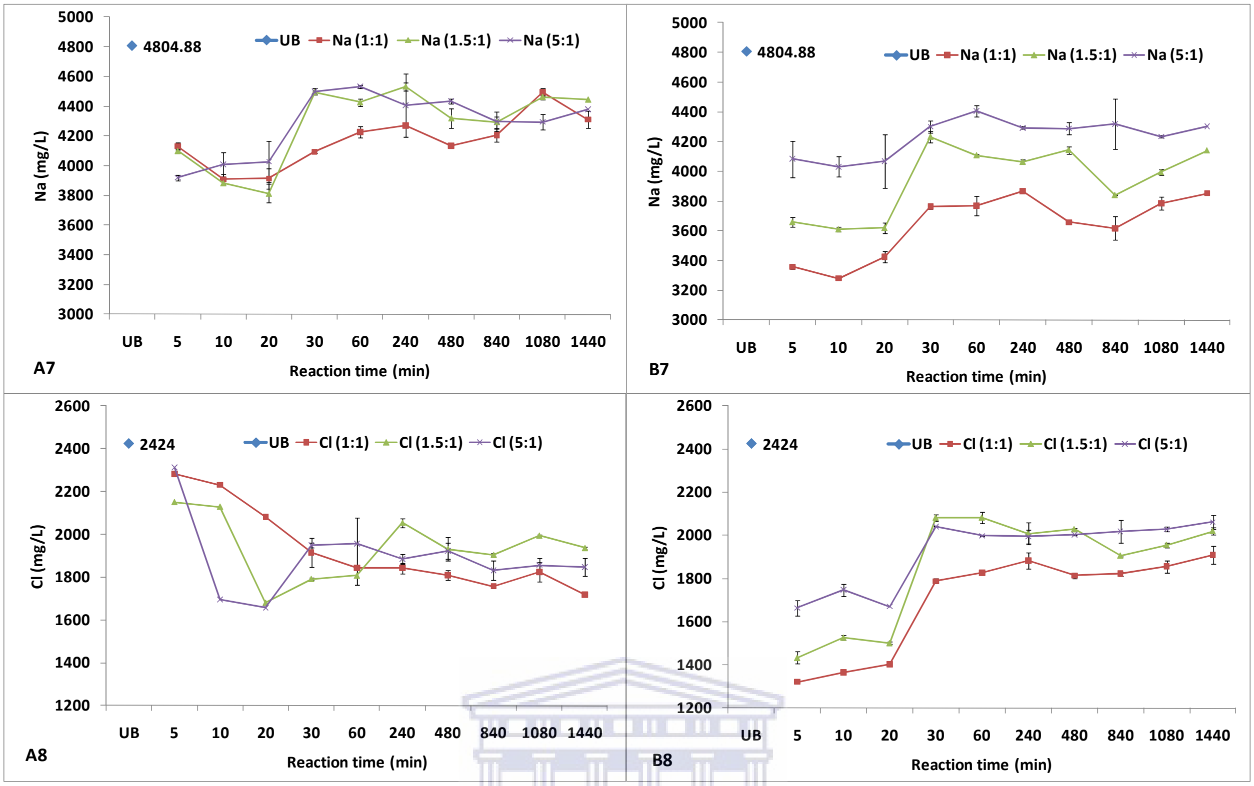

Figure 4.6: Na and Cl concentration of Secunda (A7-A8) and Tutuka (B7-B8) fly ash-brine batch reaction at L/S 1:1, 1.5:1 and 5:1 as a function of reaction time. (UB = unreacted brine)

The concentration of Na (4804.88 mg/L) in the brine solutions (UB) decreased significantly with an increase in the contact time after contact with the fly ashes (Figures 4.6 (A7 and B7)). At 10 and 20 minutes contact time, the lowest concentration of Na in the leachates was observed for Tutuka and Secunda fly ash-brine systems respectively. Concentrations of Na in the fly ash-brine leachates at L/S 1:1 was lower than what was observed at other L/S ratios (1.5:1 and 5:1) for both fly ashes. Comparison of the amount of Na in unreacted brine (UB) with Na concentrations in the fly ash-brine leachates at all contact times indicates the removal of Na ions from brine during the fly ash-brine batch reaction tests. The removal of Na in the systems could be due to the precipitation of transient phases as a result of super-saturation of Na in the fly ash-brine systems. The percentage removal of Na from the brine solution ranged between 6-19 % and 19-32 % for Secunda and Tutuka fly ash-brine systems respectively (Tables 4.4 and 4.5) over the time of the experiment. The percentage Na removal obtained shows that Tutuka fly ash has the capacity to remove more Na ions from the brine solution than Secunda fly ash. Reduction in the concentration of Na in brine after contacting brine with fly ash was observed in the study carried out by Soong *et al.* (2006). The reduction in Na concentration was attributed to the precipitation of NaCl. However, it was observed by Kirby and Rimstidt, (1994) that Na could be locked up in some solid phases such as carbonate and sulphate if formed in the system. Therefore, the removal of Na could be attributed to the super-saturation of Na ions in the solutions of the fly ash-brine systems leading to precipitation of NaCl or as a result of being locked up in the solid phases.

The Cl concentration in UB was 2424 mg/L whereas in the Secunda fly ash-brine leachates at L/S 1:1, 1.5:1 and 5:1 the Cl concentration decreased gradually at the beginning of the test [Figure 4.6 (A8)] and a minimum of 1700 mg/L was observed at 20 minutes contact time in the case of L/S 1.5:1 and 5:1 leachates. After 30 minutes contact time, the Cl concentration was almost stable for the remaining period of the test irrespective of the L/S ratio [Figure 4.6 (A8)]. In the case of Tutuka fly ash-brine systems, the concentration of Cl [Figure 4.6 (B8)] decreased abruptly at 5 minutes contact time to 1400 mg/L when compared to the UB, after which an increase (but below levels of UB) in its concentration was observed at 30 minutes. The concentration of Cl in the Tutuka fly ash-brine leachates became stable thereafter. When compared with the concentration in the unreacted brine (UB), the concentration of Cl in the fly ash-brine leachates decreased significantly in both cases. The decrease in the concentration of Cl in the brine solution after contacting the fly ashes indicates that the fly ashes were able to significantly remove the Cl ion from the brine solution during the interaction period evaluated. The percentage removal of Cl from the brine solutions ranged between 5 and 29 % for Secunda fly ash-brine leachates and between 21 and 45 % for Tutuka fly ash-brine (Tables 4.4 and 4.5). This indicates that Tutuka fly ash can significantly remove Cl ions from the brine solution than Secunda fly ash. The Tutuka trends showed a correlation similarity in the trends of Na and Cl concentration over time which could indicate removal as NaCl (Soong *et al.,* 2006) due to super-saturation of Na and Cl in the systems, but for Secunda [Figure 4.6 (A8)], apart from the precipitation of NaCl, different salts bearing Na and Cl could be responsible for the removal of Cl.

4.3.3.3 Calcium (Ca), Magnesium (Mg) and Sulphate (SO_4)

The concentrations of Ca, Mg and SO_4 in the leachates of Secunda and Tutuka fly ash-brine reactions are shown in Figure 4.7 (A9-A11 and B9-B11) respectively.

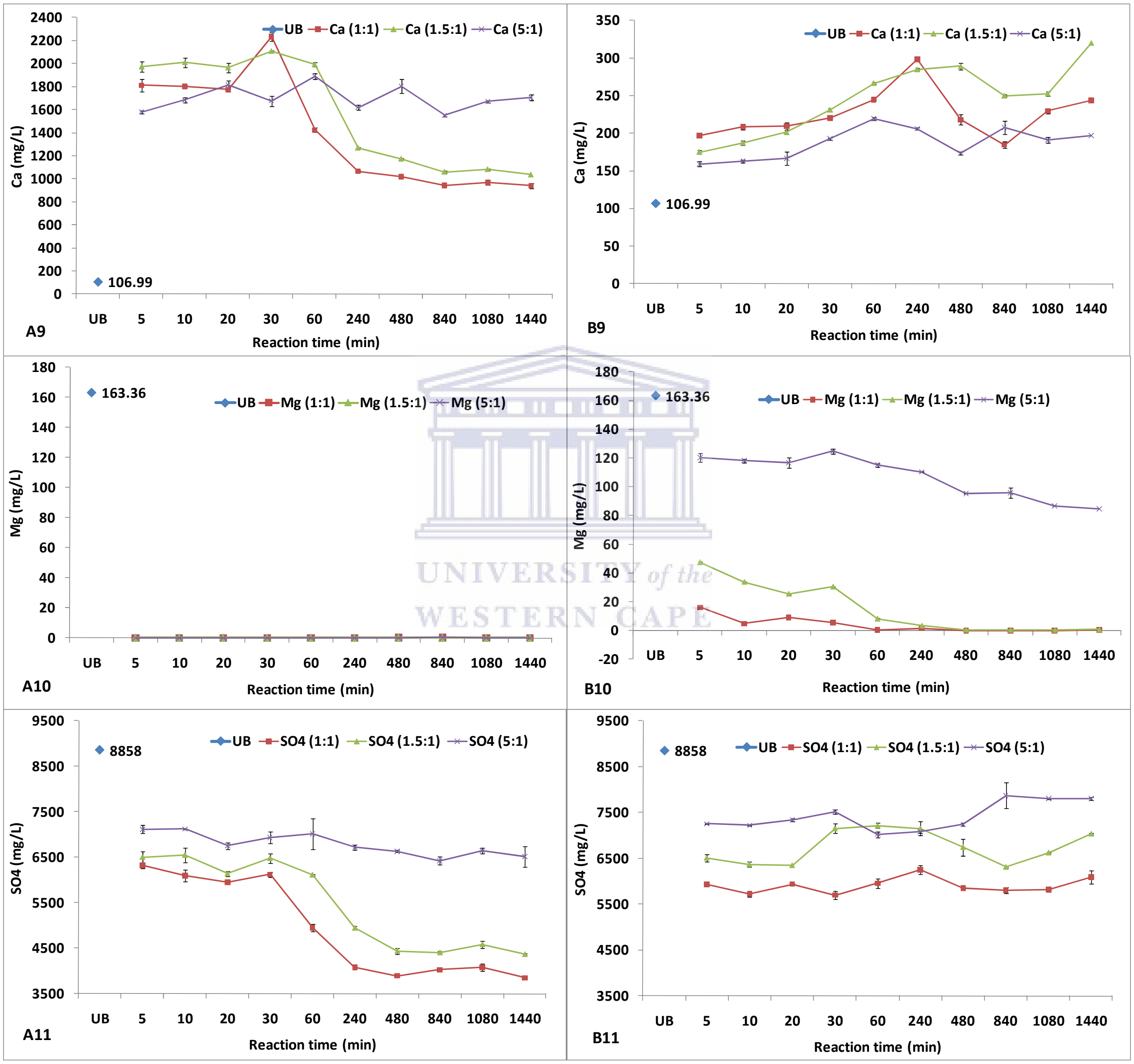

Figure 4.7: Ca, Mg and SO_4 concentration of Secunda (A9-A11) and Tutuka (B9-B11) fly ash-brine batch reaction at L/S 1:1, 1.5:1 and 5:1 as a function of reaction time. (UB = unreacted brine)

The Ca concentration in Secunda fly ash-brine leachates increased significantly from 106 mg/L in UB upon interaction with the fly ash to about 1600 to 2000 mg/L at the beginning of the experiment irrespective of the L/S ratio. The Ca concentration increased to a maximum (2236.45 mg/L) at 30 minutes (Figure 4.7) for Secunda fly ash-brine solution at L/S 1:1 [Figure 4.7 (A9)]. The concentration of Ca thereafter reduced gradually until at 840 minutes when the concentration was almost stable in the leachates at L/S 1:1 and 1.5:1. Despite the gradual decrease observed in the concentration of Ca, the value in the fly ash-brine solution was still higher than its initial concentration in the UB. This shows that the Ca containing phases in Secunda fly ash dissolved readily. The Ca concentrations in Tutuka fly ash-brine leachates gradually increased from the beginning of the experiment with increase in contact time except at 480, 840 and 1080 minutes where the concentration was slightly reduced [Figure 4.7 (B9)]. The increase observed in Ca concentration in the leachates of the fly ash-brine systems when compared with the Ca concentration in the unreacted brine (UB) shows that Ca was significantly leached from the fly ashes. The percentage of Ca leached into the brine solution from the fly ashes ranged from 700 to about 2000 % for Secunda fly ash-brine systems and from 72 to about 180 % for Tutuka fly ash-brine systems (Tables 4.4 and 4.5). The gradual decrease in Ca concentration after the initial increase in the solution of Secunda fly ash-brine indicates that some Ca ions were being removed from the system. This decrease could be attributed to the formation of Ca containing secondary mineral phases such as $CaSO_4$ and $Ca(OH)_2$ in the fly ash-brine systems (details of the possible secondary mineral phases controlling the release of species in the systems are discussed in section 4.3.4).

Ca is known to be associated with the surface of fly ash particles as a soluble salt, as well as forming part of the main components of the aluminosilicate glass fractions in fly ash, along with other major element like K and Al (Gitari *et al.*, 2009). Ca-containing phases such as CaO, which is one of the major components of fly ash, are observed to be highly soluble when in contact with aqueous solutions (Kirby and Rimstidt, 1994). Therefore the increase in the concentration of Ca in the brine solution could be ascribed to the dissolution of the easily soluble salts on the surface of fly ash particles, and as a result of the dissolution of CaO that is present in the fly ashes (Table 4.2). The concentration of Ca in Secunda fly ash-brine leachates was observed to be significantly higher than the concentration observed in Tutuka fly ash-brine leachates. This observation agrees with what was observed in the XRF data of the fly ashes, where the CaO of Secunda fly ash (9.3 %w/w) was also found to be higher than that of Tutuka fly ash (5.89 %w/w) (Table 4.2). The variation in the CaO content of the fly ashes may be due to the type of feed coal, combustion sequence and method of collection, storage and climate (Adriano *et al.,* 1980; Steenari *et al.,* 1999). The Tutuka fly ash had been irrigated with an unspecified amount of salt in the brine before the ash sample was taken, and this may have affected the CaO content or Ca containing phases in the fly ash, which in turn may affect the amount of soluble Ca available for dissolution.

The concentration of Mg in the batch reaction tests involving unreacted brine (UB) and fly ashes from Secunda and Tutuka power utilities is shown in Figure 4.7 (A10 and B10). The Mg concentration was reduced from 163 mg/L to the minimum (below detection limit) at the beginning of the batch reaction tests (at 5 minutes), for Secunda fly ash-brine systems [Figure 4.7 (A10)]. This significant reduction in Mg concentration continued until the end of the reaction. Slight differences were observed in the removal of Mg from Tutuka fly ash-brine systems. The Mg concentration in Tutuka fly ash-brine leachates was only reduced to the minimum at 60 minutes contact time for L/S 1:1 and 240 minutes for L/S 1.5:1. The low concentration of Mg in Tutuka fly ash-brine leachates at L/S 1:1 and 1.5:1 continued thereafter till the end of the experiment. At L/S ratio 5:1, the concentration of Mg was found to be reducing gradually with an increase in contact time [Figure 4.7 (B10)]. The reduction observed in the concentration of Mg in the leachates of Secunda and Tutuka fly ash-brine batch reactions when compared with the concentration of Mg in the unreacted brine (UB) shows that Mg was significantly removed from the brine after contact with fly ash during the interaction period evaluated. The percentage removal of Mg from the leachates of the fly ash-brine systems ranged between 99 and 100 % for Secunda fly ash and from 90-100 % for Tutuka fly ash (Tables 4.4 and 4.5). Mg in alkaline solution (pH >10) has been observed to exist as insoluble $Mg(OH)_2$ (Gitari *et al.,* 2009; Fatoba, 2008), and the precipitation of this insoluble Mg containing phase from solution could account for its low concentration in the leachates of the fly ash-brine systems. The rate at which Mg was removed from Secunda fly ash-brine leachates was faster than that of Tutuka fly ash-brine leachates at the beginning of the experiment [Figure 4.7 (A10 and B10)] despite the higher concentration of MgO in Secunda fly ash (Table 4.2). The observed removal trends could be attributed to the variation in the pH of the two fly ash-brine systems at the beginning of the experiment [Figure 4.5 (A5 and B5)]. The pH of Secunda fly ash-brine systems was found to be higher (>11) than that of Tutuka fly ash-brine systems (9-9.5), which could indicate that Secunda fly ash-brine systems had more hydroxyl ions (OH^-) which favoured the precipitation of more $Mg(OH)_2$. The solution pH plays a major role in metal solubility, complexation and leaching from waste materials (Van der Sloot *et al.,* 1997; Chandler *et al.*, 1997).

The concentration of SO_4 in the UB was 8858 mg/L but in Secunda fly ash-brine solution [Figure 4.7 (A11)] decreased gradually from above 7000 mg/L at the beginning of the experiment (5-30 minutes) to about 4000 mg/L for the entire period of the batch reaction tests at L/S 1:1 and 1.5:1. The concentration of SO_4 in the Tutuka fly ash-brine solution was almost stable after the initial decrease at 5 minutes contact time from 8858 mg/L in UB to between 7400 and 6000 mg/L [Figure 4.7 (B11)]. A significant amount of SO_4 was removed from the leachates of both fly ash-brine systems when compared with the SO_4 concentration in the UB (Table 4.8). The percentage SO_4 removal was found to be between 28 and 57 % for Secunda fly ash-brine systems while the percentage removal in Tutuka fly ash brine systems was between 29 and 36 % (Tables 4.4 and 4.5). The variation observed in the removal of SO_4 from the fly ash-brine leachates could be attributed to the difference in the pH of the leachates [Figure 4.5 (A5 and B5)] or as a result of the lower concentration of species such as Ca observed in Tutuka fly ash solution [Figure 4.7 (B9)], which could affect the precipitation of SO_4 and Ca-containing solid phases such as $CaSO_4$ in the fly ash-brine systems (details in section 4.3.4).

4.3.3.4 Boron (B) and Barium (Ba)

The concentrations of B and Ba in the leachates of Secunda and Tutuka fly ash-brine batch reaction tests are shown in Figure 4.8.

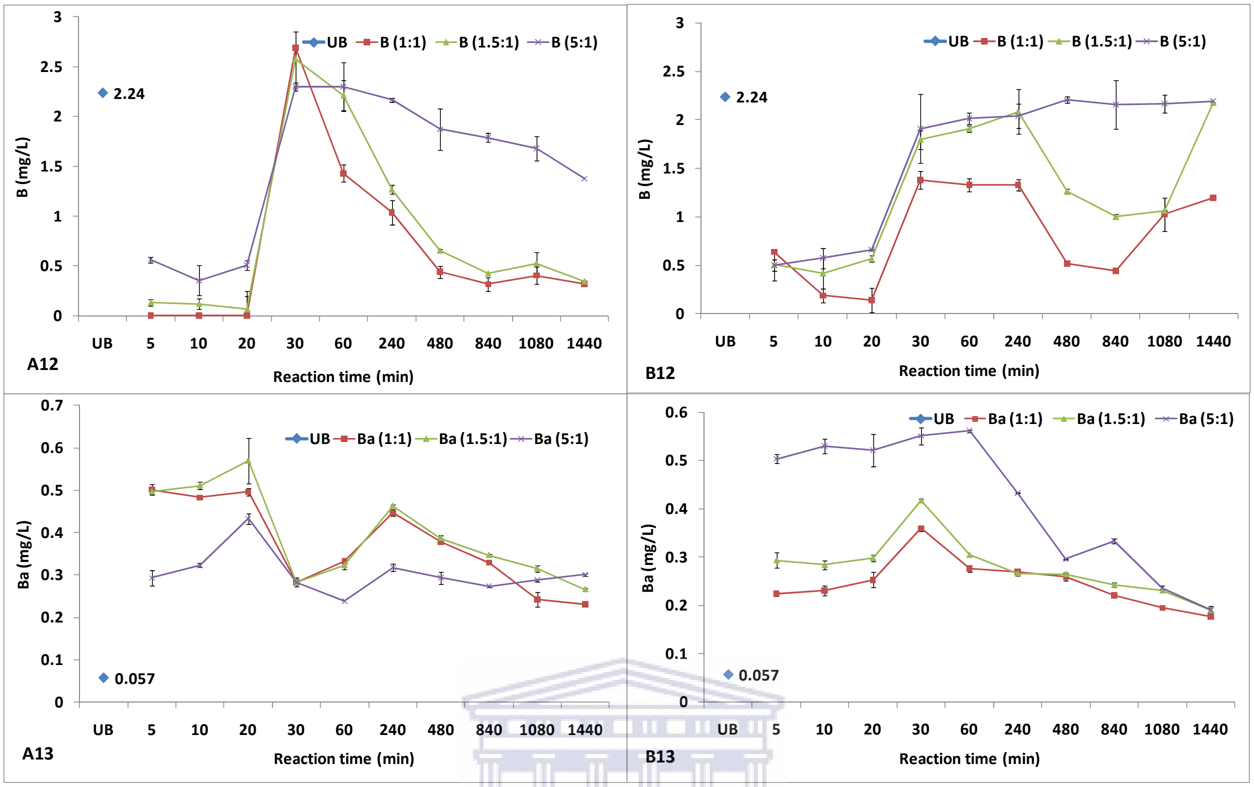

Figure 4.8: B and Ba concentration of Secunda (A12-A13) and Tutuka (B12-B13) fly ash-brine batch reaction at L/S 1:1, 1.5:1 and 5:1 as a function of reaction time. (UB = unreacted brine)

The B concentration in the fly ash-brine leachates of Secunda and Tutuka, when compared to its concentration of 2.24 mg/L in the UB, was found to decrease abruptly to below 0.5 mg/L at the beginning of the experiment up to 20 minutes contact time irrespective of the L/S ratio. The B concentration thereafter increased sharply at 30 minutes [Figure 4.8 (A12 and B12)]. B concentration in Secunda fly ash-brine solution gradually decreased after 30 minutes until the end of the batch reaction tests [Figure 4.8 (A12)]. After the initial B removal from 2.24 to 0.5 mg/L in the case of Tutuka fly ash-brine systems, the concentration of B increased to 2 mg/L and was found to be stable between 20 and 240 minutes at L/S 1:1 and 1.5:1. The concentration thereafter reduced gradually. The B concentration decreased compared to the unreacted brine (UB) after contacting with Tutuka fly ash but the trends were inconsistent as observed in Figure 4.8 (B12). The removal trends observed in the Tutuka fly ash-brine leachates were not the same with respect to the L/S ratio of the solutions after 240 minutes. The reason for the trends could be attributed to the formation of B-containing transient phases at L/S 1:1 and 1.5:1 at 480 and 840 minutes. At L/S 5:1, the concentration of B increased throughout the period of the experiment after the initial decrease. Boron was initially removed from Secunda fly ash-brine systems in the range of 36 to 100 % while in Tutuka fly ash-brine systems the percentage B removal was between 38 and 92 % (Tables 4.4 and 4.5). Boron has been observed to exist as an oxy-anion in solution at high pH (Fatoba, 2008; Jankowski *et al.*, 2006) thereby having the tendency to interact with other positively charged ions in solution. The formation of ettringite [$Ca_6Al_2(SO_4)_3.26H_2O$] in the solution of fly ash at high pH has been identified to entrap boron from the solution. According to Iwashita *et al.* (2005) and Hassett, (1994), the ettringite phase, when formed at higher pH, has the tendency of trapping oxy-anionic species such as borate by replacing its sulphate component with the borate in the solution. Fly ash with high Ca contents has been observed to reduce the concentration of B in solution due to the possible co-precipitation of B with $CaCO_3$ (Hollis *et al.*, 1988). The removal of boron from the fly ash-brine leachates could be as a result of boron entrapment by an ettringite phase or due to its interaction with Ca in the solution. The fluctuation observed in the removal of boron from Tutuka fly ash-brine leachates could be as a result of formation and dissolution of transient phases in the systems over time.

The trends observed for Ba concentration [Figure 4.8 (A13 and B13)] shows that Ba is immediately leached from the fly ashes into the brine solution (UB). It was observed that the concentration of Ba in Secunda and Tutuka fly ash-brine batch reaction increased at the beginning of the tests (5 minutes). This increase continued until at 20 and 30 minutes whereafter a decrease in the concentration was observed for Secunda and Tutuka fly ash-brine systems respectively. The concentration of Ba in Secunda fly ash-brine solution at L/S 5:1 fluctuated between 0.5 to 0.3 mg/L after the increase observed at 20 minutes reaction time [Figure 4.8 (A13)]. However, in the case of Tutuka fly ash, a gradual decrease to 0.3 mg/L was noted. Ba was significantly leached into the solutions of the fly ash-brine systems with the percentage ranging from 304 to 777 % in the case of Secunda fly ash-brine systems while the percentage leached into Tutuka fly ash-brine was found to be between 210 and 530 % (Tables 4.4 and 4.5). The leaching of Ba into the solution of brine could be as a result of the dissolution of soluble Ba-containing salts on the surface of the fly ash. Reardon *et al.* (1995) observed that the oxides of Ba dissolve readily when in contact with water thereby increasing Ba concentration in solution.

The decrease observed in the leaching trend over time could indicate the formation of secondary mineral phases such as barite during the interaction period evaluated.

4.3.3.5 Iron (Fe) and Manganese (Mn)

Figure 4.9 shows the release or removal of Fe and Mn as a result of the interactions between brine and fly ashes from Secunda and Tutuka power utilities.

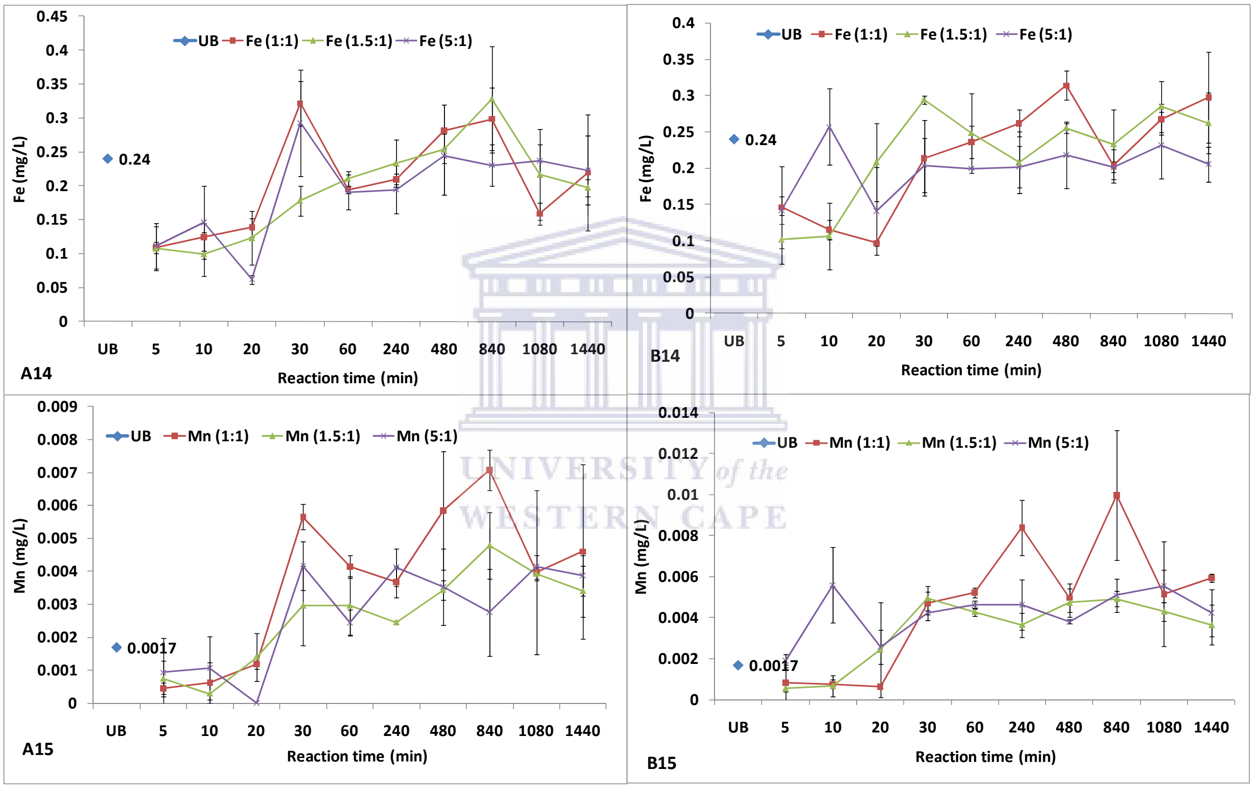

Figure 4.9: Mn and Fe concentration of Secunda (A14-A15) and Tutuka (B14-B15) fly ash-brine batch reaction at L/S 1:1, 1.5:1 and 5:1 as a function of reaction time. (UB = unreacted brine)

The trends of release or removal of Mn and Fe in the fly ash-brine leachates of the two fly ashes were similar. The concentrations of Fe and Mn [Figure 4.9 (A14-15 and B14-15)] in the leachates of Secunda and Tutuka fly ash-brine systems were found to decrease slightly from levels in UB at the beginning of the experiment (5-20 minutes). When compared to their concentrations in the UB, Fe and Mn concentrations at 5-20 minutes were observed to be lower in the systems except for Tutuka fly ash-brine solution at L/S 5:1 where an increase in Mn concentration was observed at 10 minutes. The lower concentration of these species at the beginning of the tests is an indication that they were removed from the unreacted brine solution immediately after contacting with fly ash. The percentage removal of Fe at the beginning of the tests ranged between 41 and 54 % (Secunda fly ash-brine leachates) and 37 and 60 % (Tutuka fly ash-brine leachates). The initial removal of Mn was higher with the percentage ranging between 29 and 74 % for Secunda fly ash-brine leachates and between 51 and 62 % in the solution of Tutuka fly ash-brine systems (Tables 4.4 and 4.5). A gradual increase in the concentrations of Fe and Mn in the leachates (above that of UB) was observed at 30 minutes contact time for almost all the leachates irrespective of their L/S ratios. It has been observed that Mn and Fe, when in alkaline solution, form oxy-hydroxides, which coat around the silicate grains of fly ash (Drever 1997; Gitari *et al.,* 2009). The formation of the transient oxy-hydroxides could account for the reduction observed in the concentrations of Fe and Mn in the fly ash-brine leachates at the beginning of the batch reaction tests while the gradual increase in the concentrations of Fe and Mn in the systems thereafter could be attributed to the redissolution of the transient oxy-hydroxides and the Fe and Mn minerals in the fly ashes.

4.3.3.6 Copper (Cu), Zinc (Zn) and Nickel (Ni)

Figure 4.10 (A16-18 and B16-18) presents the concentrations of Cu, Zn and Ni in the leachates of Secunda and Tutuka fly ash-brine batch reaction tests at different reaction times and at different L/S ratios.

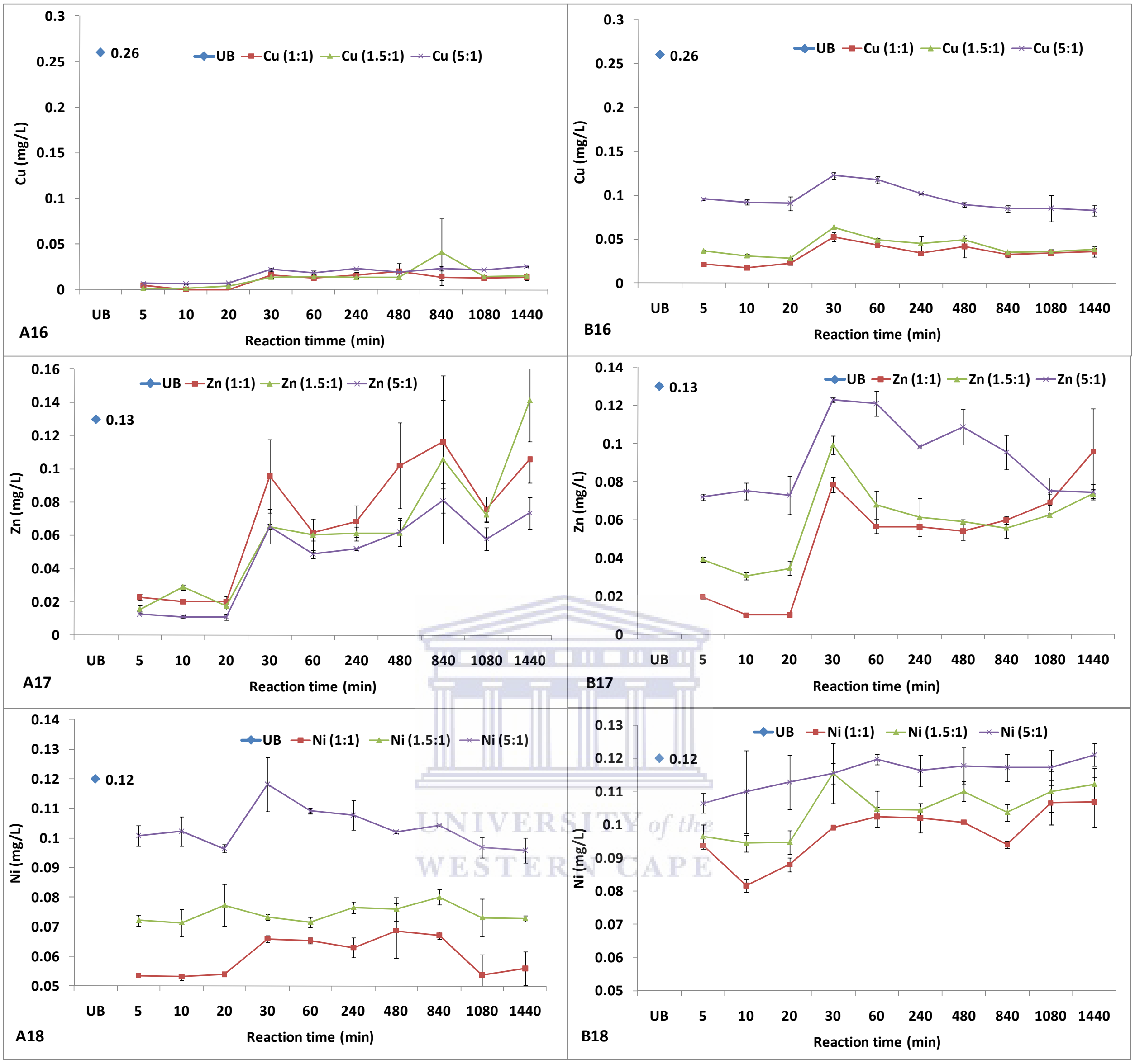

Figure 4.10: Cu, Zn and Ni concentration of Secunda (A16-A18) and Tutuka (B16-B18) fly ash-brine batch reaction at L/S 1:1, 1.5:1 and 5:1 as a function of reaction time. (UB = unreacted brine)

The concentration of Cu immediately decreased from 0.26 mg/L to almost zero on contact with the fly ashes and remained very low in Secunda fly ash-brine leachates in all the three L/S ratios used. A slight increase (not up to its concentration in the UB) at 30 minutes in Tutuka fly ash-brine systems was observed. For Zn (UB 0.13 mg/L), the initial removal to 0.02 mg/L in Secunda system and between 0.02 and 0.08 mg/L in Tutuka system was followed by an increase in the concentration (not up to its concentration in the UB) at 30 minutes in both fly ash-brine systems. Considering the effect of the L/S ratios, Ni concentration in the leachates of the fly ash-brine systems had the lowest values at L/S 1:1 after 10 minutes. The concentration of Ni was relatively stable from the beginning of the test to the end. In comparison, the concentrations of Cu, Zn and Ni in the fly ash-brine leachates were found to be lower than their concentrations in the unreacted brine (UB), which indicates that these species were removed from UB by contact with the fly ashes. The percentage removal of Cu, Zn and Ni from the leachates of Secunda fly ash-brine systems ranged between 92 and 100 %, 11 and 85 %, 43 and 56 % respectively (Table 4.4) while the removal of these species in Tutuka fly ash-brine systems ranged between 79 and 92, 26 and 92, 11 and 32 % respectively (Table 4.5). The removal was observed to be more prominent in Secunda fly ash-brine systems, where the concentration of Cu in the fly ash-brine solution was almost below detection limit at some stage. This slight difference observed in the removal capacity of the Secunda and Tutuka fly ash-brine systems could be attributed to the differences in the pH values of the systems [Figure 4.5 (A5 and B5)]. Astrup *et al.,* (2006) observed that the release of heavy metals is controlled by the pH of the solution. Several studies (Elliot and Denneny, 1982; Steenari *et al.*, 1999; Cho *et al.*, 2005; Lee and Saunders, 2003) have shown that, at high pH, the surfaces of fly ash are negatively charged. According to Alinnor, (2007), most of the positively charged heavy metal such as Ni, Cu, Pb and Zn in solution have the tendency to adsorb to the surfaces of the fly ash due to electrostatic forces of attractions between the negatively charged fly ash surface and the positively charged metal ions. Studies (Drever, 1997; Shim *et al.* 2003) have shown that heavy metals such Cu, Ni and Zn are strongly adsorbed to the surface of Fe or Mn oxy-hydroxides formed in alkaline system. The removal of Cu, Ni and Zn from the brine used in the fly ash-brine systems could also be as a result of adsorption on the fly ash surface or on Fe and Mn oxy-hydroxides formed during the interaction in the systems. The slow increase observed at some stage in the trends for Cu, Ni and Zn could be attributed to their desorption from the fly ash surfaces over time indicating the transient nature of the removal mechanisms.

4.3.3.7 Arsenic (As), Cobalt (Co) and Lead (Pb)

The concentrations of As, Co and Pb in the leachates of Secunda and Tutuka fly ash-brine batch reaction tests are shown in Figure 4.11 (A19-A21 and B19-B21).

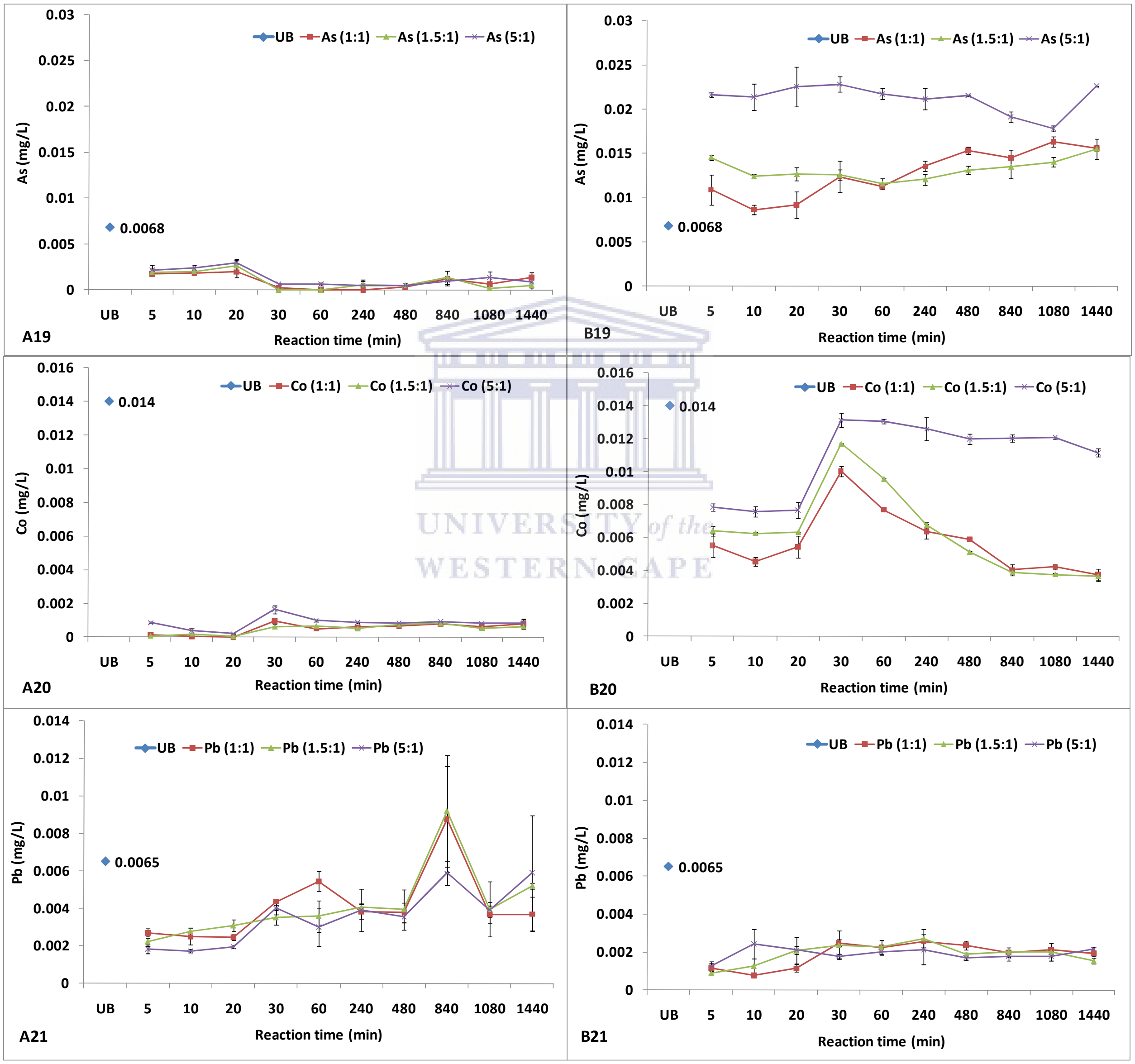

Figure 4.11: As, Co and Pb concentration of Secunda (A19-A21) and Tutuka (B19-B21) fly ash-brine batch reaction at L/S 1:1, 1.5:1 and 5:1 as a function of reaction time. (UB = unreacted brine)

It was observed that the concentrations of As, Co and Pb in the fly ash-brine leachates were reduced after contact with fly ash except for Tutuka fly ash-brine systems [Figure 4.11 (B19)] where the concentration of As was immediately increased above the concentration in the unreacted brine (UB). The increase observed in As concentration in Tutuka fly ash-brine systems shows that As was leached rapidly from Tutuka fly ash into the brine solution during the batch reaction tests. The decrease observed in the concentrations of Co, Pb and As (Secunda fly ash-brine systems) when compared with their concentrations in UB indicates their removal from the brine solution after contact with fly ash. The percentage removal of As, Co and Pb in the leachates of Secunda fly ash-brine systems ranged from 70 to 100 %, 93 to 100 % and 7 to 62 % respectively (Table 4.4) while the percentage removal of Co and Pb from Tutuka fly ash-brine systems was found to range from 29 to 74 % and 34 to 88 % respectively (Table 4.5). Comparing the removal of species by the two fly ashes, the concentrations of As and Co in Tutuka fly ash-brine leachates were higher than what was observed in the Secunda fly ash-brine leachates while the concentration of Pb in Secunda fly ash-brine solution was slightly higher. The ability of Secunda fly ash to remove more species from brine could be attributed to its higher pH values, which could in turn favour the precipitation of species from the solution or their adsorption to the fly ash surfaces. The difference in the final pH values of the fly ashes could be associated with the slight variations observed in the chemical compositions of the fly ashes either due to the pre-treatment of the fly ashes before sample collection (as described in section 3.2.2) or due to the type of coal burnt. As and Pb concentrations in alkaline environment are said to be controlled by adsorption and precipitation reactions (Goh and Lim, 2004; Jankowski *et al.,* 2006). The variable concentrations of these species in leachates could be controlled by adsorption to and desorption from the surface of fly ashes particles or transient incorporation during the formation of secondary mineral phases.

4.3.3.8 Molybdenum (Mo) and Chromium (Cr)

The concentrations of Mo and Cr in the leachates of Secunda and Tutuka fly ash-brine batch reaction systems are shown in Figure 4.12 (A22-23 and B22-23).

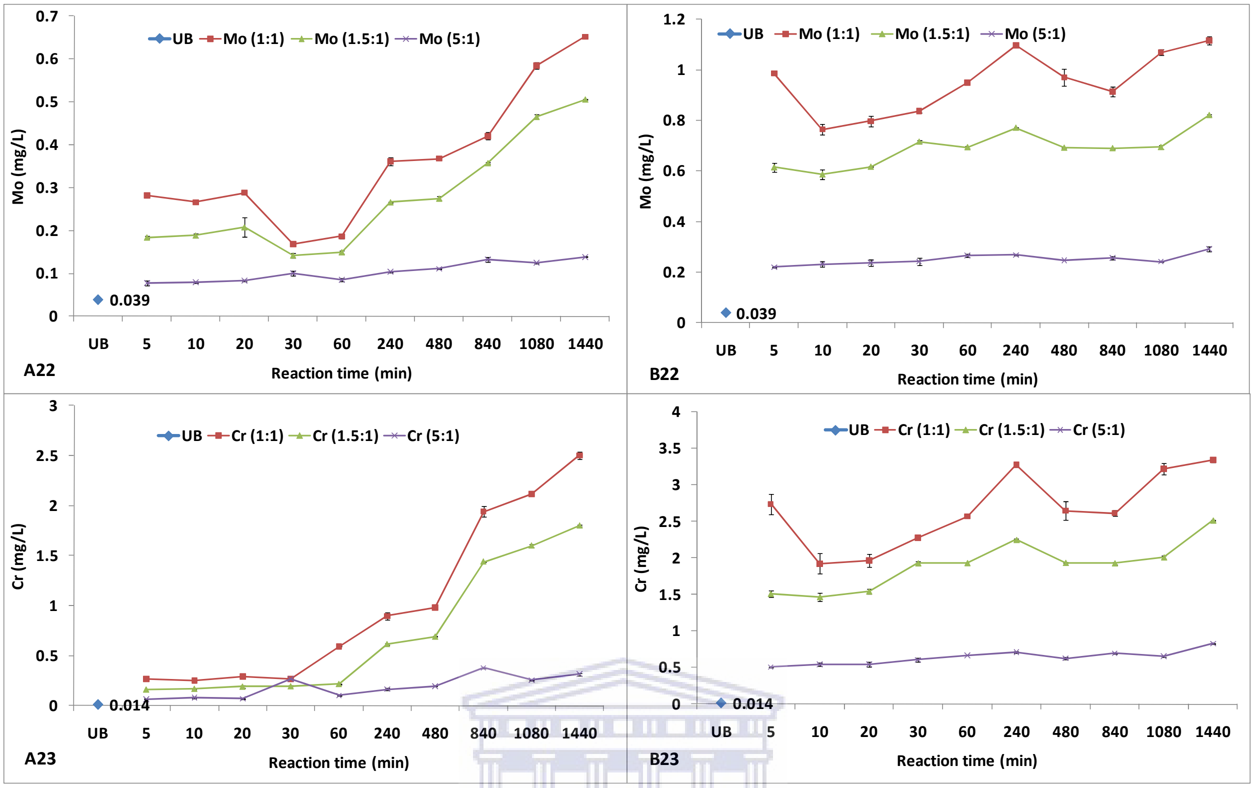

Figure 4.12: Mo and Cr concentration of Secunda (A22-A23) and Tutuka (B22-B23) fly ash-brine batch reaction at L/S 1:1, 1.5:1 and 5:1 as a function of reaction time. (UB = unreacted brine)

It was observed that the concentrations of Mo and Cr in Secunda fly ash-brine leachates increased gradually above UB levels of 0.39 and 0.014 mg/L respectively with an increase in the reaction time [Figure 4.12 (A22 and A23)]. The release pattern of Mo and Cr in the leachates of Tutuka fly ash-brine systems was slightly different. Their concentrations were variable irrespective of the L/S ratio after the initial increase in the concentrations [Figure 4.12 (B22 and B23)]. The trends of increased concentrations compared to UB indicate that Mo and Cr were leached out from the fly ashes into the leachates from the beginning of the reaction tests to the end. Interestingly, it was observed that the pattern of release of Mo into the leachates at L/S 1:1, 1.5:1 and 5:1 were the same for each ash type as the patterns observed for the release of Cr into the leachates except that the concentrations of Cr in the leachates were higher than the concentrations of Mo in the leachates. Although the total concentrations of Mo was not determined by the XRF analysis, the difference in the concentrations of Mo and Cr in the fly ash-brine leachates could be due to the difference in their concentrations in the fly ashes (Table 4.2). It has been observed that at high pH and oxidizing conditions, some species such as Mo and Cr are likely to form oxyanions (MoO_4^{2-} and CrO_4^{2-} respectively) (Astrup *et al.,* 2006; Appelo and Postma, 1994). The oxyanions of Mo and Cr are observed to be mobile in solution because of their inability to adsorb to hydrous iron (hydr) oxides or hydrous aluminum (hydr) oxides (Hyks *et al.,* 2009). The mobility of the oxyanions of Mo and Cr in the solution could account for the gradual increase observed in the leachates of Secunda and Tutuka fly ash-brine systems. The results indicate that both Secunda and Tutuka fly ashes are likely to leach Cr and Mo species when in contact with brine.

4.3.3.9 Concentrations and Percentages of species removed and leached

Figures 4.13 and 4.14 show the percentage of selected species removed from the brine solution (UB) or leached from the fly ashes at L/S 1:1 during the batch reaction experiments while Tables 4.4 and 4.5 show the percentage of selected species leached from the fly ashes at L/S 1:1 during the batch reaction experiments. The choice of L/S 1:1 was based on the fact that the removal and leaching of species was prominent in the leachates of the fly ash-brine systems at this L/S ratio. The % leached or removal of the species was calculated based on the following equation;

$$\%\, Removal\ or\ Leached = \frac{Initial\ concentration\ in\ UB - Final\ concentration\ in\ the\ leachate}{Initial\ concentration\ in\ UB} \times 100$$

$$i.e.\ \frac{Change\ in\ species\ concentration\ after\ batch\ reaction\ test}{Initial\ concentration\ of\ species\ in\ UB} \times 100$$

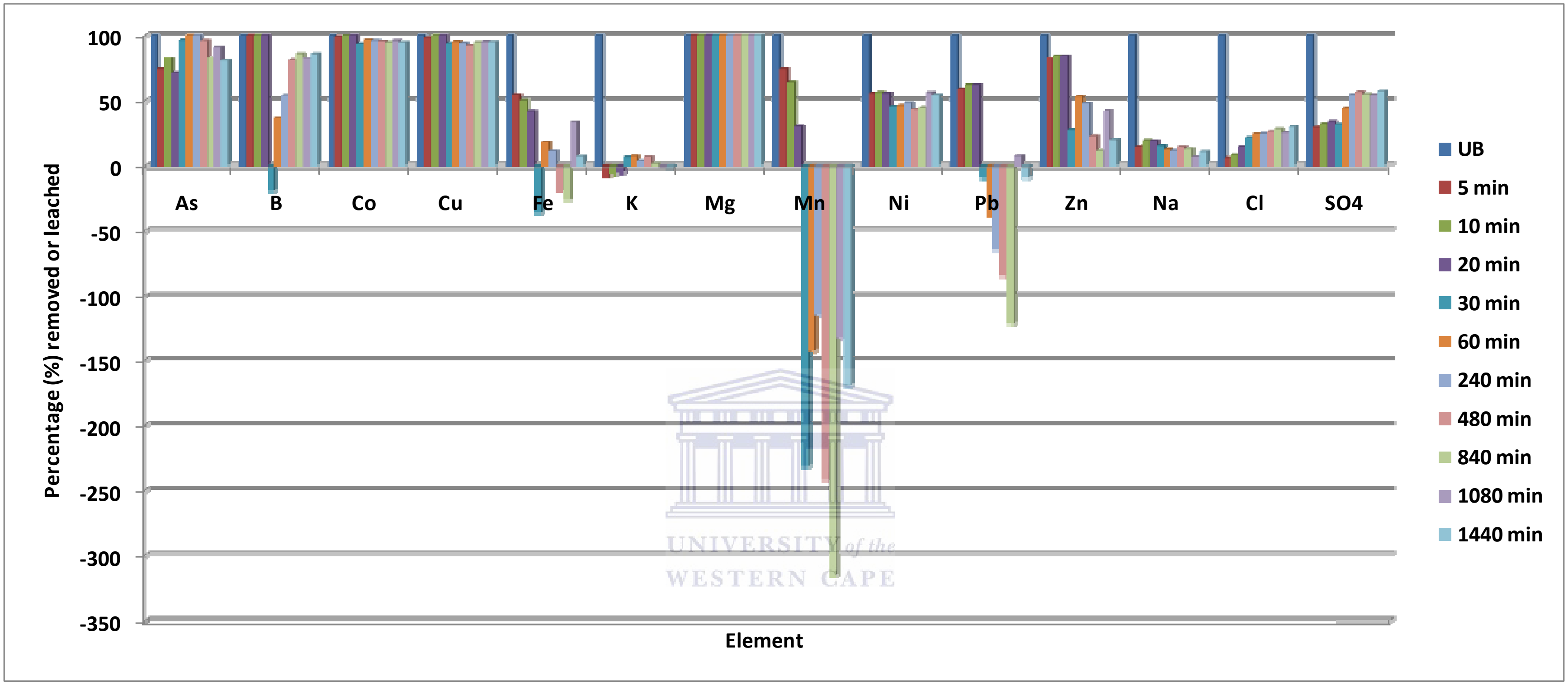

Figure 4.13: The percentage (%) of selected species removed from the brine solution or leached from Secunda fly ash during the batch reaction test at L/S 1:1 as a function of contact time; All values are in %, Negative (-) values represents % leached from the fly ash

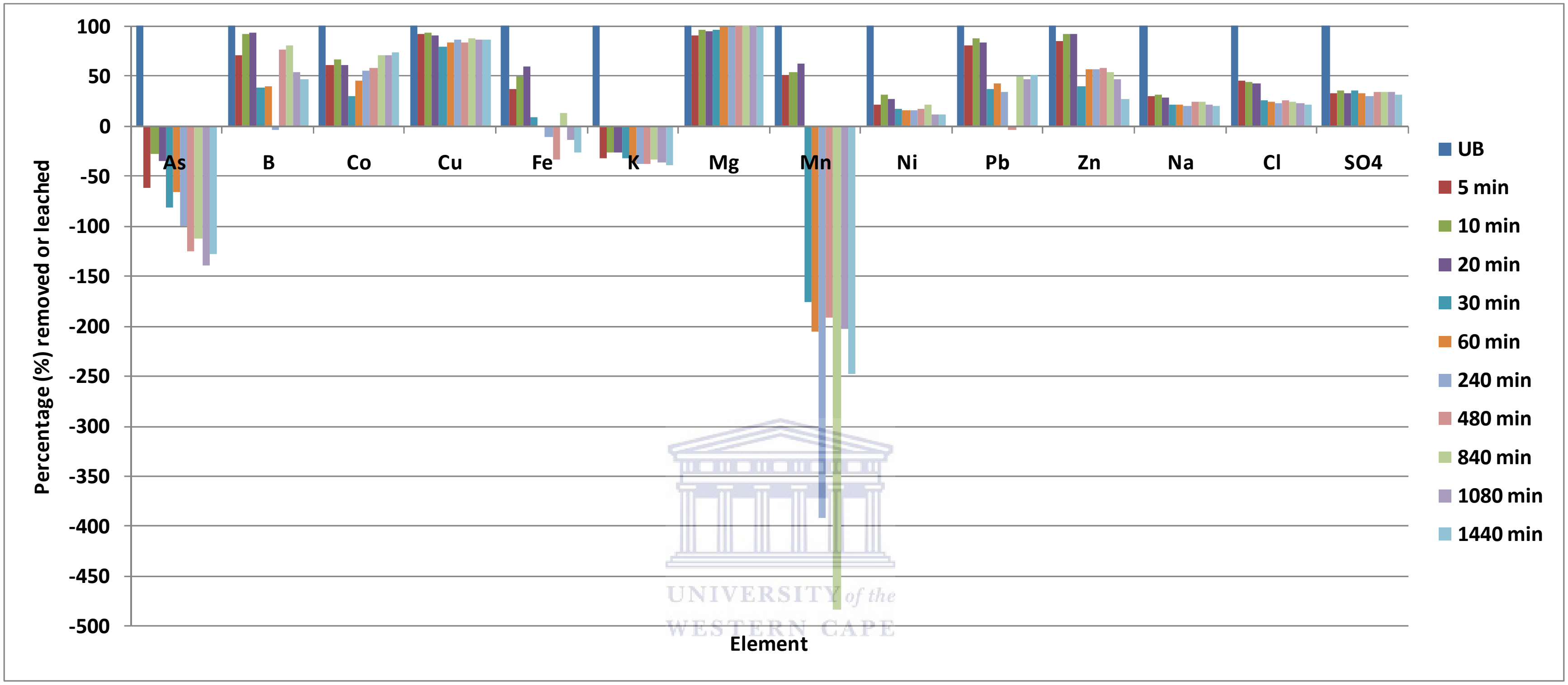

Figure 4.14: The percentage (%) of selected species removed from the brine solution or leached from Tutuka fly ash during the batch reaction test at L/S 1:1 as a function of contact time; All values are in %, Negative (-) values represents % leached from the fly ash

Table 4.4: The percentage (%) of selected species leached from Secunda fly ash during the batch reaction test at L/S 1:1 as a function of contact time (All values are in % except UB = mg/L)

Parameter/ contact time (min)	UB	5	10	20	30	60	240	480	840	1080	1440
Al	0.045	10.2	-104.082	48.98	-476.13	-427.71	-858.06	-584.7	-1739.14	-448.54	-897.22
Ba	0.057	-777.19	-742.11	-759.65	-396.35	-482.95	-682.62	-563.35	-477.41	-325.76	-304.52
Ca	106.99	-1593.7	-1584.27	-1557.44	-1990.21	-1230.29	-896.51	-850.41	-779.19	-805.17	-777.62
Cr	0.014	-1757.14	-1685.71	-1971.43	-1836.27	-4186.13	-6376.88	-6973.69	-13923.1	-15197.7	-17982.4
Mo	0.039	-617.95	-592.31	-643.59	-327.35	-374.56	-819.99	-836.49	-971.05	-1387.65	-1560.3
Sr	3.06	-1207.69	-1113.39	-1198.53	-915.72	-1052.42	-1210.21	-1390.7	-1762.69	-2148.32	-2328.65
pH	7.75	-45.29	-44.39	-44	-64.13	-63.23	-66.065	-63.48	-63.09	-64	-65.29
EC	16.69	11.68	7.13	11.32	2.16	15.04	16.72	22.05	15.99	21.63	8.87
TDS	15400	48.44	45.71	48.18	42.79	50.32	51.29	54.42	50.78	54.29	46.75

UB = unreacted brine; negative (-) sign indicates leaching

Table 4.5: The percentage (%) of selected species leached from Tutuka fly ash during the batch reaction test at L/S 1:1 as a function of contact time (All values are in % except UB = mg/L)

Parameter/ contact time (min)	UB	5	10	20	30	60	240	480	840	1080	1440
Al	0.045	-655.1	-1267.35	-838.78	-2101.36	-5921.58	-3836.81	-8617.77	-9246.09	-5060.97	-4055.3
Ba	0.057	-285.96	-303.51	-338.59	-529.98	-383.97	-371.88	-354.25	-288.014	-241.79	-210.07
Ca	106.99	-83.91	-95.07	-95.97	-105.64	-128.81	-179.11	-103.79	-72.62	-114.67	-127.97
Cr	0.014	-19471.4	-13614.3	-13900	-16332.1	-18475.1	-23605.2	-19037.3	-18804.6	-23203.5	-24090.8
Mo	0.039	-2438.46	-1874.36	-1925.64	-2032.42	-2321.19	-2694.49	-2371.61	-2230.53	-2624.22	-2742.37
Sr	3.06	-187.07	-208.35	-204.75	-222.84	-231.48	-256.44	-214.39	-184.37	-212.13	-230.02
pH	7.75	-22.45	-23.09	-23.48	-40.77	-44.65	-44	-49.68	-48.39	-47.48	-48.65
EC	16.69	36.79	38.35	49.07	55.06	55.06	54.76	64.47	62.85	63.39	59.26
TDS	15400	64.94	63.83	70.52	74.03	73.64	73.31	79.22	78.25	78.51	76.1

UB = unreacted brine; negative (-) sign indicates leaching

In Secunda fly ash-brine systems (Figure 4.13), As, B, Co, Cu, Mg, Na, Ni, Zn, Cl and SO_4 were significantly removed from the brine solution during the contact time applied with the percentage ranging from 70-100 %, 36-100 %, 93-100 %, 92-100 %, 99.9-100 %, 6-19 %, 43-56 %, 11-85 %, 5-29 %, 28-57 % respectively while Ba, Ca, Cr, Mo and Sr (Table 4.4) were leached from the fly ash in significant quantities into the brine solution. Species such as Al, Fe, K, Mn and Pb were inconsistent in their availability in the fly ash-brine solution. The trend observed in Tutuka fly ash-brine leachates was similar to that of Secunda fly ash-brine leachates. Species such as B, Co, Cu, Mg, Na, Ni, Zn, Cl and SO_4 were also removed from the brine solution during the interactions with Tutuka fly ash (Figure 4.14), and the percentage removal were 38-94 %, 29-74 %, 79-93 %, 90-100 %, 19-32 %, 11-32 %, 26-92 %, 21-45 % and 29-36 % respectively. Al, As, Ba, Ca, K, Cr, Mo and Sr were leached from the fly ash into the brine solution. As observed in the case of Secunda fly ash-brine solution, the leaching and removal of some species such as Fe, Mn and Pb were observed to be inconsistent. The results as shown in Figures 4.13 and 4.14 also revealed the optimum contact time for the removal of species from the UB by the fly ashes. It was observed that the contact times where the highest % removal of species such as B, Co, Cu, Fe, Mn, Na, Ni, Pb and Zn in Secunda fly ash-brine systems ranged from 5-20 minutes after which the % removal of these species decreased in the systems at 30 minutes showing the transient nature of the removal mechanisms. At 60 and 240 minutes, the % removal of As and K were at the maximum in Secunda fly ash-brine batch systems. The removal of Mg from the brine solution by Secunda fly ash was at almost 100 % throughout the contact time. The removal of Cl and SO_4 increased gradually until the end of the batch reaction tests (1440 minutes) (Figure 4.13). The trends observed in the case of Tutuka fly ash-brine batch reaction systems indicated that the optimum contact times for the removal of B, Cu, Fe, Mn, Na, Ni, Pb, Zn and Cl were between 5 and 20 minutes. The % removal of these species thereafter (at 30 minutes) reduced. The % removal of Na and Cl which are major species in the brine gradually decreased after 20 minutes contact time, and this shows the transient nature of the removal mechanisms. The % removal of SO_4 (a major species in the brine solution), in Tutuka batch reaction was almost stable throughout the contact time. The removal of Mg increased from 5 minutes contact time and was completely removed after 30 minutes contact time while the removal of Co from the brine by Tutuka fly ash was at its maximum at 1440 minutes (Figure 4.14). Al, Ba, Ca, Cr, Mo and Sr were leached from Tutuka fly ash to the brine solution in significant percentages (Table 4.5). The initial removal followed by a decrease in the % removal after 20 minutes contact times for some species indicates the dissolution of any transient mineral phases formed due to supersaturation during the batch reaction tests. The stable or gradual increase observed in the % removal of some species such as Mg and SO_4 could imply that the mineral phases being formed by supersaturated conditions may be slightly soluble or insoluble. The trends of Cl and SO_4 in the two fly ash-brine batch systems differ. The % removal of Cl and SO_4 in Secunda systems increased with an increase in contact time while the % removal of Cl gradually decreased after 20 minutes and the % removal of SO_4 was almost stable in Tutuka fly ash-brine batch system. This variation could be attributed to the difference in the percentage of some species such as Ca leached from the fly ash which may interact to precipitate more Cl and SO_4 out of the Secunda systems.

There was significant decrease in the TDS of the brine solution after contact with both Secunda and Tutuka fly ashes. The % removal as a function of TDS that was observed in the brine after contacting Secunda fly ash ranged between 42 and 55 % while the % removal after the contact with Tutuka fly ash was in the range of 63 and 79 %. Comparing the overall capacity of the fly ashes to remove various species from the brine solution, the removal capacity of the fly ash from Secunda seemed to be slightly higher than that of Tutuka. This could be attributed to the slight difference in the pH of the two fly ash-brine systems.

4.3.3.10 Summary

The different sources of the fly ashes used as feedstock coupled with the different pre-treatment conditions before the fly ashes were sampled could explain the variation observed in the pH values and the chemical compositions of the two fly ashes. The chemical and mineralogical characteristics of the fly ashes used in this study showed their reactivity potentials. Both Secunda and Tutuka fly ashes used for this study contain oxides which are readily soluble when in contact with brine solution. The hydrolysis and rapid dissolution of basic oxides such as CaO and MgO in the fly ashes significantly contributed to the highly alkaline pH of fly ash-brine systems. The high pH (>10) of the fly ash-brine batch systems was observed to have a significant effect on the reactivity of the species in both the fly ashes and the brine solution. The significant decrease observed in the TDS value (15400 mg/L) of the brine solution (UB) after contacting the fly ashes showed the capacity of the fly ashes to remove some major and minor soluble species from the brine solution when in contact with fly ash for a limited period of time. The TDS value of the systems was reduced to the range of 7020 mg/L (54.42 % reduction) after contacting Secunda fly ash while its contact with Tutuka fly ash reduced the TDS to about 3200 mg/L (72.22 % reduction). Even though the results of the batch leaching tests showed that some species leached from the fly ash into the fly ash-brine systems (Tables 4.4 and 4.5), the overall TDS values of the systems after the interactions revealed greater removal of species than leaching.

The results of the main batch reaction tests showed that the fly ashes from Secunda and Tutuka have the ability to remove some species from the brine solution while some species from the fly ash samples were also leached into the brine solution. The trends were variable and many species initially removed were later released into the fly ash-brine systems showing the transient nature of the removal mechanisms. The L/S ratio of the fly ash-brine systems and the contact time also played a major role in the interactions of the species in the fly ash-brine systems in most cases. The removal of major and minor species was found to be most significant at L/S 1:1. This indicates that the ratio of fly ash to brine must be equal to be able to significantly remove some of the salts in the brine solution by the fly ashes. The batch reaction tests revealed that the optimum contact time for the removal of some species from the brine solution when in contact with the fly ashes was between 5 and 20 minutes after which some of the removed species were gradually released into the fly ash-brine systems. This indicates the instability and transient forms of most mineral phases being formed during the interactions.

Species such as B, Na, Mg, Cl and SO_4 which constitute the major species of the brine solution were significantly removed; 36-100 % B, 6-19 % Na, 99-100 % Mg, 6-29 % Cl and 29-57 % SO_4 were removed by Secunda fly ash while the removal of these species by Tutuka fly ash ranged from 38-94 % B, 20-32 % Na, 90-100 % Mg, 21-46 % Cl and 29-36 % SO_4. Minor elements such as As, Co, Cu, Pb, Ni and Zn were significantly removed from the brine after which some of these species were gradually released into the fly ash-brine systems. Despite the ability of the fly ashes to remove major and minor species from brine, some species such as Ca, Ba, Sr and K were significantly leached into the brine solution from the fly ashes thereby increasing their concentration in the leachates. Cr and Mo were also very significantly leached into the brine solution from the fly ashes showing that the ashes are a source of toxic element contamination.

The batch reaction tests showed that within the space of 30 minutes of fly ash-brine interaction, significant amounts of major species could be removed from the brine solution thereby improving the quality of the brine solution. The results of the batch reaction test which models the aggressive interactions of the fly ash and brine in Secunda power utility before transport to the ash dump as slurry, indicates that significant quantities of some major and minor species may be removed from the brine solution during the mixing of the fly ash with brine as transport medium before getting to the ash dump.

The batch reaction tests gave an insight into the possible leachability or removal of species when fly ash and brine are transported together and co-disposed in the ash dump. One of the shortcomings of the co-disposal practice includes the leaching of species such as Cr and Mo, which could pose a significant environmental risk. However, in the real scenario, the L/S 1:1 where the removal of species was prominent is not practicable as the slurry will be difficult to pump. The contact time would be longer because of the distance from the mixing point to the ash dump. Therefore, the extrapolation of the results of the batch reaction tests must be causiously considered.

The geochemical process(es) responsible for the removal or release of species into the fly ash-brine batch reaction systems needs to be understood. This necessitated the application of PHREEQC geochemical modelling software to calculate the saturation indices in order to determine the solubility controlling the release or removal of species in the fly ash-brine batch systems. The possible mineral phases responsible for the removal of species during the interactions as calculated by PHREEQC will be discussed in the next section (section 4.3.4).

4.3.4 Fly ash-brine interactions systems: Solubility controlling the release of major and minor species

This section of the results and discussion presents the chemical composition (by XRF) of the solid residues recovered from the batch reaction tests and the solubility controlling the release of major and minor species in the fly ash-brine batch reaction systems. The results of the batch reaction tests as presented in the previous section (section 4.3.3) showed that some major species were removed from the brine solution during the interactions with the fly ashes while some toxic species were significantly leached from the fly ashes. The interactions of the species in the fly ash and brine resulted in effluents with reduced TDS which might be due to precipitation of soluble and insoluble phases. However, in order to understand the geochemical processes responsible for the removal and leaching of both major and minor species from the fly ash-brine systems, PHREEQC geochemical modeling software was employed to calculate the saturation indices (SI) of the possible mineral phases that may play a role in the systems. The removal capacity of species from brine by the fly ashes used in the study was observed to be more prominent at L/S 1:1. Therefore, the results of the batch reaction tests at L/S 1:1 was used for the geochemical modeling to predict the solubility controlling the release of species in the fly ash-brine systems. This section aims at understanding the solubility controlling the release of major and minor species from fly ash-brine batch reaction systems.

4.3.4.1 Chemical compositions of fresh fly ash and batch reaction solid residues

The XRF results comparing the chemical composition of the fresh fly ashes and the solid residues recovered from the main batch reaction tests (experimental details in section 3.3.2.2) are shown in Tables 4.6 and 4.7 below.

Table 4.6: Chemical compositions of Secunda fresh ash (SFA) and solid residues from Secunda fly ash-brine batch reaction tests at selected contact times (n=3)

Element (mg/kg)	SFA	10	30	60	240	480	840	1080	1440
Al	137751	132185	136639	136639	137010	136692	135793	136110	136587
Ba	2291.99	1772.24	2210.78	2233.22	2201.69	2166.33	2171.78	2194.13	2183.85
Ca	66467	63970	65181	65181	64823	64680	65038	64966	65038
Cl	73.89	865.196	1177.52	761.65	1130.57	819.68	1028.85	873.39	868.98
Co	10.48	10.84	11.38	11.32	10.14	9.86	10.93	10.10	10.33
Cr	129.76	137.56	171.51	141.55	142.08	129.66	128.05	131.90	131.77
Cu	37.00	46.78	32.60	33.15	33.20	29.75	35.47	30.67	30.28
Fe	16506	16311	16576	16576	16366	15597	16016	16156	16226
K	6724	6481	6558	6558	6558	6558	6558	6641	6558
Mg	13572	13062	13512	13512	13512	13391	13512	13512	13512
Mn	387	375	387	387	387	387	387	387	387
Na	4525	5432	5712	5712	6009	5638	5564	6751	5638
Ni	58.46	57.6	54.69	55.58	56.08	55.66	55.83	55.91	56.61
Pb	41.04	48.14	36.22	38.40	38.41	38.58	39.06	39.68	35.84
S	1378.35	2553.827	1862.65	2957.02	3707.20	3740.60	5645.98	3877.39	3845.32
Si	231787	215510	230150	230150	229589	228280	228935	228093	228982
Sr	3268.09	3476.42	3139.19	3154.59	3136.55	3149.34	3135.30	3145.14	3102.76
Zn	32.09	31.25	31.10	30.40	30.24	30.78	31.13	30.77	30.53

Table 4.7: Chemical compositions of Tutuka fresh ash (TFA) and solid residues from Tutuka fly ash-brine batch reaction tests at selected contact times (n=3)

Element (mg/kg)	TFA	10	30	60	240	480	840	1080	1440
Al	129495	122388	131030	130871	130818	129495	132141	130077	128596
Ba	983.74	880.43	999.79	1026.88	975.18	996.02	967.92	1019.68	1020.82
Ca	42096	40669	41453	42167	42024	41596	41881	41381	41167
Cl	730.26	1871.306	1896.52	1764.74	2037.10	2332.15	2257.38	1019.21	1474.67
Co	21.02	22.12	21.07	22.26	21.21	20.95	20.27	21.70	20.87
Cr	145.33	147.02	138.32	142.93	140.54	141.18	139.29	140.12	140.48
Cu	32.81	47.45	33.16	33.81	29.12	29.06	33.33	28.39	32.33
Fe	37907	36026	36299	37348	36719	36159	36928	36998	36159
K	6890	6632	6890	7139	6890	6807	6890	6890	6807
Mg	8204	7835	8324	8324	8324	8324	8264	8204	8204
Mn	387	399	387	387	387	387	387	387	387
Na	2151	3806	4229	8086	3783	3783	3561	3709	3487
Ni	62.22	59.71	58.62	60.24	58.30	57.24	58.65	58.26	60.73
Pb	50.33	61.03	51.85	54.91	52.70	53.76	53.30	53.39	52.47
S	7025.05	7391.203	6016.66	6657.95	7134.46	6097.26	8127.56	6657.37	6388.41
Si	242352	224042	241511	243381	242633	239547	243988	243100	239407
Sr	1164.44	1237.62	1152.69	1158.44	1170.08	1160.60	1161.55	1170.43	1163.94
Zn	48.53	47.32	48.02	46.79	48.02	48.01	48.72	49.30	47.83

The XRF data showing the chemical compositions (major and trace species) of Secunda and Tutuka fresh fly ash (SFA and TFA respectively) and the solid residues recovered after the Secunda and Tutuka fly ash-brine batch reaction tests at selected contact time are shown in Tables 4.6 and 4.7 respectively. The comparison of the elements in the fresh fly ashes with the solid residues from the batch reaction tests showed the effect of the fly ash-brine interactions on the chemical composition of the solid residues. Considering the concentrations of major elements in brine (Table 4.3), the concentrations of species such as Na, Mg, SO_4 and Cl in the solid residues at different contact times were higher than what was observed the fresh fly ashes. This indicates that these species were removed from the brine solution by the fly ashes thereby leading to their increase in the residues during the interaction period applied. This is in agreement with the TDS and the results of the leachates of the fly ash-brine batch reactions (Table 4.8) where the concentrations of these species were reduced when compared to UB. On the other hand, the concentrations of some species such as Al, Ca, Sr and Cr were observed to decrease in the residues, indicating that these species were leached from the fly ashes into the systems. This is also revealed in Table 4.8 where the concentrations of these species were found to be higher in the leachates of the fly ash-brine batch reaction tests than the concentrations in the UB. The difference in the concentrations of species in the fly ashes before and after the contact with brine solution could be attributed to the dissolution and precipitation of mineral phases during the interaction experiments. The detailed discussion on the possible mineral phases controlling the release of species in the fly ash-brine systems is presented in section 4.3.4.3.

4.3.4.2 Solubility controlling major and minor species

Table 4.8 shows the trend of major and minor elements that were released into the brine solution (UB) from the fly ashes and the removal of major and minor species from UB during the batch reaction tests involving fly ash and brine at L/S 1:1. Although, L/S 1:1 is the most unrealistic real co-disposal scenario, the L/S was chosen for the geochemical modeling because it was the L/S ratio where the impact of the removal of species during the fly ash-brine batch reactions was more pronounced. The analytical data defining the pH, major and minor species of Secunda and Tutuka fly ash-brine batch reaction systems at L/S 1:1 (Table 4.8) was input into the PHREEQC geochemical modelling software (see section 3.4.10 for background information) to calculate the minerals saturation indices (SI). The minteq.v4 thermodynamic database was used for all the calculations. The calculated SI was used to predict the solubility controlling the release or removal of species from the fly ash-brine batch reaction systems.

The results showing the pH, EC and TDS of the leachates from the Secunda and Tutuka fly ash-brine batch reaction systems at L/S 1:1 (used for the geochemical modeling) are briefly discussed before the discussion on the secondary mineral formation in the systems.

Table 4.8: The concentrations of major and minor species in the leachates of Secunda and Tutuka fly ash-brine batch reaction tests for extended period of 5-1440 minutes at L/S ratio 1:1 (n=3) (concentrations in mg/L except pH and EC (mS/cm))

Parameter / Reaction time (min)	Secunda fly ash-brine batch reaction at L/S 1:1											Tutuka fly ash-brine batch reaction at L/S 1:1										
	UB	**5**	**10**	**20**	**30**	**60**	**240**	**480**	**840**	**1080**	**1440**	**UB**	**5**	**10**	**20**	**30**	**60**	**240**	**480**	**840**	**1080**	**1440**
Al	0.049	0.044	0.1	0.025	0.26	0.24	0.43	0.31	0.83	0.25	0.45	0.049	0.37	0.67	0.46	0.99	2.71	1.77	3.92	4.2	2.32	1.87
As	0.0068	0.0018	0.0012	0.002	0.00027	BDL	BDL	0.00029	0.0012	0.00062	0.0014	0.0068	0.011	0.0087	0.0092	0.012	0.011	0.014	0.015	0.014	0.016	0.016
B	2.24	BDL	BDL	BDL	2.69	1.43	1.04	0.44	0.32	0.4	0.32	2.24	0.64	0.19	0.14	1.38	1.33	1.33	0.52	0.44	1.027	1.19
Ba	0.057	0.5	0.48	0.49	0.28	0.33	0.45	0.38	0.33	0.24	0.23	0.057	0.22	0.23	0.25	0.36	0.28	0.27	0.26	0.22	0.19	0.18
Ca	106.99	1812.09	1802	1773.3	2236.45	1423.37	1066.24	1016.91	940.7	968.5	939.02	106.99	196.76	208.71	209.67	220.027	244.82	298.63	218.045	184.69	229.69	243.92
Cd	0.00017	BDL	BDL	BDL	0.00015	0.000036	0.00016	0.00058	0.00021	0.00037	0.00024	0.00017	BDL	BDL	BDL	0.00061	0.00059	0.00054	0.00043	0.00066	0.00027	0.00041
Co	0.014	0.00015	0.000031	0.0000015	0.00095	0.0005	0.00059	0.00066	0.00077	0.0006	0.00078	0.014	0.0055	0.0046	0.0054	0.01	0.0077	0.0064	0.0059	0.004	0.0042	0.0038
Cr	0.014	0.26	0.25	0.29	0.27	0.59	0.9	0.98	1.94	2.12	2.5	0.014	2.74	1.92	1.96	2.27	2.57	3.28	2.65	2.62	3.23	3.35
Cu	0.26	0.0048	0.00036	0.000019	0.016	0.013	0.016	0.02	0.014	0.013	0.014	0.26	0.021	0.018	0.023	0.053	0.044	0.034	0.042	0.033	0.034	0.036
Fe	0.24	0.11	0.12	0.14	0.32	0.19	0.21	0.28	0.29	0.16	0.22	0.24	0.15	0.12	0.097	0.21	0.24	0.26	0.31	0.2	0.27	0.29
K	106.2	115.33	113.21	112.07	99.38	98.64	102.54	99.16	104.74	107.14	108.6	106.2	140.16	134.35	134.6	139.9	144.5	145.84	146.2	141.1	145.12	147.1
Mg	163.36	0.11	0.13	0.077	BDL	BDL	BDL	0.2	0.19	BDL	BDL	163.36	16.029	4.81	9.036	5.55	0.55	1.64	BDL	BDL	BDL	0.39
Mn	0.0017	0.00045	0.00062	0.0012	0.0057	0.0041	0.0037	0.0058	0.0071	0.004	0.0046	0.0017	0.00083	0.00077	0.00064	0.0047	0.0052	0.0084	0.0049	0.0099	0.0052	0.0059
Mo	0.039	0.28	0.27	0.29	0.17	0.19	0.36	0.37	0.42	0.58	0.65	0.039	0.99	0.77	0.79	0.84	0.95	1.097	0.97	0.92	1.069	1.12
Na	4804.88	4130.78	3907.94	3912.92	4093.42	4224.36	4269.28	4131.74	4205.74	4494.96	4309.9	4804.88	3357.52	3280.27	3424.71	3764.62	3768.57	3866.51	3657.04	3615.97	3785.76	3852.13
Ni	0.12	0.054	0.053	0.054	0.066	0.065	0.063	0.069	0.067	0.054	0.056	0.12	0.094	0.082	0.088	0.099	0.1	0.1	0.1	0.094	0.11	0.11
P	0.82	ND	ND	ND	1.23	0.85	0.98	1.34	1.08	0.82	1.13	0.82	ND	ND	ND	0.33	0.41	0.31	0.51	0.69	0.43	0.71
Pb	0.0065	0.0027	0.0025	0.0025	0.0044	0.0054	0.0038	0.0038	0.0088	0.0037	0.0037	0.0065	0.0012	0.00076	0.0011	0.0025	0.0022	0.0026	0.0024	0.0019	0.0021	0.0019
Se	0.005	0.046	0.047	0.039	0.055	0.016	0.018	0.037	0.043	0.014	0.029	0.005	0.032	0.019	0.024	0.023	0.02	0.035	0.029	0.038	0.041	0.028
Si	13.11	0.37	0.25	0.28	1.91	0.55	BDL	BDL	2.6	BDL	BDL	13.11	5.45	6.36	6.14	7.63	8.55	9.53	8.36	11.37	12.53	12.61
Sr	3.055	39.95	37.069	39.67	31.04	35.21	40.03	45.55	56.91	68.7	74.21	3.055	8.77	9.42	9.31	9.86	10.13	10.89	9.61	8.69	9.54	10.084
Ti	0.00069	0.0013	0.0016	0.0019	0.005	0.011	0.0049	0.01	0.055	0.0074	0.012	0.00069	0.003	0.0041	0.0028	0.0032	0.0029	0.03	0.0031	0.0066	0.0038	0.0027
V	0.019	0.009	0.0081	0.0085	0.0042	0.0045	0.0096	0.009	0.014	0.013	0.012	0.019	0.34	0.34	0.33	0.36	0.44	0.48	0.51	0.56	0.62	0.61
Zn	0.13	0.023	0.02	0.02	0.096	0.062	0.069	0.1	0.12	0.076	0.11	0.13	0.019	0.01	0.01	0.079	0.057	0.056	0.054	0.059	0.069	0.096
Cl	2424	2283.4	2231.08	2081.8	1916	1844	1842	1808	1758	1824	1718	2424	1321.68	1364	1402.76	1788	1826	1882	1814	1822	1856	1910
SO4	8858	6319	6096.88	5948.98	6122	4952	4078	3894	4026	4084	3848	8858	5934.06	5721.08	5938.7	5698	5958	6250	5856	5802	5818	6094
pH	7.75	11.26	11.19	11.16	12.72	12.65	12.87	12.67	12.64	12.71	12.81	7.75	9.49	9.54	9.57	10.91	11.21	11.16	11.6	11.5	11.43	11.52
EC	16.69	14.74	15.5	14.8	16.33	14.18	13.9	13.01	14.02	13.08	15.21	16.69	10.55	10.29	8.5	7.5	7.5	7.55	5.93	6.2	6.11	6.8
TDS	15400	7940	8360	7980	8810	7650	7500	7020	7580	7040	8200	15400	5400	5570	4540	4000	4060	4110	3200	3350	3310	3680

UB = Unreacted Brine, BDL = Below Detection Limit, ND = Not Detected

4.3.4.2.1 pH, Electrical Conductivity (EC) and Total Dissolved Solid (TDS)

The pH and EC trends of Secunda and Tutuka fly ash-brine systems at L/S 1:1 are shown in Table 4.8. The pH of the systems increased significantly at the beginning of the experiment (5 minutes) when compared with the pH of UB. The pH of Secunda fly ash-brine systems was observed to be stable till the end of the experiment after a maximum pH was reached at 30 minutes contact time while gradual increase in the pH of Tutuka fly ash-brine systems was observed throughout the contact time. The increase in the pH of the fly ash-brine systems could be attributed to the dissolution of alkalinity contributing oxides such as CaO and MgO in the fly ash samples (Gitari *et al.,* 2009; Ram *et al.,* 2007). The dissolution of oxides of Al such as Al_2O_3 has also been observed to contribute to the increase in the pH of fly ash solution (Van Herck *et al.,* 2000; Meima and Comans, 1997; Bayuseno and Schmahl, 2010). Considering the trends of the release of Ca and Al in the leachates (Table 4.8), the increase in pH corresponds to the increase in the Ca and Al concentrations in the systems thereby suggesting that the pH of the systems is dependent on the dissolution of oxides of Ca and Al. At 5-20 minutes contact time, the pH of the systems could be controlled by the dissolution of CaO as the concentration of Al in the systems was initially very low. The increase in the pH at 30 minutes could be as a result of the dissolution of Al oxide as the concentration of Al in the leachates at 30 minutes contact time increased significantly. The stability observed in the pH of the fly ash-brine systems could be attributed to the dissolution of acidic oxides such as Fe_2O_3 thereby increasing the buffering capacity of the fly ash-brine systems. Tables 4.6 and 4.7 revealed the dissolution of Fe_2O_3 as the concentration of Fe in the solid residues decreased at 30 minutes contact time compared with its concentration in the fresh fly ashes.

The EC and TDS trends of the fly ash-brine systems as shown in Table 4.8 followed the same trends. The EC and TDS of the systems decreased significantly at the beginning of the batch reaction tests (5 minutes) compared with their values in the UB. After the initial abrupt decrease, the EC and TDS of the systems was almost stable in the case of Secunda fly ash-brine systems while a slow decrease was observed in the Tutuka fly ash-brine systems up till 480 minutes. The decrease in the EC and TDS compared with the UB indicates that the ionic content in the leachates was reduced, and this could be attributed to the precipitation of secondary mineral phases or as a result of adsorption process.

4.3.4.2.2 Aluminium (Al)

The calculated SI showing the possible mineral phases controlling the release of Al in the fly ash-brine batch reaction systems are shown in Figure 4.15

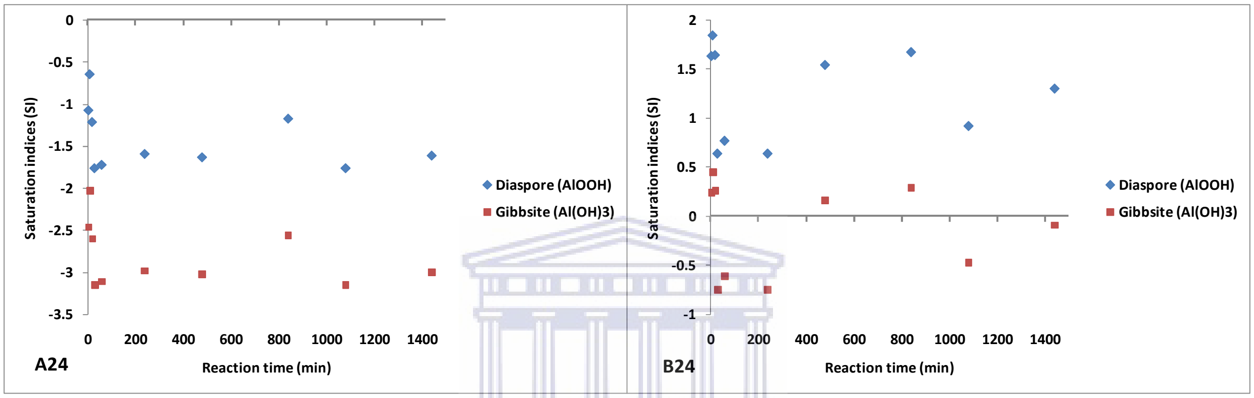

Figure 4.15: Plots of saturation indices for diaspore and gibbsite during the fly ash-brine batch reaction test at L/S 1:1 at different reaction time. Secunda (A24); Tutuka (B24)

The concentration of Al in the leachates of the Secunda and Tutuka fly ash-brine batch systems at L/S 1:1 is shown in Table 4.8. It was observed that the concentration of Al in the leachates (Table 4.8) of the two fly ash samples was higher than the concentration observed in the unreacted brine (UB) over time except at 5 and 20 minutes in Secunda fly ash-brine batch systems where a slight decrease in the concentration was observed. The slow increase noticed in most of the leachates coupled with the slight decrease observed in the solid residues (Tables 4.6 and 4.7) indicates that Al was slightly leached into the solution from the fly ashes, and this could be as a result of the dissolution of amorphous Al-bearing phases in the fly ashes. The release of Al at high pH (>9) has been observed to be a slow process (Van Herck *et al.*, 2000) as only a small soluble fraction exists as oxides on the surface of fly ash particles while the bulk exists in the form of aluminosilicates. The pH of Secunda and Tutuka fly ash-brine batch systems which was greater than 9 could be responsible for the low concentration of Al found in the leachates.

The concentration of Al in Tutuka fly ash-brine batch leachates was observed to be higher than that of Secunda fly ash-brine batch leachates. This could be attributed to the difference in the pH of the leachates (Table 4.8). The pH of Tutuka fly ash-brine batch systems (9.49-11.52) was a bit lower than that of Secunda (11.16-12.87) which could result to a faster dissolution of the Al-bearing phases in the former thereby increasing the Al concentration in the leachates. The calculated SI using PHREEQC showed that diaspore (AlOOH) and gibbsite [$Al(OH)_3$] were under-saturated in Secunda leachates [Figure 4.15 (A24)] which indicates that these mineral phases are not likely to precipitate out of the solution of Secunda fly ash-brine batch systems due to the low Al concentration. PHREEQC predicted the precipitation of diaspore (AlOOH) and gibbsite [$Al(OH)_3$] in the leachates of Tutuka fly ash-brine batch systems [Figure 4.15 (B24)] with SI values at super-saturation and near equilibrium respectively. The precipitation of these mineral phases in Tutuka fly ash-brine batch systems could be attributed to the higher concentration of Al in the systems. Meima and Comans (1997) and Dijkstra *et al.* (2006) suggested gibbsite as solubility controlling phase for Al. Diaspore (AlOOH) and gibbsite [$Al(OH)_3$] could be considered as the mineral phases controlling the release of Al in the leachates of the Tutuka fly ash-brine batch systems.

4.3.4.2.3 Calcium (Ca), Barium (Ba), Strontium (Sr) and Sulphate (SO_4)

The results of the calculated SI showing the possible mineral phases controlling the release of Ca, Ba, Sr and SO_4 in the fly ash-brine batch reaction systems are presented in Figure 4.16

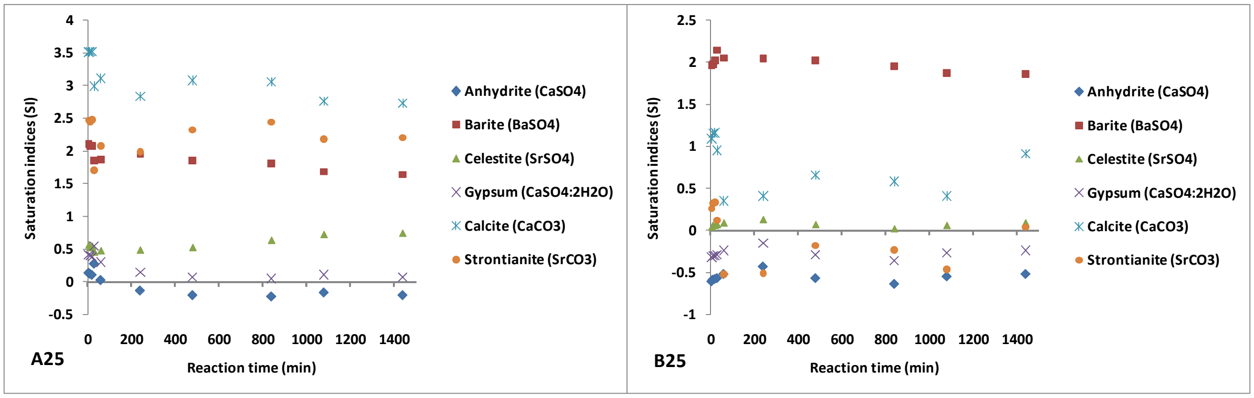

Figure 4.16: Plots of saturation indices for anhydrite, barite, celestite, gypsum, calcite and strontianite during the fly ash-brine batch reaction test at L/S 1:1 at different reaction time. Secunda (A25); Tutuka (B25)

The concentration of Ca in the leachates of Secunda and Tutuka fly ash-brine batch systems shows an increase when compared to the Ca in UB (Table 4.8). This is an indication that Ca was released in significant quantities from the fly ashes into the brine solution during the batch reaction tests. The concentration of Ca in the UB was found to be 106.99mg/L but after the interactions with fly ash, the concentration of Ca in the leachates of Secunda fly ash-brine batch systems ranged between 939 and 2236.45 mg/L while the concentration of Ca in Tutuka fly ash-brine batch systems ranged between 184 and 298.63 mg/L. The increase in Ca concentration observed in the leachates of the fly ash-brine batch systems could be attributed to the dissolution of Ca-containing soluble phases such as CaO and $CaSO_4$ in the fly ashes. The rapid increase in the concentration of Ca in the solution of fly ash has been observed to be predominantly due to the dissolution of soluble Ca-containing phases (Kirby and Rimstidt, 1994). PHREEQC geochemical modeling predicted that Secunda fly ash-brine batch systems are slightly super-saturated with respect to calcite ($CaCO_3$) while the calculated saturation indices (SI) for gypsum were at equilibrium throughout the contact time [Figure 4.16 (A25)]. Anhydrite was predicted to be at equilibrium at 5-60 minutes contact time after which anhydrite was slightly under-saturated in the systems. This indicates that the release of Ca in the leachates of Secunda fly ash-brine is being controlled by the precipitation of calcite, gypsum and anhydrite. In the case of Tutuka fly ash-brine batch systems, PHREEQC predicted that the release of Ca is controlled by calcite which was observed to be slightly super-saturated at 5-20 minutes and at equilibrium at 30-1440 minutes [Figure 4.16 (B25)]. Anhydrite and gypsum were predicted to be slightly under-saturated in Tutuka fly ash-brine batch systems, which could indicate that these phases may not control the release of Ca in the systems. The under-saturation observed with respect to anhydrite and gypsum in Tutuka fly ash-brine systems could be attributed to the lower concentration of Ca in Tutuka fly ash-brine systems. The same trend was observed in Secunda fly ash-brine batch systems where anhydrite was predicted to be slightly under-saturated at 840-1440 minutes when the concentration of Ca in the systems was lower.

The concentration of SO_4 decreased significantly in the leachates of the fly ash-brine systems when compared with the concentration of SO_4 in the UB. The concentration of SO_4 in UB was found to be 8858 mg/L while the concentration after the interactions with the fly ashes decreased to values ranging between 3848 and 6319 mg/L for Secunda fly ash-brine systems, and between 5698 and 6250 mg/L in the case of Tutuka fly ash-brine systems (Table 4.8). This indicates that SO_4 was removed from UB despite the possible dissolution of SO_4-containing soluble phases such as anhydrite, which is present in the ash immediately upon combustion (Kirby and Rimstidt, 1994). The XRF data (Tables 4.6 and 4.7) showing the total chemical compositions of the fly ash before and after the batch reaction test, revealed an increase in the concentration of S (SO_4) in the fly ashes after the batch reaction tests. This indicates that the SO_4 removed from the brine solution is being trapped in the fly ashes as solid phases. Barite ($BaSO_4$), gypsum ($CaSO_4.2H_2O$), celestite ($SrSO_4$) and anhydrite ($CaSO_4$) were predicted by PHREEQC as the mineral phases controlling the leaching of SO_4 in the fly ash-brine systems. The calculated SI indicated that barite was super-saturated irrespective of the contact time in Secunda fly ash-brine batch systems while celestite, gypsum and anhydrite were at equilibrium [Figure 4.16 (A25)], suggesting that the release of SO_4 in the systems is being controlled by the formation of these phases in the systems (Meima and Comans 1997). In the case of Tutuka fly ash-brine batch systems, the calculated SI indicated that the systems was at equilibrium and super-saturated with respect to celestite and barite respectively [Figure 4.16 (B25)] but showed slightly under-saturation for anhydrite and gypsum. This indicates that the release of SO_4 in Tutuka fly ash-brine batch system is being controlled by the precipitation of celestite and barite rather than gypsum and anhydrite. This also explains why Ca was not removed from the systems.

Despite the generally low concentrations of Ba and Sr in the leachates of the Secunda and Tutuka fly ash-brine batch systems, their concentrations were higher than what was observed in UB (Table 4.8). The concentrations of Ba and Sr in UB were respectively 0.057 and 3.055 mg/L. The concentrations of these species increased on contact with fly ash with the concentration of Ba in Secunda fly ash-brine solution ranging from 0.23 to 0.5 mg/L, and 0.18 to 0.36 mg/L in the case of Tutuka fly ash-brine leachates. Sr concentration increased in Secunda fly ash-brine batch systems from 31 to 74.21 mg/L while its concentration in Tutuka fly ash-brine batch systems ranged from 8.77 to 10.89 mg/L. The increase observed in the leachates indicates that these species were released continuously into the leachates of the fly ash-brine systems as a result of the dissolution of their soluble salts in the fly ashes. The results of the chemical compositions of the fresh fly ashes (SFA and TFA) and the solid residues from the fly ash-brine batch reactions (Tables 4.6 and 4.7) showed a slight decrease or increase in the concentrations of Ba and Sr in Secunda fly ash-brine batch reaction solid residues when compared to their concentrations in the fresh fly ash (SFA) in some cases. This agrees with the results in Table 4.8 showing that Ba and Sr were leached into the systems from the fly ashes and precipiteated as mineral phases at some stages.

PHREEQC calculations showed that the leachates of Secunda and Tutuka fly ash-brine batch systems were super-saturated with respect to barite ($BaSO_4$), and at equilibrium with respect to celestite ($SrSO_4$) [Figure 4.16 (A25 and B25)]. Strontianite ($SrCO_3$) was predicted to be super-saturated in Secunda fly ash-brine batch systems while in the case of Tutuka fly ash-brine systems, this mineral phase was at equilibrium at 5-30 minutes after which the systems was slightly under-saturated with respect to strontianite. These trends imply that the release of Ba in the leachates of both Secunda and Tutuka fly ash-brine systems is being controlled by the formation of barite. Celestite was predicted as the dominating phases controlling the release of Sr in both Secunda and Tutuka fly ash-brine systems. According to Fruchter *et al*. (1990), barite and celestite were suggested as the phases controlling the concentration of Ba and Sr respectively in alkaline fly ash leachates. Strontianite was predicted to control the release of Sr but only at 5-30 minutes in the case of Tutuka fly ash-brine systems [Figure 4.16 (B25)]. The release of Ba and Sr into the systems during the batch reaction tests (at alkaline pH) could facilitate the precipitation of barite and celestite respectively.

4.3.4.2.4 Magnesium (Mg), Sodium (Na) and Chloride (Cl)

Figure 4.17 shows the calculated SI indicating the possible mineral phases controlling the release of Mg, Na and Cl in the fly ash-brine batch reaction systems.

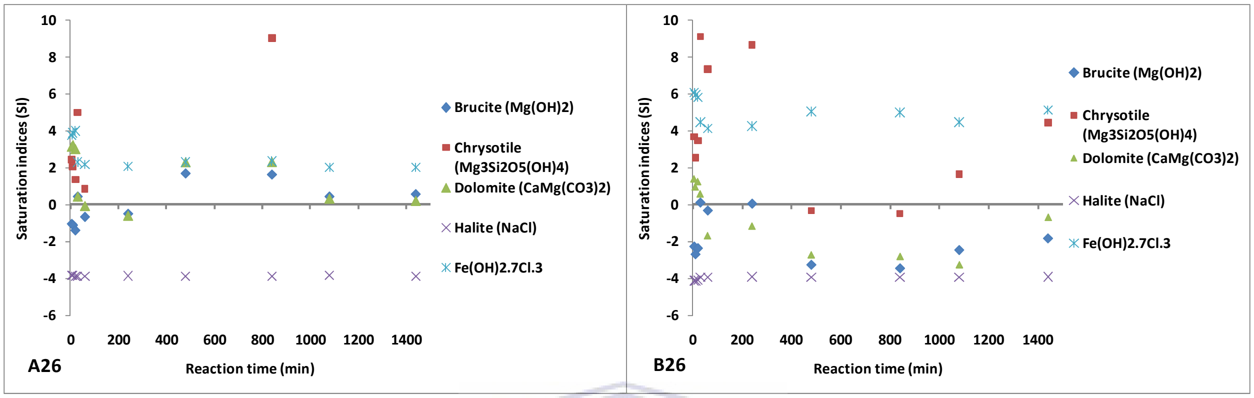

Figure 4.17: Plots of saturation indices for brucite, chrysotile, dolomite, halite and $Fe(OH)_2.7Cl_3$ mineral phases during the fly ash-brine batch reaction test at L/S 1:1 at different reaction time. . Secunda (A26); Tutuka (B26)

The concentration of Mg as observed in Table 4.8 decreased significantly when compared with the high concentration in the UB. The concentration of Mg in the UB was found to be 163.36 mg/L but after interacting with fly ash, the concentration decreased and was found to be in the range of BDL-0.19 mg/L for Secunda fly ash-brine batch systems while the concentration of Mg in Tutuka fly ash-brine batch systems was between BDL-16.029 mg/L. The reduction observed in the concentration of Mg in the two fly ash-brine batch systems is an indication that Mg was removed from UB by the fly ashes. The XRF results comparing the elemental compositions of the fresh fly ash with the residues from the batch reaction tests corroborate the removal of Mg from the systems by the fly ashes as the concentration of Mg in the residues (after the batch reaction test) was found to be slightly higher than the concentration in the fresh fly ashes (Tables 4.6 and 4.7). It was also observed that the concentration of Mg removed by Secunda fly ash was higher that the concentration removed by Tutuka fly ash. This could be attributed to the difference observed in the pH of fly ash-brine systems (Table 4.8). The pH of Tutuka fly ash-brine solution was at some stage less than 10 while the pH of Secunda fly ash-brine solution was found to be higher than 10 from the beginning of the batch reaction tests to the end (Table 4.8). The leaching of Mg into the fly ash solution is pH dependent as solubility controlling mineral phases such as brucite [$Mg(OH)_2$] precipitate mostly at pH >10 (Meima and Comans 1997; Warren and Dudas 1984; Schramke 1992). The SI calculated by PHREEQC geochemical modeling software showed that brucite [$Mg(OH)_2$], in Secunda fly ash-brine systems, was slightly under-saturated at the beginning of the tests (5-20, 60 and 240 minutes) but later found to be slightly super-saturated for the remaining period of the tests [Figure 4.17 (A26)]. The SI calculated for brucite in Tutuka fly ash-brine systems shows that brucite was under-saturated except at 30-240 minutes where near saturation was observed. This trend indicates that brucite may not control the release of Mg in the fly ash-brine batch systems. Apart from brucite, chrysotile [$Mg3Si_2O_5(OH)_4$] (with similar chemical composition as sepiolite) and dolomite [$CaMg(CO_3)_2$] were predicted by PHREEQC as solubility controlling the release of Mg in the systems of the fly ash-brine batch reaction tests. Chrysotile was found to be super-saturated in the two fly ash-brine batch systems except at 480 and 840 minutes in Tutuka fly ash-brine systems where slightly under-saturated SI values were observed [Figure 4.17 (B26)]. Dolomite was predicted to be super-saturated in the Secunda fly ash-brine leachates except at 60 and 240 minutes where near-saturation values were observed [Figure 4.17 (A26)]. The precipitation of dolomite was also predicted at the beginning of the experiment in the case of Tutuka fly ash-brine systems. Meima and Comans (1997) and Rai (1987) suggested that the formation of sepiolite ($Mg_2Si_3O_6(OH)_4{\cdot}1.5H_2O$) may control Mg leaching in alkaline condition (pH 8-10) in coal fly ash and MSWI bottom ash. Mg can also be incorporated in other mineral phases such as calcite (Schramke 1992), which may exert control on the release of Mg in the systems. Sepiolite was predicted to be slightly super-saturated at some stage in the systems (not included in the Figure). Sepiolite may control the release of Mg in the systems rather than chrysotile because the latter could only form at very high temperature. The formation of magnesioferrite (Fe_2MgO_4) (Figure 4.18) and dolomite may control the leaching of Mg in the leachates of the fly ash-brine batch systems.

The release of Na in the leachates of both Secunda and Tutuka fly ash-brine batch systems followed the same trends. The concentration of Na in the UB was found to be 4804.88 mg/L. After the interactions experiments at different reaction times, the concentration of Na in the fly ash-brine batch systems reduced significantly with Na concentration in Secunda fly ash-brine batch systems ranging from 3907.94-4494.96 mg/L while Na concentration in Tutuka fly ash-brine batch leachates ranged from 3280.27-3866.51 mg/L. The trend shows that Na was removed from the UB, and this could be due to the formation of secondary mineral phases as a result of super-saturation of Na in the fly ash-brine systems. Tables 4.6 and 4.7 further showed the capacity of the fly ashes to remove Na from UB as the concentration of Na in the fly ashes increased significantly after the batch reaction test. The concentration of Cl in the leachates of both Secunda and Tutuka fly ash-brine batch systems was also found to decrease when compared with the concentration of Cl in the UB. The concentration of Cl in the UB was significantly high with the value of 2424 mg/L (Table 4.8). The concentration of Cl in Secunda fly ash-brine batch systems was found to be between 1718 and 2283.4 mg/L while the Cl concentration in Tutuka fly ash-brine systems was in the range of 1321.68 and 1910 mg/L. This shows that Cl was also removed from UB during the fly ash-brine interaction experiments. The removal could also be due to the super-saturation of Cl in the systems. Comparison of the chemical compositions of the fresh fly ashes and the residues from the batch reaction tests revealed that Cl was removed from UB by the fly ashes as the concentration of Cl in the residues after the batch reaction tests increased significantly (Tables 4.6 and 4.7). Due to the high concentration of Na and Cl in the systems as a result of their concentrations in the brine solution (UB) (Table 4.8) coupled with the increase in Na and Cl concentrations observed in the residues (Tables 4.6 and 4.7), it could be assumed that the removal of Na and Cl is controlled by the formation of halite. However, the saturation index (SI) calculated for halite (NaCl) in the fly ash-brine batch systems showed that halite was under-saturated. The unsaturation observed for halite could be due to high soluble this phase is when formed. Apart from the formation of halite, PHREEQC predicted the formation of $Fe(OH)_2.7Cl_3$, and the calculated SI for $Fe(OH)_2.7Cl_3$ was found to super-saturated in the range of 2-3.99 (Secunda systems) and 4-6.09 (Tutuka systems) (Figure 4.17). Incorporation of Cl in the iron hydroxide phase [$Fe(OH)_2.7Cl_3$] could also control the release of Cl in the fly ash-brine batch systems.

4.3.4.2.5 Iron and Manganese

The calculated SI showing the possible mineral phases controlling the release of Fe and Mn in the fly ash-brine batch reaction systems are shown in Figure 4.18

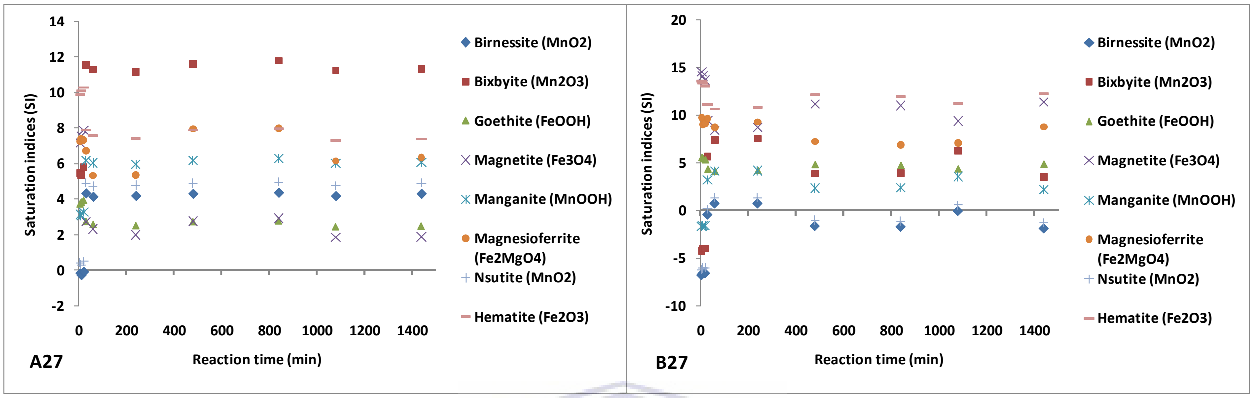

Figure 4.18: Plots of saturation indices for birnessite, bixbyite, goethite, magnetite, manganite, magnesioferrite, nsutite and hematite during the fly ash-brine batch reaction test at L/S 1:1 at different reaction time. Secunda (A27); Tutuka (B27)

The concentration of Fe in the UB was found to be 0.24 mg/L. The concentration of Fe in the leachates of both Secunda and Tutuka fly ash-brine batch systems at the beginning of the experiment decreased but were later found to be higher than the concentration in UB at 30, 480 and 840 minutes in the case of Secunda fly ash-brine batch systems while Fe concentration in Tutuka fly ash-brine batch systems was higher than what was observed in the UB at 240, 480, 1080 and 1440 minutes (Table 4.8). This trend shows that Fe was only removed transiently from the systems at the beginning of the batch reaction tests. The removal of Fe at the beginning of the tests could be attributed to the formation of transient mineral phases. The higher concentration observed at some later stages could be due to the dissolution of the transient mineral phases formed as well as from the Fe-containing minerals in the fly ashes. In alkaline solution, Fe forms iron oxides (oxyhydroxides), which occur as coatings around the silicate grains of fly ash and as discrete grains of oxide mineral (Fatoba, 2008). Upon reduction, Fe oxyhydroxides could re-dissolve into solution (Drever, 1997) thereby causing an increase in the concentration of Fe in the systems. The calculated SI shows that the leachates of the fly ash-brine batch systems was super-saturated with respect to goethite (FeOOH), magnetite (Fe_3O_4), magnesioferrite (Fe_2MgO_4) and hematite (Fe_2O_3) in both fly ash-brine batch systems (Figure 4.18). Roy and Griffin (1984) suggested that the concentration of the Fe in fly ash leachates is controlled by precipitation of their hydroxides. The formation of goethite (FeOOH), magnetite (Fe_3O_4), magnesioferrite (Fe_2MgO_4) and hematite could therefore be considered as mineral phases that may control the release of Fe in the fly ash-brine batch systems.

The trends of Mn concentration were found to be similar to that of Fe in the leachates of the fly ash-brine batch systems. The concentration of Mn at the beginning of the tests (5-20 minutes) showed a decrease when compared with the Mn concentration in the UB (0.0017 mg/L). Mn concentration was in the range of 0.00045-0.0012 mg/L and 0.00064-0.00083 mg/L in Secunda and Tutuka fly ash-brine batch systems respectively (Table 4.8). Mn concentration thereafter (at 30-1440 minutes) increased beyond what was contained in the UB in the range of 0.0037-0.0071 mg/L for Secunda fly ash-brine batch systems, and 0.0047-0.0099 mg/L in the case of Tutuka fly ash-brine batch systems. The initial decrease in the concentration of Mn in the systems at the beginning of the tests indicates the removal of Mn from the systems, which could be attributed to the formation of hydrous manganese (Fatoba, 2008). The increase observed in the concentration observed at 30-1440 minutes could be due to the dissolution of the hydrous manganese as well as Mn incorporated in the solid phases of the fly ashes. The calculated SI values (Figure 4.18) indicate that birnessite and nsutite (MnO_2) were slightly under-saturated and at equilibrium respectively at 5-20minutes in Secunda fly ash-brine batch systems after which the systems became supersaturated with respect to birnessite and nsutite. PHREEQC calculations show that bixbyite (Mn_2O_3) and manganite (MnOOH) were super-saturated in Secunda fly ash-brine systems. The SI values calculated with respect to these mineral phases are slightly different in Tutuka fly ash-brine batch systems. Birnessite was predicted to be under-saturated in Tutuka fly ash-brine batch systems except at 60 and 240 minutes where the system was at equilibrium [Figure 4.18 (B27)]. Bixbyite and manganite were under-saturated at 5-20 minutes after which Tutuka fly ash-brine systems became super-saturated with respect to these phases. According to Roy and Griffin (1984) who suggested that the concentration of the Fe and Mn in fly ash leachates is controlled by precipitation of their hydroxides, the solubility controlling the release of Mn in the fly ash-brine batch systems could be manganite, bixbyite, birnessite and nsutite at different stages.

4.3.4.2.6 Copper, Zinc and Nickel

The results of the calculated SI showing the possible mineral phases controlling the release of Cu, Zn and Ni in the fly ash-brine batch reaction systems are shown in Figure 4.19.

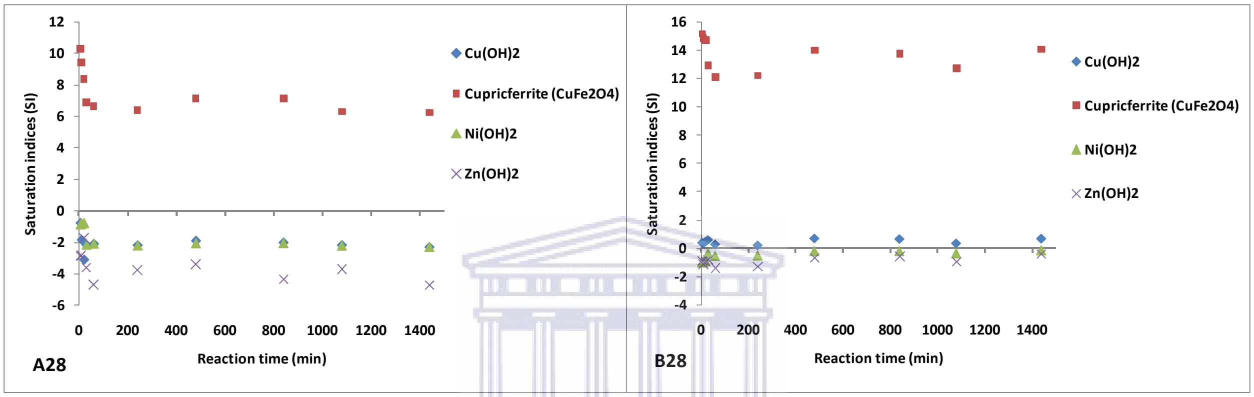

Figure 4.19: Plots of saturation indices for $Cu(OH)_2$, cupricferrite, $Ni(OH)_2$ and $Zn(OH)_2$ during the fly ash-brine batch reaction test at L/S 1:1 at different reaction time. Secunda (A28); Tutuka (B28)

The release of Cu in the leachates of the two fly ash-brine batch systems shows that Cu was significantly removed from the systems (Table 4.8). The concentration of Cu in UB was 0.26 mg/L. After the batch reaction tests, the concentration of Cu in Secunda fly ash-brine batch systems was reduced to concentrations ranging from 0.000019 and 0.02 mg/L while the concentration of Cu in Tutuka fly ash-brine batch systems ranged between 0.018 and 0.086 mg/L. The removal of Cu from the systems could be attributed to the formation of secondary mineral phases. The leachates of Secunda fly ash-brine batch systems were under-saturated with respect to $Cu(OH)_2$ irrespective of the contact time while cupricferrite ($CuFe_2O_4$) was found to be super-saturated in the systems (Figure 4.19). PHREEQC geochemical modeling predicted that Tutuka fly ash-brine batch systems was at equilibrium with respect to $Cu(OH)_2$, and super-saturated with respect to cupricferrite ($CuFe_2O_4$). Cu concentration in alkaline solution has been predicted to be controlled by surface complexation to Fe and Al-(hydr)oxides (Meima and Comans 1998; Dijkstra *et al.* 2006), and by the precipitation of $Cu(OH)_2(s)$ at pH >8 (Dijkstra *et al.,* 2008; Rai *et al.,* 1987). Surface complexation or co-precipitation with Fe-mineral phases (cupricferrite ($CuFe_2O_4$)) and the precipitation of $Cu(OH)_2$ could control the concentration of Cu in the fly ash-brine batch systems.

The concentration of Zn in the systems of Secunda and Tutuka fly ash-brine was found to be lower than the concentration of Zn in UB (0.13 mg/L) (Table 4.8). Zn concentration was found to be within the range of 0.02-0.1 mg/L in Secunda fly ash-brine batch systems while in the case of Tutuka fly ash-brine batch systems, the concentration of Zn ranged between 0.01 and 0.096 mg/L. The trend indicates that, during the batch reaction tests, Zn was removed from the brine by the two fly ashes. The removal of Zn from the UB during the interaction could be due to the precipitation of secondary mineral phases. According to Meima and Comans (1998) and Dijkstra *et al.*, (2006a), the release of Zn in solution is being controlled by surface precipitation on Fe and Al-(hydr)oxides. The calculated SI (Figure 4.19) shows that the systems is under-saturated with respect to $Zn(OH)_2$ in the case of Secunda fly ash-brine batch systems irrespective of the contact time. A slight difference was observed in the SI values for Tutuka fly ash-brine batch systems as PHREEQC predicted $Zn(OH)_2$ to be at near-saturation except at 10, 60 and 240 minutes where the calculated SI for $Zn(OH)_2$ was slightly under-saturated. Although co-precipitation of Zn with Al or Fe hydroxides was not predicted by PHREEQC, Zn concentration in the systems could be controlled by the precipitation of $Zn(OH)_2$ or as Al or Fe-hydroxides co-precipitates.

Ni concentration in the leachates of the fly ash-brine batch systems was found to be lower than the concentration in the UB (0.12 mg/L). The concentration of Ni in Secunda fly ash-brine batch systems was in the range of 0.054 and 0.067 mg/L while the concentration of Ni in Tutuka fly ash-brine batch systems was found to be between 0.082 and 0.11 mg/L (Table 4.8). The release of Ni in the case of Secunda fly ash-brine batch systems was observed to be stable while the concentration of Ni in Tutuka fly ash-brine batch systems increased with increase in contact time. The lower concentration of Ni in the systems, when compared with the concentration in the UB, indicates that Ni was removed from the brine solution (UB). The removal of Ni from UB during the fly ash-brine batch reaction tests could be as result of secondary mineral formation or adsorption to the surface of the fly ash particles. PHREEQC geochemical modeling (Figure 4.19) predicted that $Ni(OH)_2$ was near saturation at 5-20 minutes after which the leachates were under-saturated with respect to $Ni(OH)_2$ in Secunda fly ash-brine batch systems. In the case of Tutuka fly ash-brine batch systems, the systems were near equilibrium throughout the contact time. Ni was also observed to be controlled by the surface complexation on Fe and Al-(hydr)oxides and by the precipitation of $Ni(OH)_2(s)$ (Dijkstra *et al.*, 2006a; 2008). The precipitation of $Ni(OH)_2$ in the solution of the Tutuka fly ash-brine systems could control the release of Ni while the removal of Ni in the case of Secunda fly-brine systems could be as a result of surface complexation on Fe and Al-(hydr)oxides (Astrup *et al.*, 2006).

4.3.4.2.7 Arsenic, Cobalt and Lead

Figure 4.20 shows the calculated SI indicating the possible mineral phases controlling the release of As, Co and Pb in the fly ash-brine batch reaction systems.

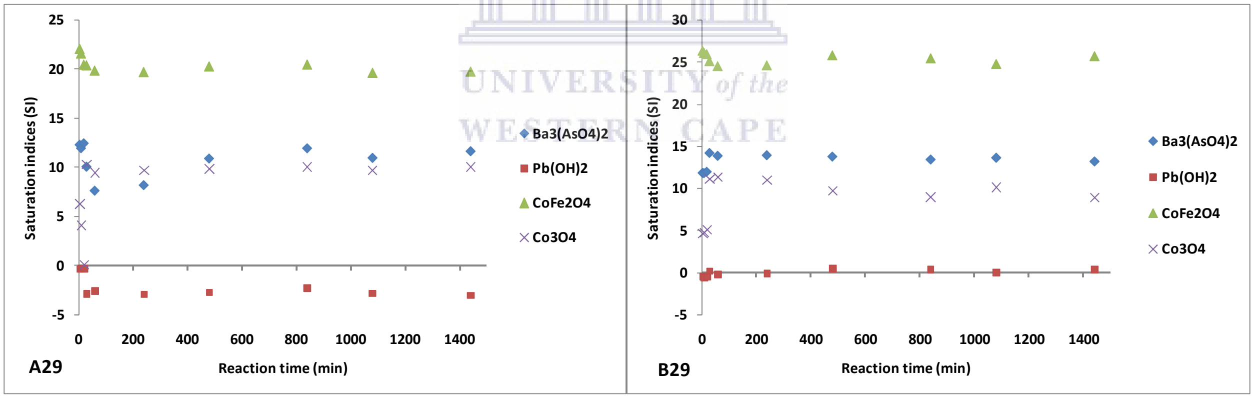

Figure 4.20: Plots of saturation indices for $Ba_3(AsO_4)_2$, $Pb(OH)_2$, $CoFe_2O_4$ and Co_3O_4 during the fly ash-brine batch reaction test at L/S 1:1 as a function of reaction time. Secunda (A29); Tutuka (B29)

The As concentration in UB was found to be as low as 0.0086 mg/L (Table 4.8). After the interaction of UB with Secunda fly ash, the concentration of As in the leachates was found to be lower and at some stage found to be below the detection limit. The concentration of As in Tutuka fly ash was observed to be higher than its concentration in UB (Table 4.8). In the case of Tutuka fly ash-brine systems, the As concentration was found to be between 0.0087 and 0.016 mg/L. The trend of As in the leachates indicates that As was removed from Secunda fly ash-brine batch systems while As was released into the Tutuka fly ash-brine systems. The removal of As from Secunda fly ash-brine batch systems could be as result of formation of secondary mineral phases while the increase in As concentration in the case of Tutuka fly ash-brine batch systems could be attributed to the preconditioning of the Tutuka fly ash before being sampled (see section 4.2.1). The SI calculated by PHREEQC shows that leachates of both Secunda and Tutuka fly ash-brine systems were super-saturated with respect to $Ba_3(AsO_4)_2$. This indicates that As in the leachates is being controlled by the formation of $Ba_3(AsO_4)_2$. The gradual dissolution of As-containing mineral phases in Tutuka fly ash-brine systems could be due to the dissolution of the sorbed As during the pre-treatment of Tutuka fly ash before being sampled. Barium arsenate [$Ba_3(AsO_4)_2$] has been proposed as a solubility-controlling phase for As in a solution where Ba concentration is at equilibrium with $BaSO_4$ (Eary *et al.*, 1990; Wagemann 1978; Essington 1988). The release of As in the fly ash-brine batch systems could be controlled by the precipitation of $Ba_3(AsO_4)_2$.

The concentration of Co in the leachates of the fly ash-brine batch systems was found to be lower than the concentration in UB. The Co concentration in UB was 0.014 mg/L but after the contact with fly ashes, the concentration of Co in both Secunda and Tutuka fly ash-brine systems decreased significantly (Table 4.8). The Co concentration in Secunda fly ash-brine batch systems was found to be in the range of 0.0000015 and 0.00095 mg/L while in the case of Tutuka fly ash-brine batch systems, the concentration ranged between 0.0038 and 0.0077 mg/L except at 30 minutes where the concentration (0.01 mg/L) was almost the same as in UB (Table 4.8). This trend indicates that Co was removed from UB by the fly ashes. Tables 4.6 and 4.7 also revealed the removal of Co by the fly ashes as the concentrations of Co in the residues from the batch reaction tests increased at some stage when compared with its concentration in the fresh fly ashes. This removal could be attributed to co-precipitation and formation of secondary mineral phases in the systems. PHREEQC geochemical modeling predicted the formation of $CoFe_2O_4$ and Co_3O_4 as the mineral phases controlling the release of Co in the systems (Figure 4.20). The calculated SI indicates that $CoFe_2O_4$ and Co_3O_4 were super-saturated in both Secunda and Tutuka fly ash-brine systems.

Pb concentration in UB was found to be 0.0065 mg/L (Table 4.8). The concentration of Pb after the batch reaction with Secunda fly ash was found to be in the range of 0.0025 and 0.0054 mg/L while in Tutuka fly ash-brine batch systems, the concentration ranged between 0.00076 and 0.0026 mg/L. The trends of these results showed that Pb concentration in the UB was reduced after contact with the fly ashes irrespective of the contact time. The removal of Pb in the solution could be as a result of solubility controlling phases in the systems. Dijkstra *et al.* (2008) observed that the concentration of Pb in solution of municipal solid waste incineration (MSWI) ash (similar composition as fly ash) at pH >11 could be predicted by the solubility of pure $Pb(OH)_2$(s) rather than adsorption on the surface of the ash particles. It was also suggested that the concentration of heavy metals such as Pb may be controlled by sorption to neo-formed iron- and aluminium (hydr)oxides such as lepidocrocite [FeO(OH)] and gibbsite $Al(OH)_3$ (Bayuseno and Schmahl, 2010) or by the formation of mineral phases such as $Pb(OH)_2$ (Meima and Comans 1997). The calculated saturation indices (SI) (Figure 4.20) in Secunda fly as-brine batch systems shows that $Pb(OH)_2$ was near-equilibrium at 5-20 minutes after which it became under-saturated at 30-1440 minutes. The calculated SI for $Pb(OH)_2$ in the case of Tutuka fly ash-brine batch systems was near-equilibrium at 5-20 and 60-240 minutes after which it was at equilibrium at 30, 480-1440 minutes. The removal of Pb from the leachates of Secunda fly ash-brine batch systems may therefore be controlled by sorption to either Fe or Al- hydroxide phases (lepidocrocite [FeO(OH)] (not shown) and gibbsite $Al(OH)_3$) formed in the systems rather than by the formation of $Pb(OH)_2$ while in the case of Tutuka fly ash-brine systems, Pb could be controlled by the combination of sorption on Fe- or Al-hydroxide and by the formation of $Pb(OH)_2$ at different stages.

4.3.4.2.8 Molybdenum (Mo) and Chromium (Cr)

The results of the calculated SI showing the possible mineral phases controlling the release of Mo and Cr in the fly ash-brine batch reaction systems are shown in Figure 4.21.

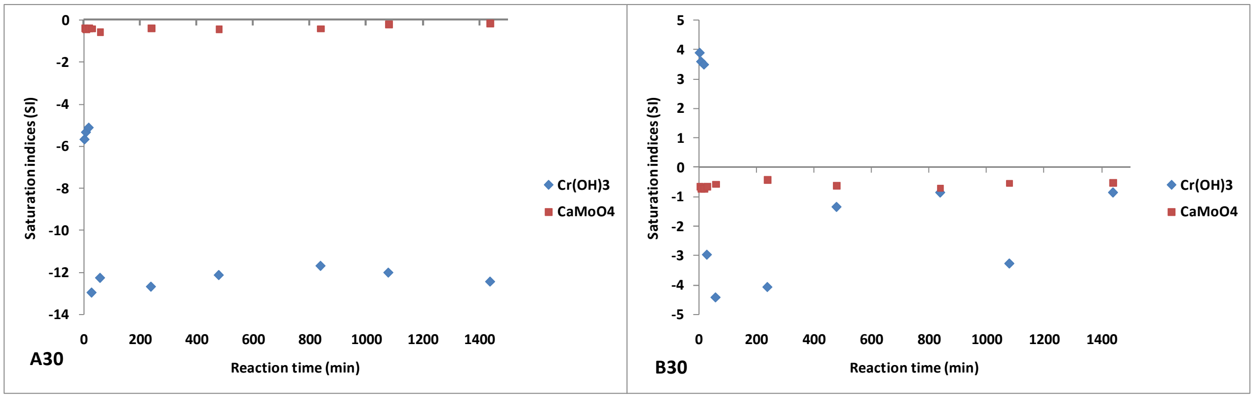

Figure 4.21: Plots of saturation indices for $Cr(OH)_3$ and $CaMoO_4$ during the fly ash-brine batch reaction test at L/S 1:1 at different reaction time. Secunda (A30); Tutuka (B30)

Mo concentration in the UB (0.039 mg/L) was found to be lower than its concentration in the leachates of Secunda and Tutuka fly ash-brine batch systems. The Mo concentration in Secunda fly ash-brine batch systems was found to be between 0.17 and 0.65 mg/L while its concentration in Tutuka fly ash-brine was in the range of 0.77 and 1.12 mg/L. The result, as shown in Table 4.8, indicates that Mo was leached into the systems from the fly ashes. PHREEQC geochemical modeling (Figure 4.21) predicted that the leachates of the both Secunda and Tutuka fly ash-brine systems were slightly under-saturated with respect to $CaMoO_4$ irrespective of the contact time. This indicates that the release of Mo in the systems is not likely to be controlled by $CaMoO_4$. The concentration of Mo in solution at high pH has been suggested to be controlled by weak surface complexation, and by the formation of secondary mineral phases at low pH (Dijkstra *et al.*, 2008). The trend of release of Mo as observed in Secunda and Tutuka fly ash-brine batch systems could be controlled by surface complexation rather than the formation of $CaMoO_4$ due to the high pH (Table 4.8) of the fly ash-brine systems.

The release of Cr in the fly ash-brine batch reaction systems followed the same trend as that of Mo. The concentration of Cr in UB was 0.014 mg/L. On contact with the fly ashes, the concentration of Cr in Secunda fly ash-brine batch systems was in the range of 0.25 and 2.5 mg/L, while the concentration of Cr in the case of Tutuka fly ash-brine batch systems increased to between 1.92 and 3.35 mg/L (Table 4.8). Thus a significant increase was observed in the concentration of Cr when compared with its concentration in UB, which indicates that Cr was significantly leached into the systems from the fly ashes. Contrary to the low concentration of Cr expected in the solid residues due to the increase observed in the leachates, the concentration of Cr in Secunda solid residues was higher than the concentration observed in Secunda fresh fly ash (SFA) in most cases (Table 4.6). Although, the oxidation state of the Cr in the systems was not determined, the trend observed in the concentration of Cr in Secunda solid residues could indicate the existence of Cr in different oxidation states in the respective fly ashes. Cr (III) is observed to be insoluble while Cr (IV) is easily available in solution (Tiruta-Barna *et al.,* 2006; Drever 1997). The difference in the release of Cr based on its oxidation could account for the difference observed in the leaching trend of Cr in the fly ashes, and this could indicate that Tutuka fly ash is dominated by Cr (IV) thereby causing its increase in the leachates and decrease in the solid residues. PHREEQC modeling predicted that the leachates of Secunda and Tutuka fly ash-brine batch systems was under-saturated with respect to $Cr(OH)_3$ (Figure 4.21) and $BaCrO_4$ (not presented). Metal oxy-anions such as Cr and Mo in alkaline systems may be trapped by the presence of secondary minerals such as barite ($BaSO_4$) either by precipitation as $BaCrO_4$ or $Ba(S,Cr)O_4$ (Bayuseno and Schmahl, 2010). Despite the under-saturation of the systems with respect to $Cr(OH)_3$ and $BaCrO_4$, the presence of barite in the fly ash-brine systems and the high pH of the systems which could cause weak sorption (Johnson *et al.,* 1995), thus precipitation of $Cr(OH)_3$ and $BaCrO_4$ could be the phases controlling the leaching of Cr in the system.

4.3.4.3 Summary

Although, the laboratory experiments do not exactly correlate with the leaching scenario expected in the field due to factors such as greater L/S ratio, non-aggressive leaching processes and other environmental conditions of the latter, the batch reaction tests gives an insight to the effect of fly ash-brine interactions on the removal and leaching of species in a co-disposal systems. The results of the batch reaction tests revealed that species such as Na, Mg, Cl, SO_4, B, As, Cd, Co, Cu, Ni, Pb and Zn could be significantly removed from the brine solution during the fly ash-brine batch reaction tests while Ca, Ba, Sr, Cr, Mo and Se were released into the leachates during the fly ash-brine batch reaction tests. The release of species such as Fe, Mn and Al was not consistent.

The pH of the systems increased to alkaline level upon contact with the fly ashes despite the near-neutral pH of the brine solution (Table 4.8). The pH of the fly ash-brine systems contributed to a large extent to the removal of some species in the batch reaction systems, as at very high pH, the precipitation of most of the species as secondary mineral phases is highly favoured. Apart from the high pH of the fly ash-brine batch systems, the high concentrations of some species such as Ca, Na, Cl, SO_4 and Ba in the systems could play a major role in the precipitation of most of secondary mineral phases due to the super-saturation level of these species in the systems.

The calculated saturated indices using PHREEQC geochemical modeling software provides information on the solubility-controlling phases that influenced the release of both major and minor species from fly ash-brine batch reaction systems. The study revealed that the release of major and minor species from the fly ash-brine systems at alkaline pH could be significantly controlled by precipitation/dissolution or adsorption/desorption processes. PHREEQC modelling predicted that mineral phases such as diaspore, gibbsite, barite, celestite, gypsum, anhydrite and brucite may control the release of major species such as Al, Ba, Sr, Ca, SO_4 and Mg in the fly ash-brine systems. The minor species such as Fe, Mn, Cu, Ni and Zn among others were predicted to be controlled by the precipitation of mineral phases such as goethite, hematite, cupricferrite, $Ni(OH)_2$ and $Zn(OH)_2$. Although, the formation of secondary mineral phases were predicted to control the release of major and minor species in the fly ash-brine batch reaction systems, the reduction in the % removal after 20 minutes contact time (in most cases) (Figures 4.13 and 4.14) and the reduction in the concentrations of most of the species in the solid residues (Tables 4.6 and 4.7) with increase in contact time showed the instability of the mineral phases formed during the interactions tests. Therefore, most of the mineral phases formed during the time frame of the batch reaction tests could be transient and re-dissolution may occur in most cases over time.

Genrally, the batch reaction tests gave a clear indication that some major and minor species in the brine can be removed when in contact with fly ash by forming transient mineral phases. The limitation of the batch reaction tests compared to the real scenario is that the L/S ratio used may not be practicable in the real co-disposal scenario. This study was carried out in a period of 24 hours whereas in the real co-disposal scenario where the slurry is being pumped to the ash dump after the aggressive aggitation, the fly ash-brine contact time is longer. At the ash dump, it takes longer time for the brine to percolate through the fly ash-brine systems, and there is need to understand the effect of the long-term fly ash-brine interactions on the removal or leaching of species in the systems. The need to understand the removal or leaching of species from the fly ash-brine systems without aggressive agitation and for longer contact time motivated the application of the long-term fly ash-brine interaction tests and the up-flow percolation tests. The results of the long-term fly ash-brine interaction tests and the up-flow percolation tests are presented in chapters 5 and 6 respectively.

Having observed the removal or leaching of some major and minor species when the fly ash-brine systems were aggressively agitated for a short period varying from 5 minutes to 1440 minutes (24 hours), there is need to determine the effects of the long-term fly ash-brine interactions, in static (not agitated) condition, on the removal or leaching of species in fly ash-brine systems. The next chapter (chapter 5) deals with the results and discussion of the long-term fly ash-brine interactions experiments carried out to determine the effects of long-term fly ash-brine interactions in closed and static systems on the removal of species from the brine solution. The results of the ANC tests carried out on the solid residues generated from the long-term fly ash-brine interaction experiments to determine the stability of the species removed during the interactions experiments will also be discussed in the next chapter.

Chapter 5

Long-term fly ash-brine interactions: A closed and static system

5 Introduction

This aspect of the study deals with the long-term interactions of species in fly ash and brine solution when in contact for a period of time varying from 1 week to 12 months. The approach used in this chapter was borne out of the way some power utilities co-dispose fly ash and brine with the aim of using fly ash to capture the ‘salts’ in brine. For instance, ESKOM power generation in South Africa pre-condition their fly ash with about 16 % brine in dry disposal systems in order to suppress dust before conveyed to the ash dump, and at the ash dump, the fly ash is being irrigated with brine. The fly ash conditioned with a small amount of brine is deposited in the ash dump at different times and seasons thereby creating a scenario where there is an old section of the dump and new ash placement. Therefore, a controlled simulative experiment was carried out to investigate the effect of short and long-term interactions of fly ash and brine on the leaching of species from the fly ash samples and the removal of species from the brine solution under a closed and static condition. The idea of the closed and static systems was aimed at investigating the effect of the fly ash-brine interactions on the mineralization, removal and leaching of species if fresh brine or rain water is not allowed to come in contact after the initial fly ash-brine contact. The long-term fly ash-brine interaction experiments described in this chapter is different from the batch reaction tests presented and discussed in the previous chapter (4). The former is non-aggressive and carried out in closed and static systems while the latter is an aggressive fly ash-brine interaction system.

According to the experimental procedure as described in section 3.3.3, the brine solution was mixed with Secunda or Tutuka fly ash in ratio 1:1 and allowed to stand at ambient conditions in closed containers for different contact times of 1 week, 1 month, 6 months and 12 months. The excess leachate decanted from the solid residues after the long-term interaction experiments was analyzed in order to determine the effect of the fly ash-brine interactions on the quality of the brine solution after a specific period of time. The solid residues from the fly ash-brine interaction experiments were characterized to determine the effect of the fly ash-brine interactions on the physical, chemical and mineralogical composition of the solid residues. The acid neutralization capacity (ANC) tests were carried out on the solid residues recovered from the long-term fly ash-brine interaction experiments to determine the mobility of species in the solid residues when in contact with solutions of different pH values.

Apart from the sections that deal with the overview and the materials and methods (experimental details in chapter 3), the results and discussion of this chapter is divided into two (2) sections, namely sections 5.3.1 and 5.3.2. Section 5.3.1 presents and discusses the chemical composition of the excess brine decanted from the solid residues after the interactions experiments, and the characterization of the long-term fly ash-brine solid residues. Section 5.3.2 deals with the results and discussion of the acid neutralization capacity tests (ANC) carried out to determine the mobility of species from the solid residues when in contact with solutions of different pH.

5.1 Overview

The combustion of coal for power generation is on the increase due to the increase in demand for electricity in some countries in the world. Huge amounts of fly ash are produced as a result of the increase in coal combustion. According to US Coal Combustion Product (CCP) Production & Use Survey Report in 2008, US power plants produced about 70 million tons of fly ash annually, of which nearly 45 % was beneficially used (ACAA, 2008). In South African, one of the power utilities produce about 40 million tons of fly ash annually (ESKOM report, 2009), out of which less than 10 % is utilized. Despite the fact that fly ash is beneficially used for agricultural purposes, waste stabilization, additive to cement, road construction among others (Iyer and Scott 2001; Kumpiene *et al.,* 2007; Campbell, 1999; Foner *et al.,* 1999), significant amounts of fly ash are being disposed of in ash dump. Fly ash contains major and minor species such as Ca, Na, Mg, K, SO_4, Cl, As, Pb, Cu, Cr, Fe, Mo, Mn etc., and these species could leach out in significant quantity from fly ash when in contact with aqueous solution (Ilic *et al.,* 2003; Baba and Kaya, 2004; Polettini and Pomi, 2004; Adriano *et al.,* 1980). Due to the possible release of contaminants to the surrounding soils, surface and groundwater, the disposal of fly ash has environmental impacts. Apart from fly ash generated in the power stations in South Africa, brine (a hyper-saline wastewater), is also generated in large quantities. Brine contains some major and trace species such as Na, Mg, K, SO_4, Cl, As, Pb, Cu, Se, Cr, in significant quantities. The regulation guiding the disposal of brine has regulated its disposal due to its chemical composition. South African power stations have been practicing the co-disposal of fly ash and brine. One of the reasons for co-disposing brine and fly ash is that the interactions of the species in the waste materials is thought to lead to the formation of secondary mineral phases thereby reducing the mobility of contaminants to the surrounding soils and groundwater. Several studies have shown that interactions of fly ash with contaminated water could lead to the removal of species from wastewater. For instance, Gitari *et al.* (2006) observed that some contaminants were removed from acid mine drainage (AMD) when in contact with fly ash. The studies in chapter 4 have revealed that fly ash can remove some species from brine solutions (section 4.2). The removal of species by fly ash was observed to be either by adsorption/desorption processes or by precipitation of secondary mineral phases (section 4.3.4.2).

The objectives of this section of the study are; a) to determine the effect of the long-term fly ash-brine interactions under closed and static conditions on the removal of species from the brine solution, b) to identify secondary mineral phases if any, that may form as a result of the long-term interactions between fly ash and brine species under closed and static conditions, and c) to determine the stability of the secondary mineral phases formed and determine the mobility of species in the solid residues when in contact with solutions of different pH values.

To achieve these objectives, several analytical and experimental methods such as XRF, XRD, SEM-EDS and acid neutralization capacity (ANC) were employed on the solid residues recovered from the fly ash-brine interaction experiments.

The pH of a system is one of the key parameters controlling the leaching process. The release of species from fly ash systems is primarily controlled by the solubility of various solid phases at different pH levels (van Herreweghe, *et al.*, 2002). Acid neutralization capacity (ANC) tests have been carried out to determine the mobility of species at different pH from municipal solid waste incineration (MSWI) ash and fly ash (Vítková *et al.* 2009; Kirby and Rimstidt 1994; Fleming *et al.* (1996; Astrup *et al.* 2006; Baba *et al.* 2008). The interactions between ash particles and a leaching solution can lead to partial or complete dissolution of the mineral phases that constitute the ash particles, or can result in partial chemical equilibrium between the ash constituents and leachant, depending on factors such as the pH of the leachant. The application of the ANC gives an insight into the release of metals from waste by-products of a coal-fired thermal power plant in acidic conditions. In this study, the ANC test was applied to determine the mobility of species in the solid residues when in contact with solution of different pH conditions.

5.2 Materials and Methods

The description of the samples, the experimental procedures and the analytical techniques used in this chapter are presented in chapter 3. The XRD, XRF and SEM-EDS are presented in section 3.4.7, 3.4.8 and 3.4.9 respectively. The experimental procedures for the total acid digestion, long-term fly ash-brine interaction tests and the acid neutralization capacity (ANC) tests are presented in sections 3.3.1, 3.3.3 and 3.3.4 respectively. The anion and cation analyses of the leachates from the experiments were done using IC and ICP-MS respectively (see sections 3.4.5 and 3.4.6 respectively).

5.3 Results and discussion

As mentioned above (section 5), the results and discussion is divided into two sections (sections 5.3.1 and 5.3.2).

5.3.1 Chemical composition of the excess brine decanted from the solid residues and the characterization of long-term fly ash-brine interactions solid residues

This section (5.3.1) presents and discusses the chemical composition of the excess brine decanted from the long-term fly ash-brine interactions experiments and the physical, chemical and mineralogical compositions of the solid residues from the long-term fly ash-brine interactions experiments. This section is expected to give an insight into the quality of excess brine on top of the solid residues after the interaction with the fly ashes, and the changes in the physical, mineralogical and chemical characteristics of the fly ashes after extensive contact with a fixed volume of brine solution.

The chemical composition of excess brine solutions decanted from the solid residues after the long-term fly ash-brine interactions experiments was determined using IC and ICP-MS. The physical, chemical and mineralogical compositions of the fresh fly ash and the solid residues from the long-term fly ash-brine interactions experiments were determined using scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS), x-ray diffraction (XRD) and x-ray fluorescence (XRF) techniques. This section will discuss the effects of long-term fly ash-brine interactions on the morphology of the fly ash samples, and the presence and relative proportions of amorphous and some crystalline phases present in the fly ash and fly ash-brine interactions residues, and the concentrations of species before and after the fly ash-brine interaction tests.

5.3.1.1 Chemical composition of unreacted brine and excess brine decanted from the solid residues

Tables 5.1 and 5.2 present the elemental composition of the excess brine decanted from the solid residues after the long-term fly ash-brine interaction experiments. Figures 5.1 and 5.2 present the percentage (%) of selected species leached into the brine solutions or removed from the brine solutions by the fly ashes during the long-term fly ash-brine interaction experiments.

The concentration and percentage of species leached or removed from the brine solutions was calculated using this formula

$$Concentration\ of\ species\ leached\ or\ removed\ (CLR) = \frac{CUB - CDB}{CUB}$$

$$Percentage\ (\%) leached\ or\ removed = \frac{CLR}{CUB}\ X\ 100$$

where *CUB, CDB* and *CLR* are concentration of the unreacted brine solution, concentration of species in the decanted brine solution and concentration of species leached or removed respectively.

Table 5.1: Chemical composition of unreacted brine and the excess brine solution decanted from the solid residues after the long-term Secunda fly ash-brine interactions experiment; (concentration in mg/L except pH and EC (mS/cm))

Element	UB	SAC(L)	SBC(L)	SCC(L)	SDC(L)
Al	0.016	0.057	104.9	141.5	132.15
As	0.0036	0.0015	0.027	0.044	0.101
B	1.39	BDL	0.58	BDL	3.47
Ba	0.029	0.22	0.17	0.094	0.037
Ca	101.27	977.52	245.57	5.24	8.062
Co	0.0072	BDL	0.0013	BDL	0.0026
Cr	0.0063	1.55	1.29	0.38	0.161
Cu	0.1004	BDL	0.0054	0.0049	0.0086
Fe	0.043	0.098	0.24	0.104	0.55
K	56.37	143.92	181.6	232.1	244.16
Mg	75.44	0.109	0.13	0.03	BDL
Mn	0.043	0.00049	0.0061	0.0026	0.017
Mo	0.019	0.38	0.67	1.28	1.61
Na	4475.07	4411	4372.05	3658.36	2935.2
Ni	0.057	0.046	0.062	0.031	0.04
Pb	0.00093	0.00037	0.00066	0.00035	0.00023
Si	7.27	0.56	71.11	48.2	399.57
Sr	2.93	50.58	10.75	1.96	0.16
Zn	0.051	0.013	0.027	0.048	0.022
Cl	2424	2089.05	1950	1730	1780
SO4	8858	4835.18	1000	652	705.33
pH	7.75	12.54	12.3	12.98	12.46
EC (mS/cm)	16.69	34.75	34	32.84	27.68

UB = unreacted brine solution; SAC(L) = excess brine decanted from SAC (1 week); SBC(L) = excess brine decanted from SBC (1 month); SCC(L) = excess brine decanted from SCC (6 months); SDC(L) = excess brine decanted from SDC (12 months).

Table 5.2: Chemical composition of unreacted brine and the excess brine solution decanted from the solid residues after the long-term Tutuka fly ash-brine interactions experiment; (concentration in mg/L except pH and EC (mS/cm))

Element	UB	TAC(L)	TBC(L)	TCC(L)	TDC(L)
Al	0.016	0.43	4.73	3.29	6.43
As	0.0036	0.0087	0.015	0.015	0.013
B	1.39	0.14	0.84	BDL	0.8
Ba	0.029	0.17	0.16	0.12	0.18
Ca	101.27	194.72	73.87	110.18	95.32
Co	0.0072	0.0028	0.0027	0.0018	0.002
Cr	0.0063	2.087	2.7	2.56	1.53
Cu	0.1004	0.015	0.016	0.007	0.018
Fe	0.043	0.067	0.29	0.13	0.042
K	56.37	147.88	147.36	154.55	145.89
Mg	75.44	1.47	0.14	0.13	0.065
Mn	0.043	0.00081	0.0043	0.00072	0.0012
Mo	0.019	0.79	0.98	1.034	1.2
Na	4475.07	3639.29	3273.57	3607.78	3240.41
Ni	0.057	0.091	0.11	0.087	0.096
Pb	0.00093	0.00085	0.00064	0.00025	0.0009
Si	7.27	9.01	16.78	20.98	26.66
Sr	2.93	9.053	4.47	7.39	5.79
Zn	0.051	0.01	0.031	0.016	0.011
Cl	2424	1608.08	1860	1797.51	1768
SO4	8858	6161.83	5388	5770.41	5112
pH	7.75	11.07	11.46	12.11	11.5
EC (mS/cm)	16.69	15.44	17.52	12.67	16.4

UB = unreacted brine solution; TAC(L) = excess brine decanted from TAC (1 week); TBC(L) = excess brine decanted from TBC (1 month); TCC(L) = excess brine decanted from TCC (6 months); TDC(L) = excess brine decanted from TDC (12 months).

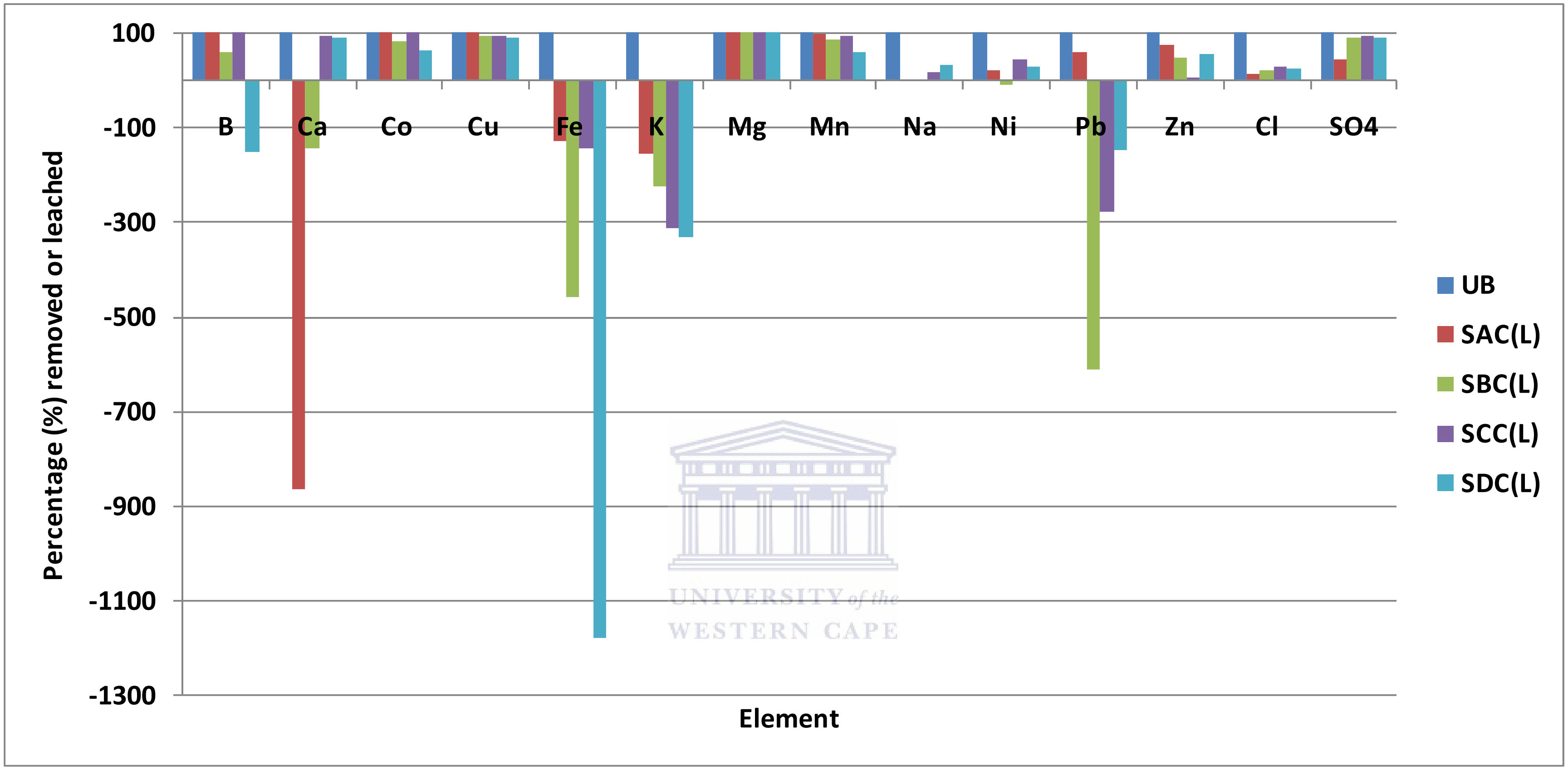

Figure 5.1: Percentage of selected species removed or leached into the excess brine solution decanted from the Secunda solid residues after the long-term fly ash-brine interactions experiment; (negative (-) values means % leached)

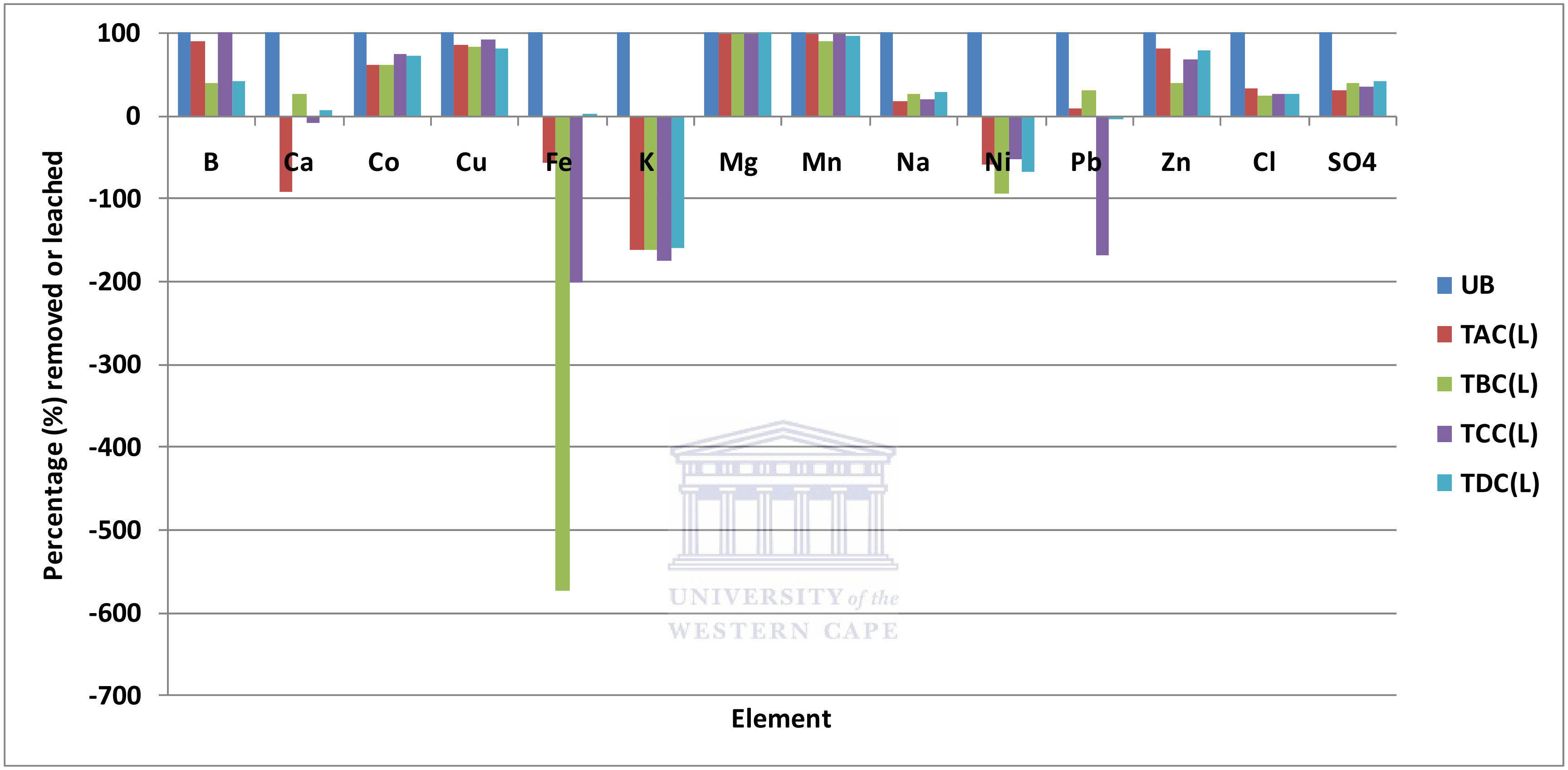

Figure 5.2: Percentage of selected species removed or leached into the excess brine solution decanted from the Tutuka solid residues after the long-term fly ash-brine interactions experiment; (negative (-) values means % leached)

Despite the static and closed conditions of the long-term fly ash-brine interaction tests, some species such as Al, Ca, K, Ba, Sr, Cr and Mo were leached out of the fly ashes into the brine solutions thereby causing an increase in their concentrations in the decanted brine solutions compared with their concentrations in the unreacted brine (UB) (Table 5.1 and 5.2). On the other hand, some species were removed from the brine solutions by the fly ashes during the long-term fly ash-brine interactions experiments. For instance, species such as B, Co, Cu, Mg, Mn, Zn, Cl and SO_4 were significantly removed from the brine solutions by Secunda fly ash during the long-term fly ash-brine interactions experiments irrespective of the period of the interactions experiments. Although Na and Ni were removed from the brine solution by Secunda fly ash, the concentrations removed were lower than those of other species mentioned above (Table 5.1 and 5.2). In the case of Tutuka systems, B, Co, Cu, Mg, Mn, Na, Zn, Cl and SO_4 were significantly removed from the brine solution by Tutuka fly ash. Pb was initially removed from the brine solution but later leached into the brine at 1 month and 6 months for Secunda and Tutuka long-term interactions respectively. Ni, which was removed from the brine solution by Secunda fly ash, was leached from Tutuka fly ash into the brine solution (Figures 5.1 and 5.2; Tables 5.1 and 5.2). The removal of these species from the brine solution could be as a result of precipitation, co-precipitation or adsorption processes in the fly ash-brine systems. The % of Mg removed from the brine solutions by Secunda and Tutuka fly ashes ranged between 98 and 100 % (Figures 5.1 and 5.2). In alkaline solution, the formation of insoluble $Mg(OH)_2$ (Reardon *et al.* 1995) could responsible for the removal of Mg from the brine solution. The removal of B from the brine solutions was in the range of 39 and 100 % (Figures 5.1 and 5.2). Due to the high concentration of Ca leached into the brine at the beginning of the experiment (1 week), co-precipitation of B with $CaCO_3$ in the systems could account for the removal of B from the brine solution (Hollis *et al.,* 1988). However, the formation of ettringite [$Ca_6Al_2(SO_4)_3.26H_2O$] in the highly alkaline solutions (pH >11) due to the availability of its components (Al, Ca and SO_4) in the brine solution, can also reduce the concentration of B (Iwashita *et al.,* 2005; Hassett, 1994). Mn was removed significantly from the brine solutions in percentage ranged between 60 and 98 % (Figures 5.1 and 5.2) but gradually reduced with increase in the interactions period. The removal of Mn could be associated with the possible formation of Mn-oxyhydroxides in the alkaline systems (Drever, 1997). The percentage removal of Cu, Co and Zn from the brine solutions was found to range between 82 and 100 %, 61 and 100 %, and 5 and 80 % respectively

(Figures 5.1 and 5.2). The removal of Co, Cu and Zn could be attributed to adsorption on the Mn-oxyhydroxides in the systems or as a result of the adsorption of these species on the negatively charged surfaces of the fly ash particles (Alinnor, 2007; Papandreou *et al.*, 2007). The removal of Na (1-34 %) and Cl (13-34 %) from the brine during the long-term fly ash-brine interaction experiments (Figures 5.1 and 5.2) could be due to the formation of Na and Cl-rich mineral phase such as halite in the systems. The percentage removal of SO_4 was found to be in the range of 30 and 93 % (Figures 5.1 and 5.2). The removal of SO_4 could be as a result of the precipitation of SO_4-rich mineral phases such as $CaSO_4$, Na_2SO_4 and $BaSO_4$ during the long-term fly ash-brine interactions experiments. The % removal of Na, Cl and SO_4 from the brine solution by the fly ashes increased with increase in the interaction periods. This indicates that the period of interaction could have a positive effect on the removal of Na, Cl and SO_4 from the brine solution if the fly ash-brine system is left undisturbed for a longer period of time. Comparison of the removal capacity of the two fly ashes showed that Secunda fly ash could removed more SO_4 than Tutuka fly ash while on the other hand, Tutuka fly ash showed higher removal capacity for Na and Cl than Secunda fly ash. The concentrations of species such as Al, Si, Ba, Ca, Sr, As, Mo, Cr, and Fe were observed to increase in the excess brine decanted after the long-term fly ash-brine interactions experiments when compared with their concentrations in unreacted brine solution (Tables 5.1 and 5.2). After 1 month of the fly ash-brine interactions, the concentrations of Ca, Ba and Sr were found to decrease in the excess brine decanted indicating that these species initially released into the systems were removed gradually from the systems. The removal of these species over time indicates the possible interactions with other species in the brine solution to form new mineral phases. The formation of SO_4-rich mineral phases such as $CaSO_4$, $BaSO_4$ and $SrSO_4$ could be responsible for the decrease in the concentrations of Ca, Ba and Sr respectively. The decrease in the concentration of SO_4 in the excess brine (Tables 5.1 and 5.2) and the increase observed in the % removal of SO_4 from the brine solution (Figures 5.1 and 5.2) by the fly ashes after 1 month of interactions supports this assumption.

Considering the pH and EC values of the brine decanted from the solid residues after the long-term fly ash-brine interactions experiments (Tables 5.1 and 5.2), an increase in the pH and EC of the systems was observed. The increase in the pH of the systems could be attributed to the dissolution of alkalinity-contributing oxides such as CaO and MgO in the fly ashes. The increase in the pH of the systems due to the dissolution of alkalinity-contributing oxides from the fly ashes influenced the reactivity of the species in the systems as high pH favours the precipitation of most of the phases. The increase observed in the EC of the excess brine decanted from the Secunda solid residues after the long-term fly ash-brine interaction experiments could be as a result of the leaching of some species from the fly ashes into the brine solutions during the experiments.

In conclusion in this section, the results of the elemental composition of excess brine decanted from the solid residues after the long-term fly ash-brine interaction experiments and the % removal of species (Tables 5.1 and 5.2; Figures 5.1 and 5.2) showed that some species B, Co, Cu, Mg, Mn, Zn, Na, Cl and SO_4 were removed from the brine solutions by Secunda and Tutuka fly ashes (static and closed conditions) without the systems being aggressively agitated. The % removal of Na, Cl and SO_4 which are the major components in brine increased with an increase in the interaction period. This shows that when the fly ash-brine systems are left undisturbed for a longer period, more Na, Cl and SO_4 species may be removed from the brine solution. Despite the fact that some species were removed from the brine solution by the fly ashes, it was shown that some species such as Al, Ca, Ba, Sr, Mo, Cr and Fe were leached out of the fly ashes into the brine solution even under static conditions over time. The removal and the leaching of species observed in the long-term interaction systems is evidence of chemical interactions between the species in the systems.

The assumption that the removal of species from the brine solutions was as a result of the interactions of brine components with the fly ashes needs to be investigated and ascertained. Therefore, analysis showing the chemical composition of the solid residues recovered from the long-term fly ash-brine interactions experiments is necessary to determine the effect of the interactions on the fly ashes and to ascertain the assumption that the fly ashes removed some species from the brine solution during the experiments. The results of the chemical composition (as measured by XRF) of the solid residues from the long-term fly ash-brine interactions experiments are presented and discussed in the next section.

5.3.1.2 Chemical composition of fresh fly ash and the fly ash-brine interaction solid residues

The total elemental composition of the fresh Secunda and Tutuka fly ashes (SFA and TFA) and the solid residues recovered from the long-term fly ash-brine interactions experiments carried out at different contact times ranging from 1 week (SAC and TAC), 1 month (SBC and TBC), 6 months (SCC and TCC) and 12 months (SDC and TDC) are presented in Figures 5.3 to 5.8. The results of the total elemental compositions of Secunda and Tutuka fresh fly ashes and the solid residues from the long-term fly ash-brine interactions experiments were determined by XRF analytical technique except As and Mo which were determined by the total acid digestion tests (experimental details in section 3.3.1). The results represent the mean of the triplicate analysis.

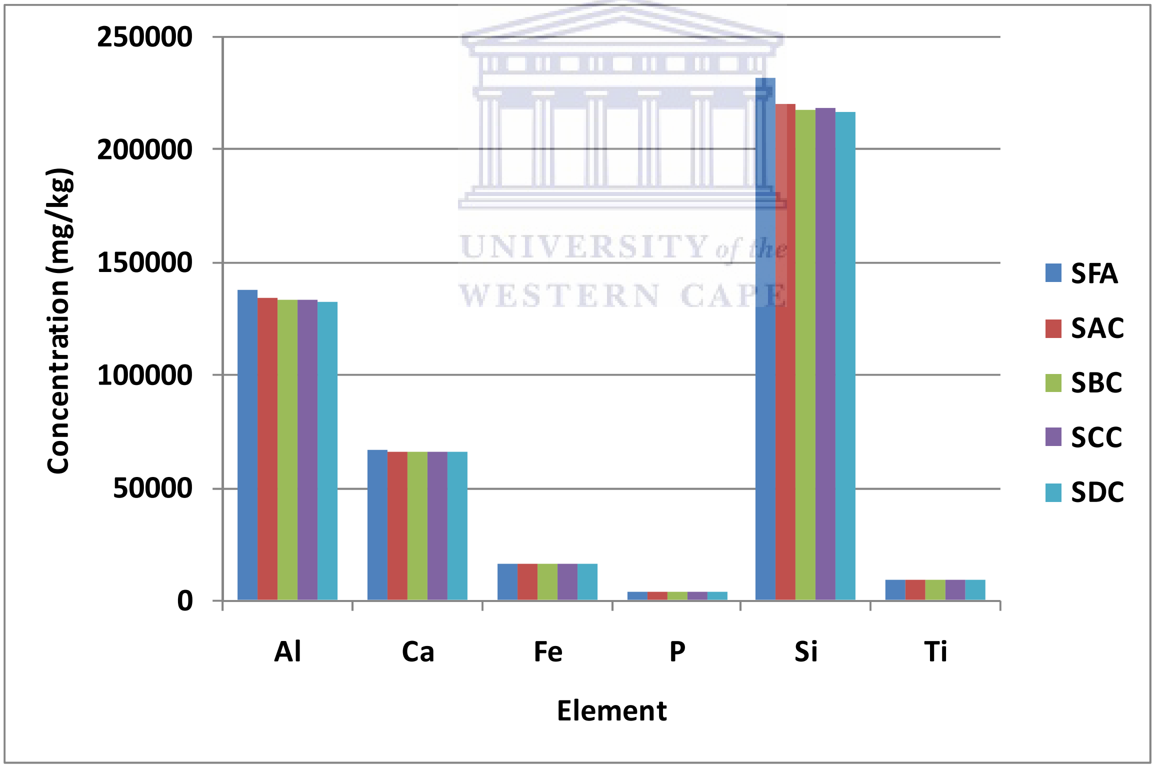

Figure 5.3: Concentrations of Al, Ca, Fe, P, Si and Ti (mg/kg) in Secunda fresh fly ash (SFA) and solid residues recovered from Secunda fly ash-brine long-term interactions experiments; SAC = solid residue at 1 week, SBC = solid residue at 1 month, SCC = solid residue at 6 months, SDC = solid residue at 12 months (*n=3*)

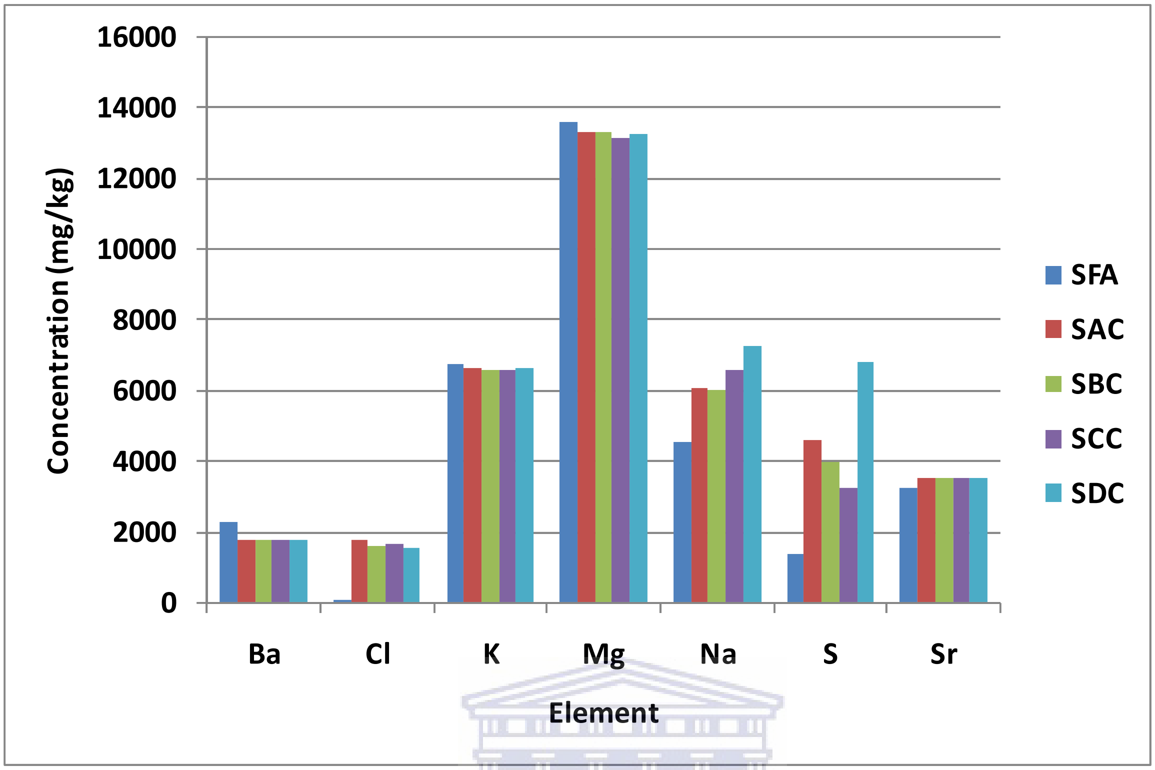

Figure 5.4: Concentrations of Ba, Cl, K, Mg, Na, S and Sr (mg/kg) in Secunda fresh fly ash (SFA) and solid residues recovered from Secunda fly ash-brine long-term interactions experiments; SAC = solid residue at 1 week, SBC = solid residue at 1 month, SCC = solid residue at 6 months, SDC = solid residue at 12 months (*n*=3)

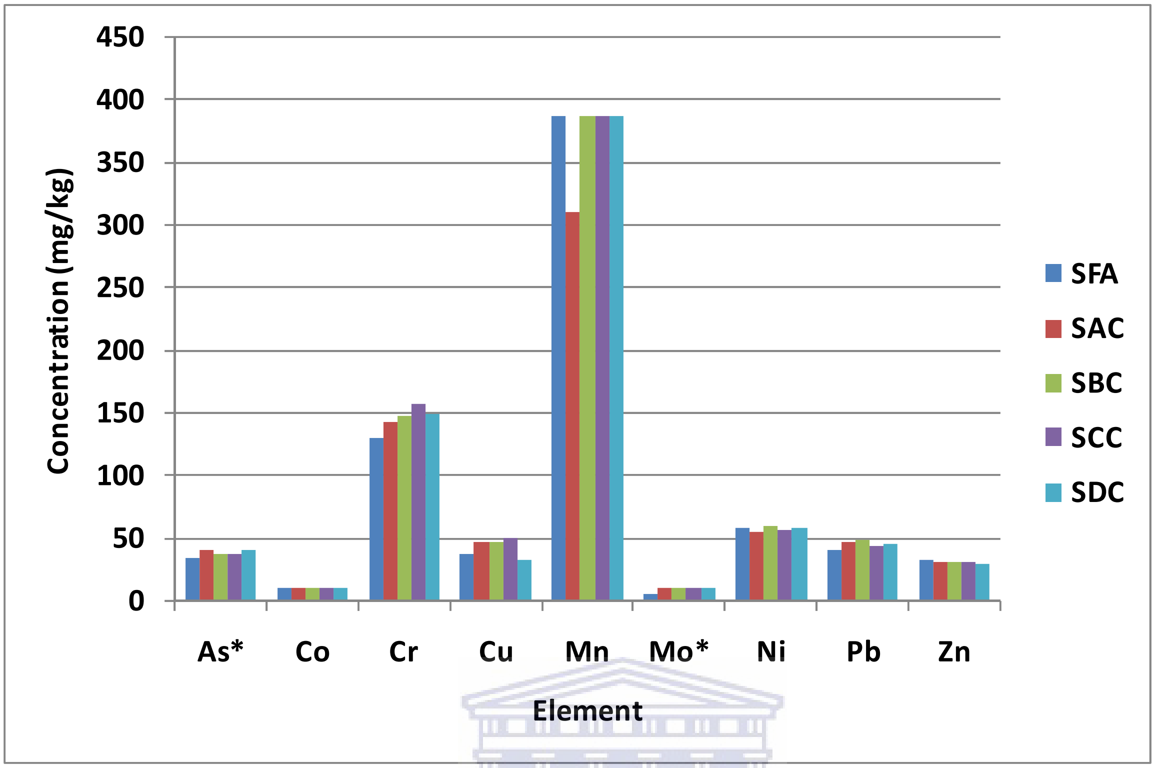

Figure 5.5: Concentrations of As, Co, Cr, Cu, Mn, Mo, Ni, Pb and Zn (mg/kg) in Secunda fresh fly ash (SFA) and solid residues recovered from Secunda fly ash-brine long-term interactions experiments; SAC = solid residue at 1 week, SBC = solid residue at 1 month, SCC = solid residue at 6 months, SDC = solid residue at 12 months; (*n*=3); * Data from total acid digestion tests

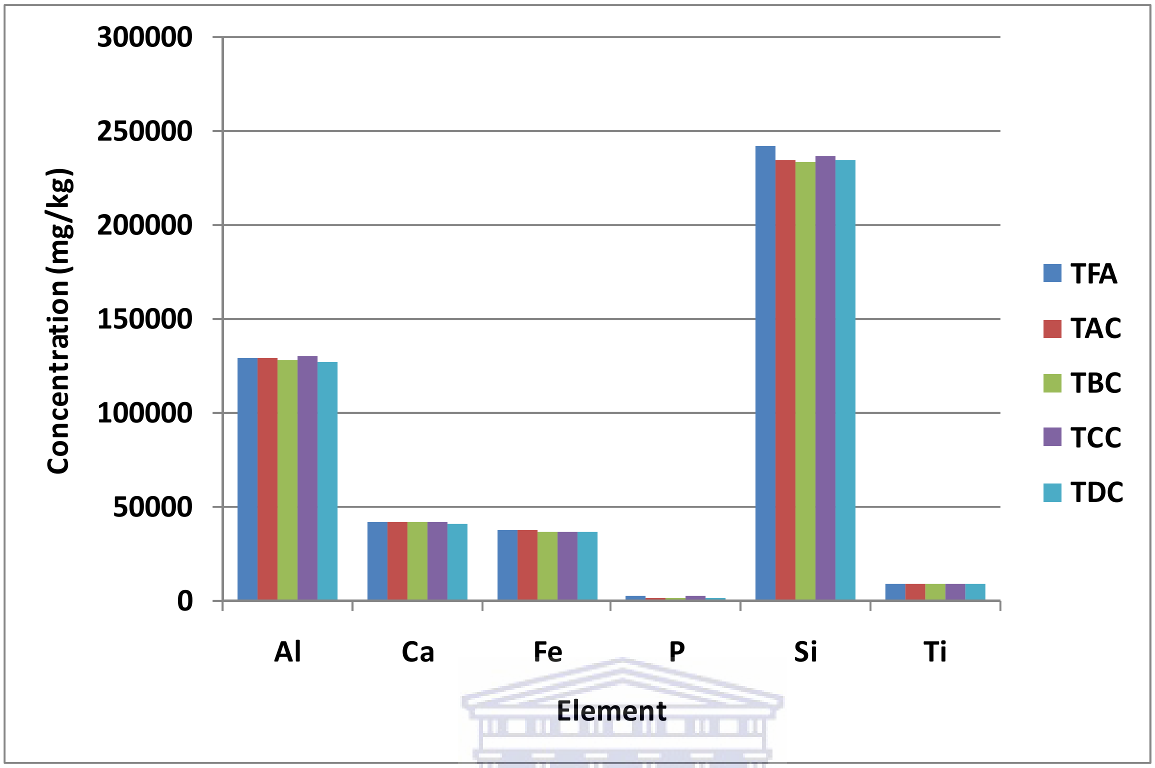

Figure 5.6: Concentrations of Al, Ca, Fe, P, Si and Ti (mg/kg) in Tutuka fresh fly ash (TFA) and solid residues recovered from Tutuka fly ash-brine long-term interactions experiments; TAC = solid residue at 1 week, TBC = solid residue at 1 month, TCC = solid residue at 6 months, TDC = solid residue at 12 months (*n*=*3*)

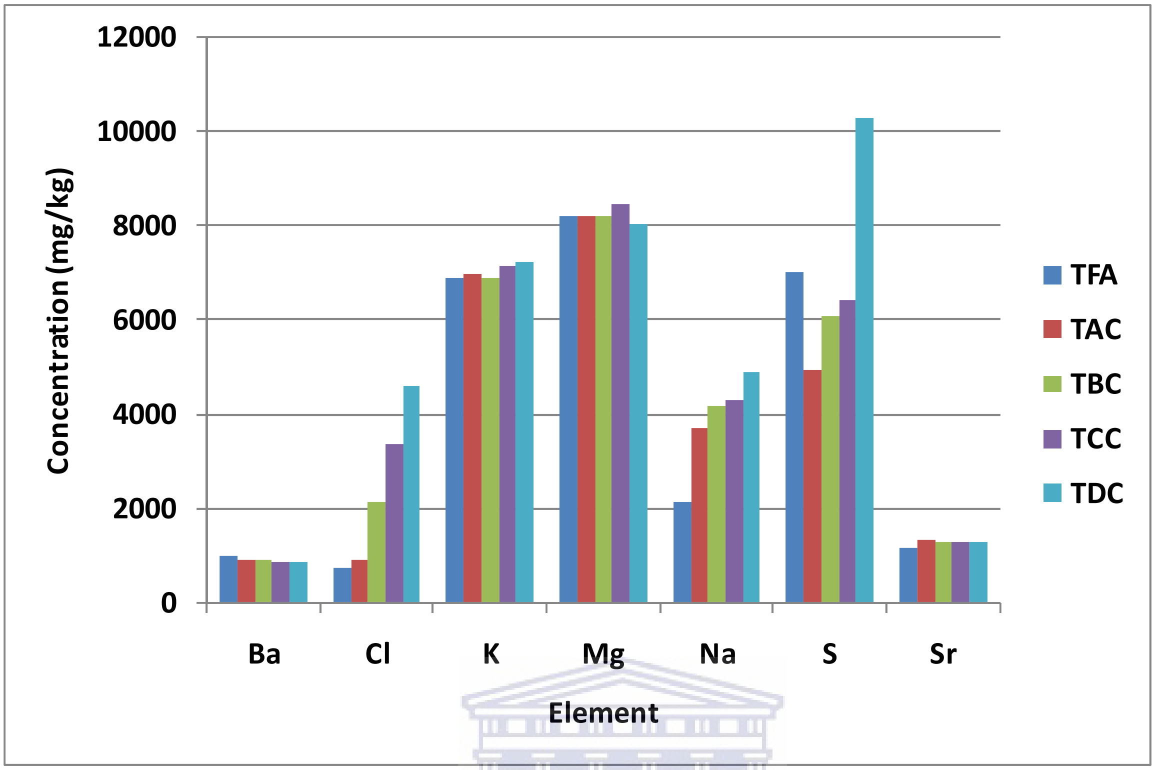

Figure 5.7: Concentrations of Ba, Cl, K, Mg, Na, S and Sr (mg/kg) in Tutuka fresh fly ash (TFA) and solid residues recovered from Tutuka fly ash-brine long-term interactions experiments; TAC = solid residue at 1 week, TBC = solid residue at 1 month, TCC = solid residue at 6 months, TDC = solid residue at 12 months (*n*=*3*)

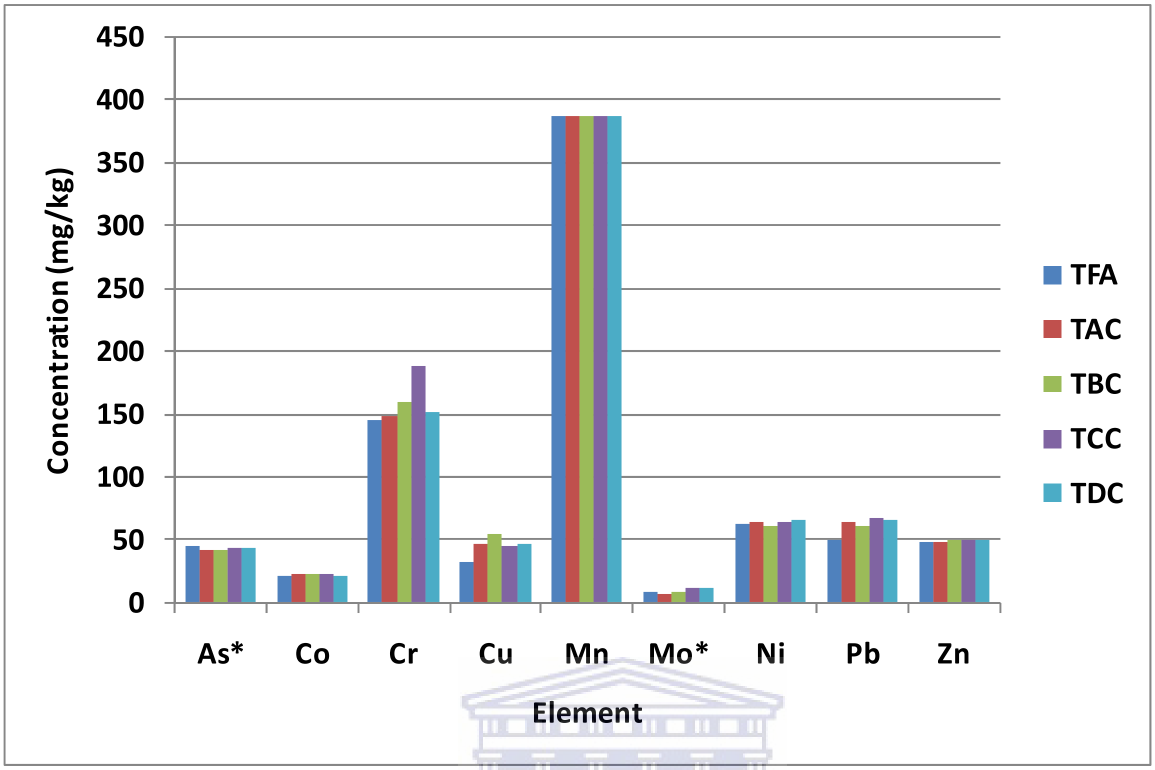

Figure 5.8: Concentrations of As, Co, Cr, Cu, Mn, Mo, Ni, Pb and Zn (mg/kg) in Tutuka fresh fly ash (TFA) and solid residues recovered from Tutuka fly ash-brine long-term interactions experiments; TAC = solid residue at 1 week, TBC = solid residue at 1 month, TCC = solid residue at 6 months, TDC = solid residue at 12 months; (*n*=3); * Data from total acid digestion tests

The results showed that the total concentrations of some of the elements such as Al, Ba, Ca, Fe, K, Mn, Mg, Na, Si, S and Sr in the fresh fly ashes (SFA and TFA) are generally very high (Figures 5.3 to 5.8). It was observed from the XRF data that the concentrations of species such as As, Cr, Cu, Mo, Pb, (Figure 5.5) Na, Cl, S and Sr (Figure 5.4) in Secunda fly ash-brine solid residues (SAC, SBC, SCC and SDC) increased significantly upon long-term contact with brine compared with their concentrations in the fresh fly ash (SFA). The concentration of Al, Ba, K, Si and Zn in Secunda solid residues were observed to decrease compared with their concentrations in SFA while there was no significant change observed in the concentrations of Ca, Mg, Fe, Mn, Co and Ni in the Secunda solid residues (Figures 5.3 to 5.5). Similar trends were observed when the concentrations of species in Tutuka fresh fly ash was compared with the concentrations of species in the solid residues from Tutuka long-term fly ash-brine interactions experiments. The concentrations of Cl, K, Mg, Na, S, (Figure 5.7) Cr, Mo, Cu, Pb and Zn (Figure 5.8) in Tutuka solid residues increased compared with their concentrations in the fresh fly ash. The concentration of Al, Ba and Si were observed to reduce in the solid residues recovered from Tutuka long-term interaction experiments.

The increase in the concentrations of most of the species such as Na, Mg, Na, S, Cu and Pb in the solid residues must result from their removal from the brine solution and the subsequent uptake by the fly ashes either by adsorption or precipitation processes. The results of the chemical composition of the excess brine decanted from the solid residues after the long-term interactions experiments showed that the concentrations of the above mentioned species were lower than what was observed in the unreacted brine solution (UB) (Tables 5.1 and 5.2). The results of the chemical composition of the excess brine decanted (Tables 5.1 and 5.2) coupled with the XRF results (Figures 5.3 to 5.8) give evidence that species such as Na, Cl, Mg, S and Cu were removed from the brine solution by the fly ashes during the long-term interactions experiments over 12 months. On the other hand, the increase in the concentrations of Al, Ba, K and Si in the excess brine decanted from the solid residues increased coupled with slight decrease in the concentrations of these species in the solid residues showed that these species were leached from the fly ashes into the brine solution during the long-term interactions experiments over 12 months. Although, the concentrations of species such as Ca, Ba, Mg and Sr in the solid residues were expected to decrease significantly due to their high solubility when in contact with water, the slight change observed in their concentrations in the solid residues compared with their concentrations in the fresh fly ashes could indicate that these species formed new phases under static conditions after being leached from the fly ashes. The formation of new mineral phases is possible due to the interactions of these species with other species such as SO_4 contained in the brine solution. The assumption of formation of new mineral phases was supported by the decrease observed in the concentrations of Ca, Ba and Sr species in the excess brine decanted from the solid residues after the initial increase (Tables 5.1 and 5.2). The formation of Fe and Mn oxy-hydroxides after the leaching of these species from the fly ashes could also account for their stable concentrations in the solid residues.

Apart from the high pH (Tables 5.1 and 5.2) of the fly-ash-brine interactions systems that could favour the precipitation of some mineral phases, the fact that the experiments were carried out in closed and static systems for a longer period of time gave sufficient contact time for the species to interact to form secondary mineral phases. Ahmaruzzaman (2010) also suggested that the adsorption of heavy metals by fly ash depends on the pH, initial concentration of heavy metals and contact time. Studies on the application of fly ash in wastewater treatment revealed the potential of fly ash to remove most of the species in the wastewater due to its major chemical components, which are alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties such as porosity, particle size distribution and surface area (Ahmaruzzaman, 2010). Investigation revealed that metal ions such as ions, Ni, Cr, Pb, As, Cu, Zn and Cd are removed by fly ash from wastewater by adsorption process (Dasmahapatra *et al.,* 1996; Bhattacharya *et al.,* 2006; 2008; Bayat, 2002). Therefore, the removal of species such as Cu, Cr, Pb, Co, As and Ni could be attributed to adsorption process in the long-term fly ash-brine systems. The slight decrease in the concentrations of species such as Al, Ca and Ba could be attributed to the dissolution of the easily soluble phases of these species in the fly ashes. Significant quantities of these species that may be present in their easily soluble phases could easily dissolve when in contact with aqueous solution.

The effect of the interaction periods was revealed in the concentrations of Na, Cl and S in the solid residues. Interestingly, the concentration of Na, Cl and S in the solid residues was observed to increase with the increase in the period of the interaction. This observation was in agreement with what was observed in the chemical analysis of the excess brine decanted from the solid residues where the % removal of Na, Cl and SO_4 (Figures 5.1 and 5.2) in the brine solution increased with an increase in the interaction periods. This indicates that the longer the interaction periods of the fly ashes and the brine solution in closed and static conditions, the higher the amount of Na, Cl and SO_4 that could be removed from the brine solution.

Generally, the results of the chemical composition of the excess brine decanted from the solid residues (section 5.3.1.1) and the elemental analysis of the solid residues (section 5.3.1.2) revealed that some species such as Na, Cl and SO_4, which are major constituents of the brine solution, could be significantly removed from the brine solution when the fly ash-brine systems is allowed to stay undisturbed for some times. These results also revealed that some species such as Ca, Ba, Al, Si, Cr and Mo could leach out of the fly ashes into the brine solution. Having observed an increase in the concentrations of some species in the solid residues generated from the long-term fly ash-brine interactions experiments which indicate their removal from the brine solution, the mineral phases responsible for this removal need to be identified. The need to identify the mineral phases therefore called for the use of XRD analytical technique. The results of the XRD analysis carried out on the solid residues to identify the crystalline mineral phases in the solid phases are presented and discussed in the next section (5.3.1.3).

5.3.1.3 Mineralogical composition of the solid residues from the long-term fly ash-brine interaction experiments: XRD analysis

The X-ray diffractograms presenting the mineralogical composition of the fresh fly ashes and the solid residues from the fly ash-brine interaction experiments are shown in Figures 5.9 and 5.10.

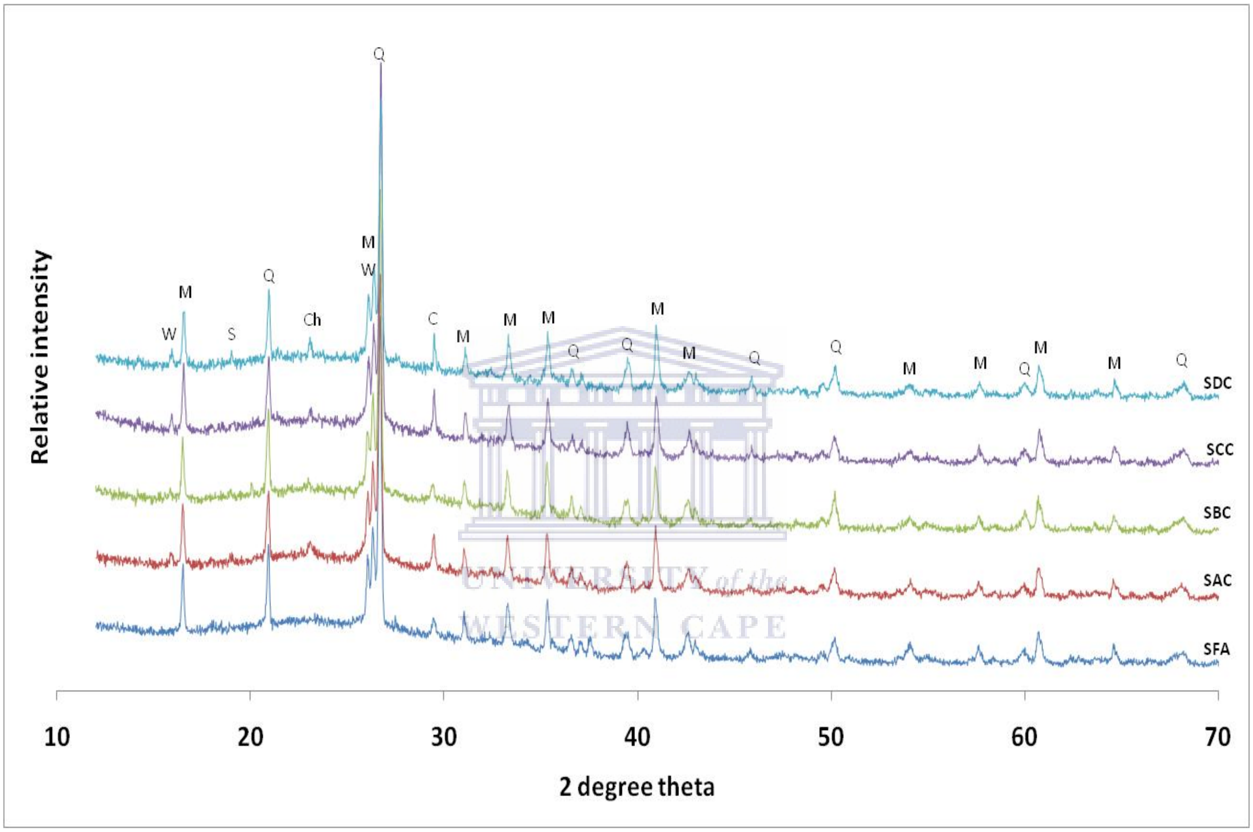

Figure 5.9: X-ray diffractograms for SFA- Secunda fresh ash; SAC - long-term Secunda ash-brine interactions for 1 week; SBC – long-term Secunda ash-brine interactions for 1 month; SCC – long-term Secunda ash-brine interactions for 6 months; SDC – long-term Secunda ash-brine interactions for 12 months. Peaks labelled are: M (mullite), Q (quartz), C (calcite), W (wairakite), Ch (charlesite), S (spinel).

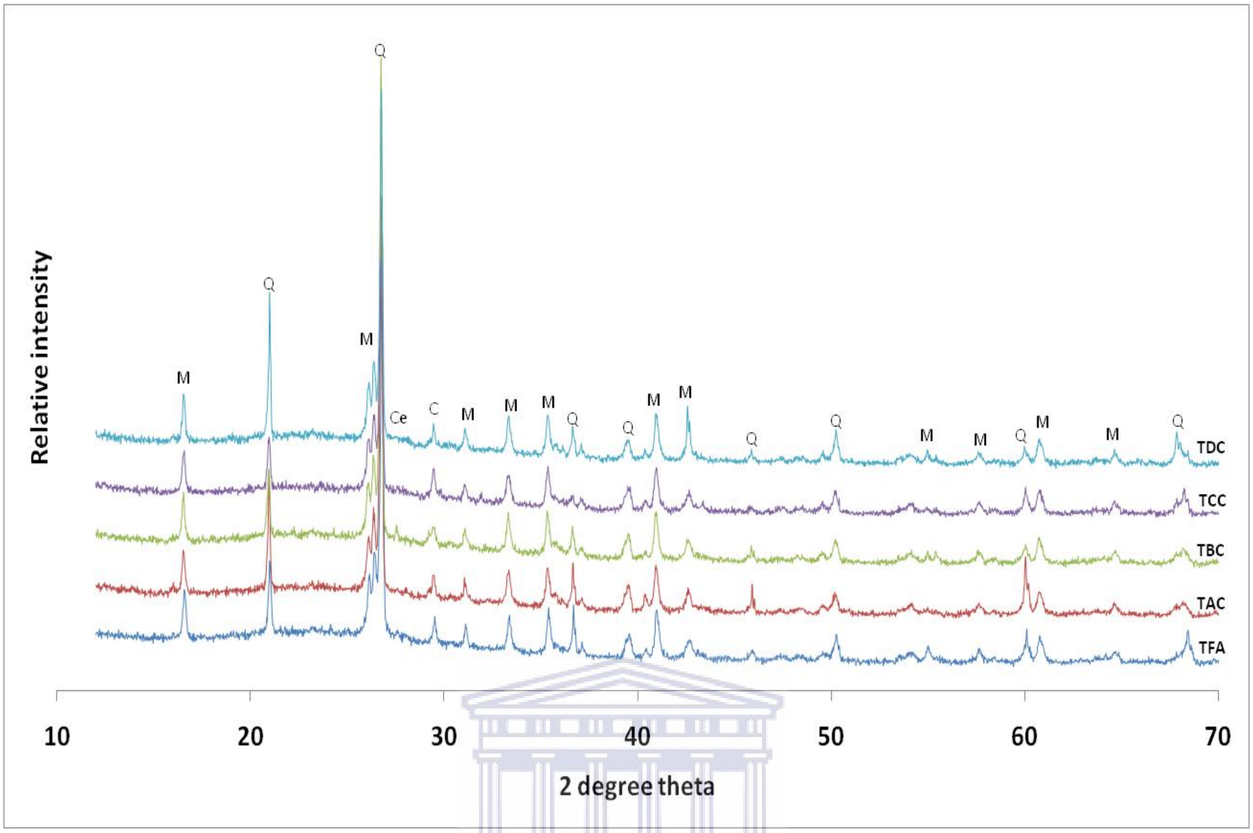

Figure 5.10: X-ray diffractograms for TFA- Tutuka fresh ash; TAC - long-term Tutuka ash-brine interactions for 1 week; TBC – long-term Tutuka ash-brine interactions for 1 month; TCC – long-term Tutuka ash-brine interactions for 6 months; TDC – long-term Tutuka ash-brine interactions for 12 months. Peaks labelled are: M (mullite), Q (quartz), C (calcite), Ce (celestine).

The mineralogical composition of the fresh fly ashes and the solid residues from the fly ash-brine interactions experiments was determined using XRD (Figures 5.9 and 5.10). Peaks assigned to quartz (SiO_2), mullite ($Al_6Si_2O_{13}$) and calcite ($CaCO_3$) were easily identified in the diffraction patterns of Secunda and Tutuka fresh fly ash and the fly ash-brine interactions residues. Some poorly-defined peaks were identified as wairakite [$CaAl_2Si_4O_{12}.2(H_2O)$], charlesite [$Ca_6(Al,Si)_2(SO_4)_2B(OH)_4(OH,O)_{12}.26(H_2O)$] and spinel ($MgAl_2O_4$) in Secunda fly ash-brine interactions residues; and celestine ($SrSO_4$) was identified in the case of Tutuka fly ash-brine interactions residues. Quartz, mullite and calcite are the major mineral phases in fresh fly ash

[Figure 5.9 (SFA) and Figure 5.10 (TFA)] while phases such as wairakite, charlesite, spinel and celestine that were identified in the solid residues could be attributed to the interactions of the fly ash and brine. Comparison of the fresh fly ashes (SFA and TFA) with the fly ash-brine interactions residues at different contact times revealed that new mineral phases were being formed over time during the interactions despite the static condition of the fly ash-brine systems.

Generally, the results of the XRD showed the formation of new mineral phases in the solid residues due to the fly ash-brine interactions. This in turns showed that the removal of some of the species from the brine solution by the fly ashes was as a result of formation of new mineral phases in the fly ash-brine systems. Due to the high concentrations of species such as Na and Cl in the brine, the mineral phase(s) containing these species were expected to be identified by the XRD analysis in the solid residues after the fly ash-brine interactions, but were not identified. The non-identification of Na or Cl-rich mineral phases did not indicate the non-existence of these species in the solid residues but rather showed the limitation of the XRD analysis. The non-identification of some mineral phases could be as a result of their presence in amorphous forms in the solid residues which may not be detectable by the XRD or as a result of the low quantity in the solid residues. Further analysis of the solid residues using SEM-EDS was carried out which was expected to give more insight into the presence of some elements associated with some specific mineral phases in the solid residues. The results of the SEM-EDS analysis are presented and discussed in the next section (5.3.1.4**).**

5.3.1.4 Morphological and elemental compositions of the residues from the long-term fly ash-brine interactions experiments: SEM-EDS analysis

The SEM-EDS analysis was carried out on the solid residues from long-term fly ash-brine interactions experiments in order to observed the morphological changes and qualitatively identify some elements that are present in the solid residues which could be associated with some mineral phases that were not identified by XRD in the solid residues. The SEM-EDS analysis is expected to give more insight into the elements contained in the solid residues of the long-term fly ash-brine interactions experiments.

SEM is one of the most widely used characterization techniques to determine the morphology and physical appearance of fly ash (Vassilev and Vassileva, 2005). The morphology of fresh fly ash particles is controlled by the combustion temperature and the cooling rate of the particles. The use of the EDS detector incorporated in the SEM is capable of detecting elements with atomic number equal to or greater than six. The intensity of the peaks in the EDS is not a quantitative measure of elemental concentration, although relative amounts can be inferred from relative peak heights (Kutchko & Kim, 2006). Two spots were analyzed on each of the SEM micrographs by EDS. The EDS analysis was used for a qualitative determination of different elements to establish whether some morphologies were associated with specific elemental composition.

The SEM micrographs of the fresh fly ashes and the solid residues from the long-term fly ash-brine interactions experiments are shown in Figures 5.11 and 5.12 while the elemental composition of the EDS analyzed spots (weight %) are shown in Tables 5.3 and 5.4.

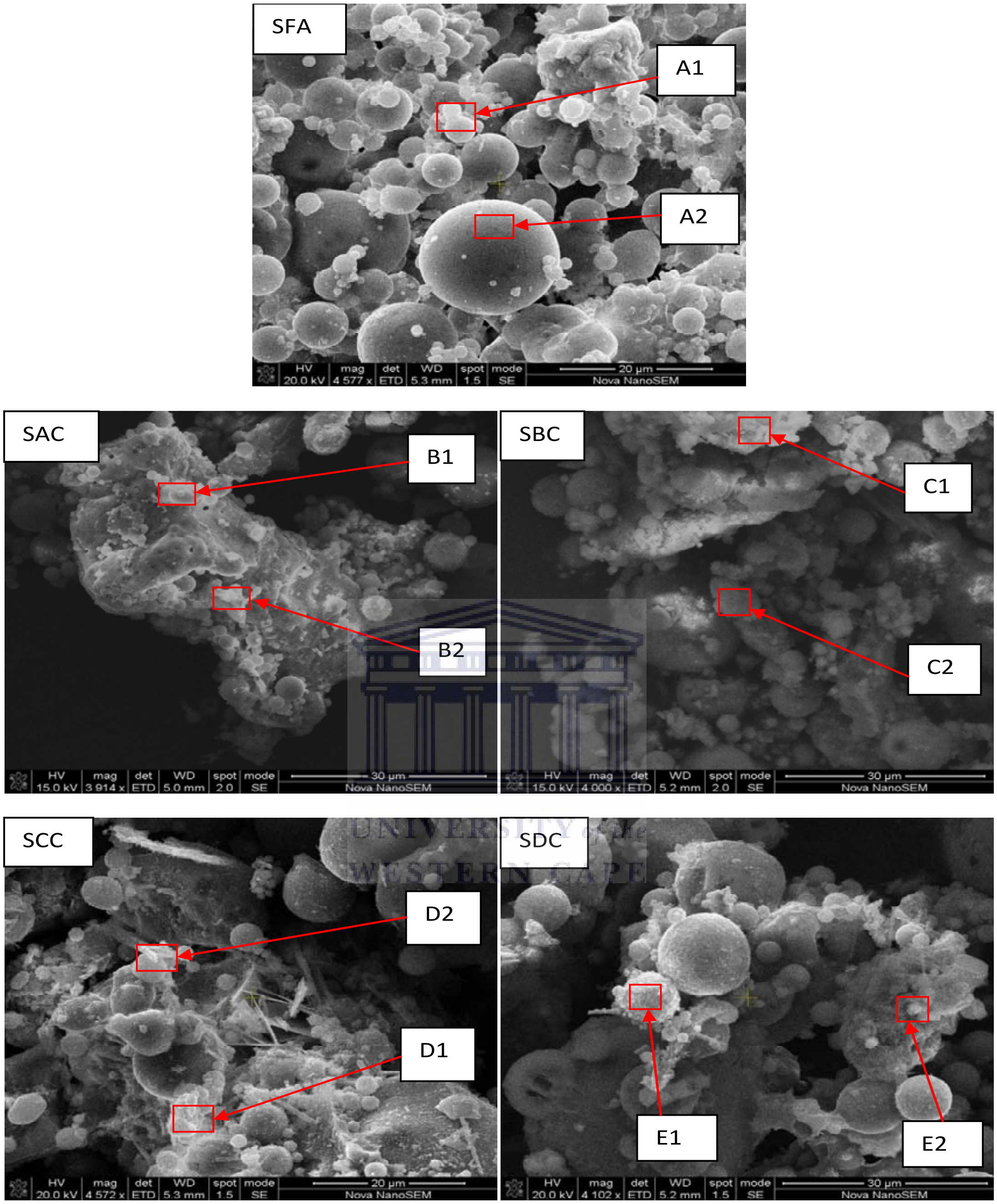

Figure 5.11: SEM-EDS micrograph of Secunda fresh fly ash and fly ash-brine long-term interaction residues showing the spots for EDS analysis; SFA - Secunda fresh ash; SAC - long-term Secunda ash-brine interactions for 1 week; SBC – long-term Secunda ash-brine interactions for 1 month; SCC – long-term Secunda ash-brine interactions for 6 months; SDC – long-term Secunda ash-brine interactions for 12 months.

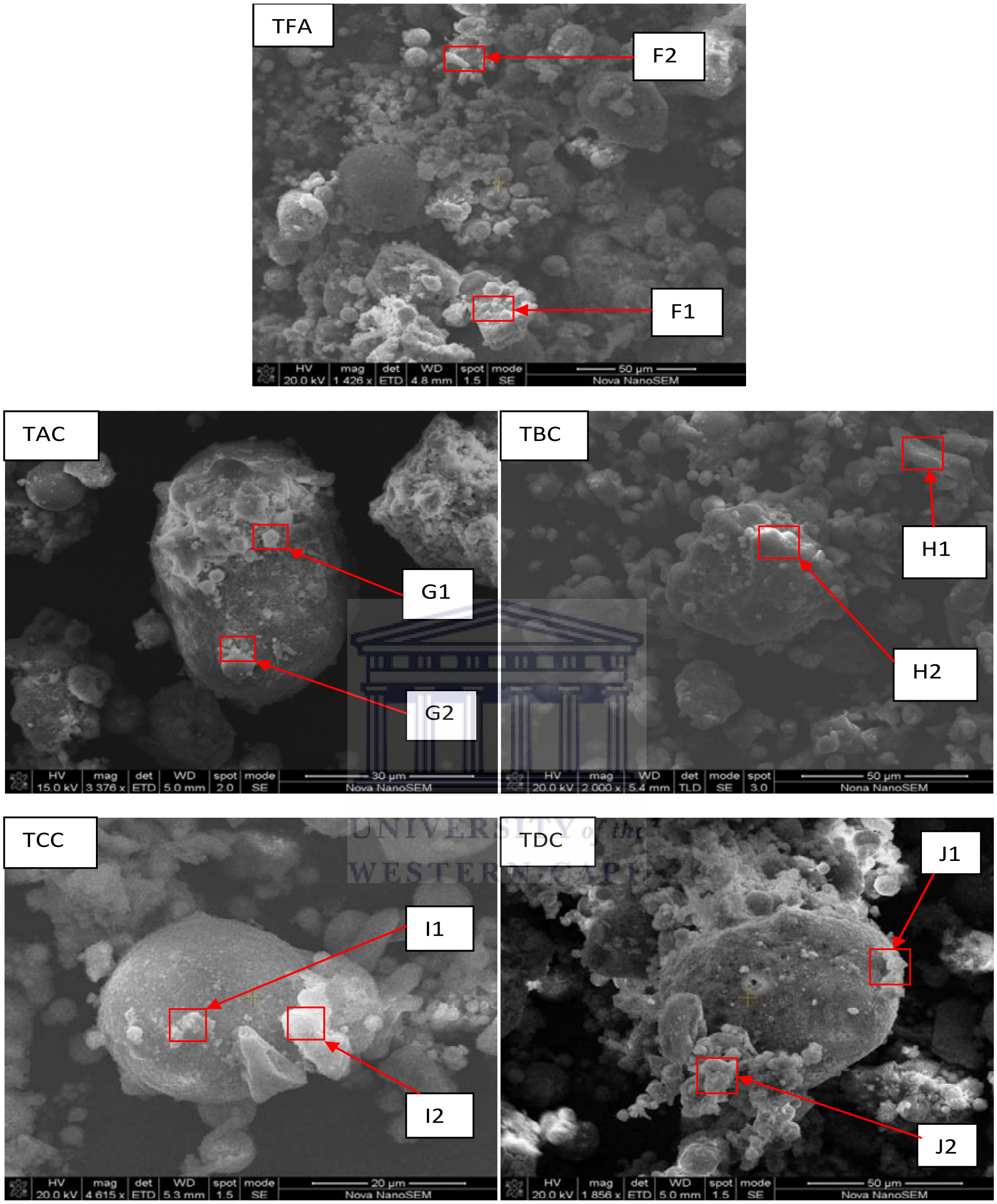

Figure 5.12: SEM-EDS micrograph of Tutuka fresh fly ash and fly ash-brine long-term interaction residues showing the spots for EDS analysis; TFA- Tutuka fresh ash; TAC - long-term Tutuka ash-brine interactions for 1 week; TBC – long-term Tutuka ash-brine interactions for 1 month; TCC – long-term Tutuka ash-brine interactions for 6 months; TDC – long-term Tutuka ash-brine interactions for 12 months.

Table 5.3: SEM-EDS spot analysis (weight %) of Secunda fresh fly ash and fly ash-brine long-term interaction residues

	SFA		SAC		SBC		SCC		SDC	
Element	A1	A2	B1	B2	C1	C2	D1	D2	E1	E2
O	52.61	55.15	58.33	59.36	55.84	49.61	57.83	57.31	52.31	54.27
Na	0.77	0	0.83	0.63	0.74	0.81	0.65	0.57	0.61	0.76
Mg	0.46	0.69	0.78	0.66	0.45	0.64	1.11	0.77	0.53	0.84
Al	14.75	12.56	7.3	6.67	15.65	5.93	11.19	15.13	17	13.28
Si	25.92	23.73	9.35	7.71	19.43	32.21	21.54	19.95	22.67	21.72
S	0	0	2.85	3.26	0.4	0.77	0.67	0	0.83	0.5
K	0.74	0.74	0	0	0.72	0.64	0.46	0.54	0.47	0.76
Cl	0	0	0.54	0.57	0	0	0	0	0	0
Ca	3.08	5	18.65	20.21	4.92	6.61	5.61	3.24	3.95	5.07
Ti	0.77	1.03	0.87	0.43	0.97	2.04	0.5	1.51	0.71	0.82
Fe	0.89	1.11	0	0	0.88	0.74	0	0.98	0.92	1.18

SFA = Secunda fresh ash; SAC = long-term Secunda ash-brine interactions for 1 week; SBC = long-term Secunda ash-brine interactions for 1 month; SCC = long-term Secunda ash-brine interactions for 6 months; SDC = long-term Secunda ash-brine interactions for 12 months.

Table 5.4: SEM-EDS spot analysis (weight %) of Tutuka fresh fly ash and fly ash-brine long-term interaction residues

	TFA		TAC		TBC		TCC		TDC	
Element	F1	F2	G1	G2	H1	H2	I1	I2	J1	J2
O	55.25	55.55	50.89	55.79	51.94	50.09	55.33	51.87	51.14	52.09
Na	0	0	1.08	0	0.88	0.78	0.49	0	1.28	0.72
Mg	0	1.04	0.79	1	0.58	0.47	0	0.9	0.6	0.9
Al	15.96	15.89	14.76	11.14	15.9	14.89	18.17	15.48	12.25	8.17
Si	19.77	19.06	21.53	22.4	21.45	24.3	21.76	22.24	18.39	27.56
S	0.44	0.46	0.61	1.44	0.9	1.12	0.61	0.87	1.69	1.73
Cl	0	0	0	0	0	0.41	0	0	0	0
K	0.6	0.52	0.68	0.53	0.52	1.25	0.44	0.55	0.44	0.65
Ca	4.71	3.47	5.28	4.94	5.6	4.39	2.07	3.66	5.62	5.4
Ti	0.86		0.89	1.04	1.23	0.88	0.66	0.99	1.13	0.5
Fe	1.89	4.02	3.48	1.73	0.99	1.4	0.46	3.43	7.46	2.27

TFA = Tutuka fresh ash; TAC = long-term Tutuka ash-brine interactions for 1 week; TBC = long-term Tutuka ash-brine interactions for 1 month; TCC = long-term Tutuka ash-brine interactions for 6 months; TDC = long-term Tutuka ash-brine interactions for 12 months.

The surfaces of most of the particles of Secunda fresh fly ash were smooth and spherical in shape [Figure 5.11 (SFA)] while some agglomerated and irregular shaped particles characterized the morphology of particles of Tutuka fresh fly ash [Figure 5.12 (TFA)]. The interactions of the fresh fly ashes with the brine solution at different periods of time were observed to have had an effect on the surfaces of the fly ash particles. The observed roughened surfaces of the ash particles after the long-term interactions [Figure 5.11 (SAC, SBC, SCC and SDC)] and [Figure 5.12 (TAC, TBC, TCC and TDC)] could be attributed to the dissolution of the soluble phases on the surface of the fly ash particles upon contact with brine over time. Apart from the rough surface of the fly ash particles, agglomeration of particles and irregularly shaped amorphous particles were observed. This observation could be as a result of inter-particle cementing (Kutchko & Kim, 2006) during the interactions experiments.

As determined by the EDS, the predominant major elements in the fresh Secunda were Al, Si, Ca and O while minor amounts of the elements such as Mg, K, Na, Fe and Ti were determined (Tables 5.3). The analyzed spots (A1 and A2) in Secunda fresh fly ash (SFA) revealed the aluminosilicate composition of the fresh ash and the absence of species such as S and Cl. The absence of S and Cl at the analyzed spots did not indicate that these species were not present in the fly ash but may have been present in small amounts.

In SAC (residue at 1 week), spots B1 and B2 analyzed showed irregularly shaped crystalline materials on top of the aggregated particles (Table 5.3). The high concentrations of Ca and S at these spots coupled with the decrease in the Al and Si concentration suggests the precipitation of Ca-S rich phases. Compared to the analyzed spots on Secunda fresh fly ash (A1 and A2), Cl was associated with higher concentration of Na indicating the presence of Na-Cl salt. The presence of Cl and increased Na concentration in the analyzed spots of the residue could indicate the formation of halite as a result of interactions of the fly ash with brine.

Analysis of spots C1 and C2 on SBC (residue at 1 month) showed high concentrations of Al and Si (Table 5.3). The analyzed spots also showed lower concentration of Ca, Na, S, Mg, Ti and Fe. The high concentration of Al and Si suggests the formation of amorphous alumino-silicate phase during the interactions experiments. The presence of lower concentrations of Ca, Mg, S and Na when compared to the concentrations of Al and Si could indicate the formation of Ca-Mg-S rich or Na-rich phases embedded in the amorphous particles.

Analyzed spots D1 and D2 represent crystal-like and agglomerated particles (Figure 5.11) on the SCC residue. The analyzed spots showed the high concentration of A, Si and O. Lesser amounts of Ca and Mg were also present. The trend observed in the analyzed spots for SDC (E1 and E2) was similar to the analyzed spots for SCC. Spots E1 and E2 contained high concentrations of Al, Si and O. The elements present in the analyzed spots in the two residues (SCC and SDC) suggest alumino-silicate phases mixed with Ca-Mg rich or Ca-S-rich phases. The presence of Na also suggests that the analyzed spots contain Na salts, which could be as a result of the interactions of the fly ash with brine.

The EDS analysis on the fresh fly ash from Tutuka (TFA) showed that the predominant elements were Al, Si, Ca and O. The concentrations of Mg, S, K, Ti and Fe were lower in the analyzed spots F1 and F2 (Table 5.4). Na and Cl were missing in the analyzed spots which did not indicate their non-existence in the fly ash but that these elements were not contained in the analyzed spots. Actually, significant amounts of Na and Cl were expected in the fresh fly ash from Tutuka due to conditioning resulting in its contact with brine solution before being sampled (section 3.2). This discrepancy gives an insight into the limitation of EDS. The elements at any analyzed spot may not represent the total elements present in the fly ash.

Analysis of spots G1 and G2 (TAC) showed that the small spherical phases on the surface of the agglomerated particles contained Al, Si and O, which suggested the presence of amorphous alumino-silicate phases (Figure 5.12). Apart from the Al, Si and O, elements such as K, Na, Fe, Mg, Ca and S were present in spots G1 and G2. The presence of these elements also suggested that Ca-S or Ca-Mg-rich phases could be present in the analyzed spots. The presence of Na (G1) and an increased concentration of S (G1 and G2), compared with the TFA (F1 and F2), could be attributed to the effect of the fly ash-brine interactions. The interactions of fly ash with the brine solution could result in the precipitation of Na salt due to super-saturation.

The EDS analysis of spots H1 and H2 on TBC showed amorphous irregular shaped material which predominantly contained Al, Si and O. An increase in the concentrations of Ca and S at spots H1 and H2, compared to the analyzed spots on TFA, suggested the precipitation of Ca-S-rich phases during the interaction experiments. Na and Cl were observed in the analyzed spots which could indicate the presence of Na-Cl-rich salts as a result of the interactions of the fly ash with brine.

Spots I1 and I2 on TCC (Table 5.4) represented mineral aggregates which showed the presence of elements such as Al, Si and O in higher quantities with a lower amounts of Ca, K, Fe, S, Na and Mg. The abundance of Al, Si and O suggested the presence of Al-Si or Si-O rich minerals such as quartz.

Analyzed spots J1 and J2 on TDC showed the presence of Al, Si and O in significant quantities which could suggest the alumino-silicate phase. Ca and S concentrations were also observed but in lower concentrations. These spots show high Fe concentration which suggested the formation of an iron-rich phase. Significant Ca, Mg and Si concentrations in the analyzed spots (J1 and J2) indicated the possible formation of Ca-Mg-Si rich glassy phases (Table 5.4).

The EDS data were consistent with the XRD data. The EDS analysis (Tables 5.3 and 5.4) verified the presence of all the elements contained in the mineral phases identified by XRD. The EDS analysis revealed the enrichment of Al, Si and O in the residues which suggested the presence of aluminosilicate phases while the presence of Ca and S in the solid residues could indicate the precipitation of hydrated or anhydrous calcium suphate phases. Significant quantities of Na and Cl that were identified in the solid residues by EDS could suggest the presence of mineral phases such as halite. The EDS analysis revealed the possibility of having some mineral phases in the solid residues that could not be identified by the XRD either because of their non-crystalline forms or as a result of their low quantities in the residues. The EDS analysis showed that some species such as Na and Cl were significantly present in the solid residues but seemed to be absent in the fresh fly ashes. The significant presence of these species in the solid residues could be attributed to the interactions between the fly ashes and the brine solution.

5.3.1.5 Summary

The analysis of the brine solution and the excess brine decanted from the solid residues after the long-term fly ash-brine interactions experiments showed that some species in the brine solution were captured in the fly ashes during the static and closed conditions of the systems. Minor species such as Cr, Mo and As were observed to increase in the excess brine decanted from the solid residues when compared with their concentrations in the unreacted brine. This implies that while some species were captured by the fly ashes, some species were also leached from the fly ashes into the brine solution. On the other hand, the characterization of the solid residues recovered from the long-term fly ash-brine interaction experiments gave an insight into the interactions of fly ash and brine causing possible capture of brine components by the fly ashes. The results of the total elemental composition (as determined by the XRF analysis) of the fresh fly ashes and the solid residues from the fly ash-brine interactions experiments showed that the concentrations of some species such as Na, Cl, SO_4, Co, Cu, Pb and Zn in the solid residues increased after the interactions experiments. This showed that the fly ashes could remove these species from the brine solution under static conditions where a fixed volume of brine was co-disposed with ash in a 1:1 ratio, which may be due to either adsorption or precipitation mechanism. Although further work needs to be carried out to determine other processes (out of the scope of this study) responsible for the removal of species from the brine solution, previous studies (Fatoba, 2008) on the interactions of fly ash and water, and the batch reaction tests in the previous chapter of this study (Chapter 4) predicted the precipitation of mineral phases as a factor responsible for the removal of species from the fly ash-water systems and fly ash-brine systems respectively. The effect of the interaction periods was shown on the removal of Na, Cl and SO_4 which are the major constituents of brine as an increase was observed in the % removal of these species from the brine solution with increased interaction periods. This shows that if fixed volumes of fly ash and brine are mixed together and left undisturbed for a longer period of time, the amounts of Na, Cl and SO_4 that will be captured will continuously increase over one year.

The XRD data showed that a very small amount of new mineral phases were formed as a result of the fly ash-brine interactions. Apart from the small amount of the new mineral phases identified by the XRD in the solid residues, the possibility of other newly formed phases that were not identified cannot be ruled out. Despite the high concentrations of Na and Cl in the solid residues, which indicates their removal from the brine solution by the fly ashes, the formation of phases containing Na and Cl were not detected by the XRD. Similar case was observed in the batch reaction tests (chapter 4) where the concentrations of Na and Cl in the solid residues increased significantly indicating that these species were captured by the fly ashes, but the geochemical modelling predicted halite to be under-saturated. The limitations of XRD at detecting amorphous phases or phases present in small amounts in fly ash could be responsible for not detecting other possible phases formed during the long-term interactions. Nevertheless, the XRD analysis showed that the formation of secondary mineral phases during the interactions of the species in the fly ashes and brine solution could be responsible for the removal of some of the species from the brine solution.

The morphology of the solid residues as analyzed by SEM-EDS revealed the effect of the dissolution of the soluble phases on the surfaces of the fly ash particles. Some amorphous phases and mineral aggregates which may not be detected by the XRD were shown in the SEM micrograph and EDS analysis. The abundance of species such as Na, Cl and S in the spots analyzed on the solid residues' micrographs showed that these species were removed from the brine solution by the fly ashes.

In conclusion, on this section, the results of the analyses carried out on the excess brine and the solid residues showed that the interaction of fly ash and brine solution under static and closed conditions could remove significant amounts of major species from the brine solution. The major concern is the leaching of contaminants such as Cr and Mo from the fly ashes into the brine solution during the interaction. Although the concentration of these contaminants leached into the brine solution, especially Cr (Tables 5.1 and 5.2), was gradually reduced with an increase in the interaction period, and this is an indication that these species, although leached at the beginning of the interaction, may be removed from the systems over time.

Having observed the removal of species from the brine solution by the fly ashes, the need arose to determine the stability and mobility of the species removed from the brine solution by the fly ashes. This necessitated the application of acid neutralization capacity (ANC) tests on the solid residues recovered from the long-term fly ash-brine interaction experiments. The results of the ANC tests are expected to give an insight into the mobility of the species removed from the brine solution by the fly ashes when in contact with solutions of different pH. The detailed results of the acid neutralization capacity (ANC) tests will be discussed in the next section (5.3.2).

5.3.2 Long-term ash-brine interactions: Effect of leachant pH on the retention and removal of species from the fly ash-brine interactions residues

This section (5.3.2) presents and discusses the results of the ANC tests carried out on the fly ash-brine interactions solid residues. The results of the ICP-MS and IC analysis carried out on the excess brine decanted (section 5.3.1.1) and the XRF analysis (section 5.3.1.2) carried out to determine the chemical composition of the solid residues recovered after the long-term fly ash-brine interactions experiments showed that some species in the brine solution were captured by the fly ashes under the applied conditions. The need to determine the mobility of species captured in the solid residues when in contact with solutions of different pH values necessitated the ANC tests. The detailed descriptions of the ANC tests were given in sections 3.3.4.

5.3.2.1 The acid consumption capacity of the solid residues

The pH profiles showing the acid neutralization capacity of the solid residues from the long-term fly ash-brine interactions experiments are shown in Figure 5.13.

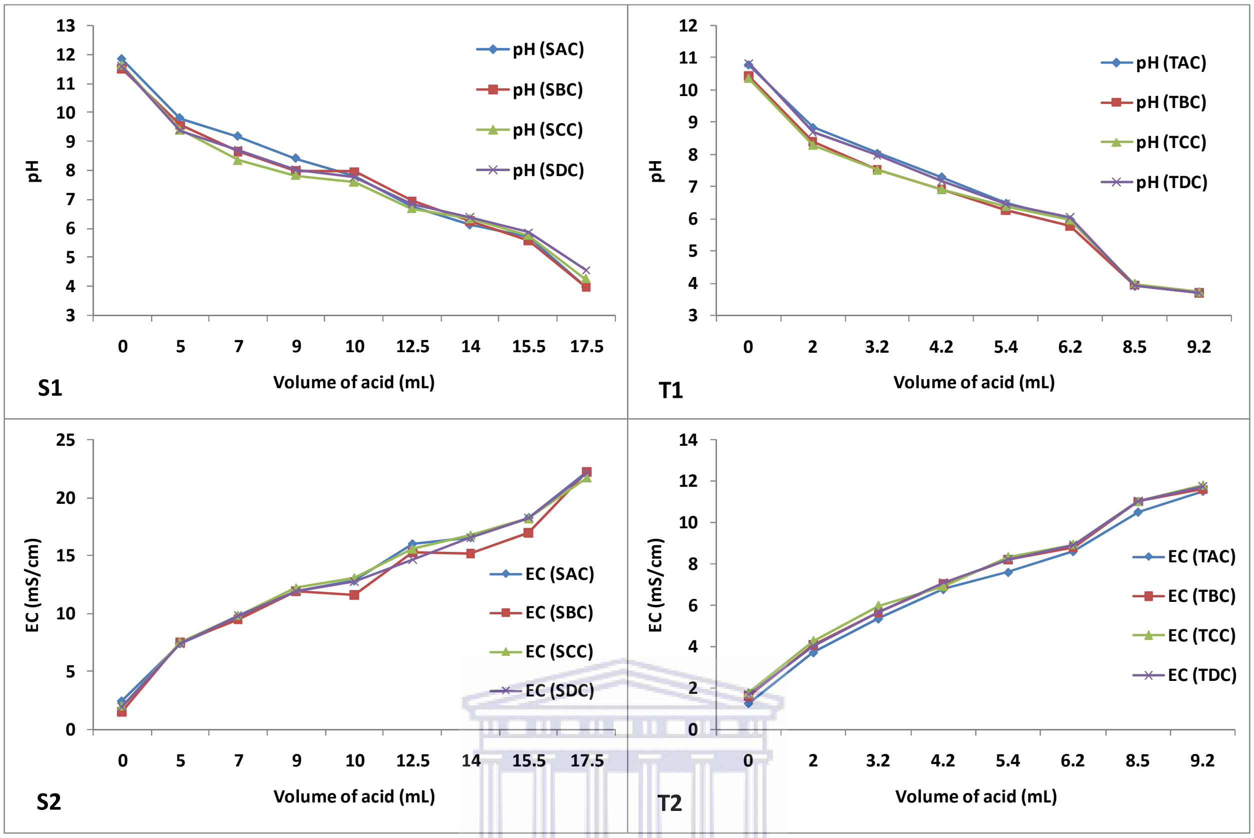

Figure 5.13: pH and EC profiles of Secunda (S1 and S2) and Tutuka (T1 and T2) long-term fly ash-brine interaction residues as a function of volume of acid added.

The acid neutralization capacity tests (ANC) were carried out by adding pre-determined quantities of acid (2M HNO_3) to the residues for a period of 48 h to achieve the desired pH values (prEN 14429) (experimental details in section 3.3.4). When in contact with ultrapure water (no acid added), the pH of the solid residues irrespective of the period of interactions was found to be greater than 11 in the case of Secunda while the pH of Tutuka solid residues were between 10 and 11 (Figure 5.13). The pH of both Secunda (SAC, SBC, SCC and SDC) and Tutuka (TAC, TBC, TCC and TDC) fly ash-brine interaction solid residues decreased with an increase in the volume of acid in the leachants. Comparing the pH trends of the solid residues, it was observed that the pH profiles of the solid residues at 1 week (SAC and TAC) were slightly higher than the pH profiles of solid residues recovered at 1 month, 6 months and 12 months. This implies that the acid neutralization capacity of the solid residues at 1 week is higher than that of the solid residues at 1 month, 6 months and 12 months. Being a closed and static system, the 1

week period may not be enough for the complete and rapid dissolution of the alkalinity-contributing oxides in the fly ashes during the long-term fly ash-brine interactions, thereby leaving some oxides such as CaO in the solid residues. Longer interactions periods (1-12 months) could cause the dissolution of more alkalinity-contributing oxides from the fly ashes during the long-term interaction experiments, and could also stabilize the new mineral phases formed in the residues. This dissolution of more CaO or MgO at longer interactions period could account for the slightly lower pH of the solid residues SBC, SCC, SDC, TBC, TCC and TDC.
It was observed that the volume of acid required to achieve the final pH 4 in Secunda solid residues (SAC, SBC, SCC and SDC) was higher, and almost double the volume of acid required for Tutuka residues (TAC, TBC, TCC and TDC) to achieve the same pH. This implies that the neutralization capacity of Secunda solid residues is higher than that of Tutuka solid residues. This phenomenon could be attributed to the higher percentages of CaO and MgO as recorded in Secunda fly ash (Tables 4.2). These oxides are the major alkalinity contributors in fly ash, and the concentrations of these basic oxides in the fly ash determine the pH of the fly ash when in contact with aqueous solution.

The increase in the EC values as shown in Figure 5.13 (S2 and T2) correlated directly with the increase in the volumes of acid added. This showed the effect of the pH of the leachants on the dissolution of components in the solid residues. The consistent increase in the EC with increase in volumes of acid added suggested that apart from the dissolution of the easily soluble phases in the solid residues, phases insoluble at high pH were dissolved thereby increasing the concentrations of species in solution. Dijkstra *et al.* (2002) suggested that increased protonation at low pH causes a lower affinity of the species on the surfaces of the ash particles. The low affinity at low pH could result in an increase in the concentrations of species in solution which will directly lead to increase in the EC of the systems.

5.3.2.2 The influence of pH on the release of major and minor species

The release of major and minor species from the solid residues when in contact with solutions of different pH will be discussed in this part of the study. This aspect of the study is aimed at determining the mobility of the species such as Na, Cl, SO_4, Cu and Pb that were captured in the solid residues when in contact with ultrapure water and solutions of different pH. The ANC test is expected to give an insight into whether the species captured in the fly ashes will be released immediately the solid residues contact ultrapure water or whether they can only be released when in contact with solutions of lower pH. Although some species such as Al, Si, Ca, Ba, Mo and Cr that were observed to leach out of the fly ashes into the brine solution during the long-term interactions experiments were presented, the aim of presenting these species was to determine the possibility of their continuous mobility when in contact with ultrapure water or solution of lower pH.

5.3.2.2.1 Aluminum and Silicon

Figure 5.14 presents the leaching of Al and Si from the solid residues recovered from Secunda and Tutuka fly ash-brine interaction experiments.

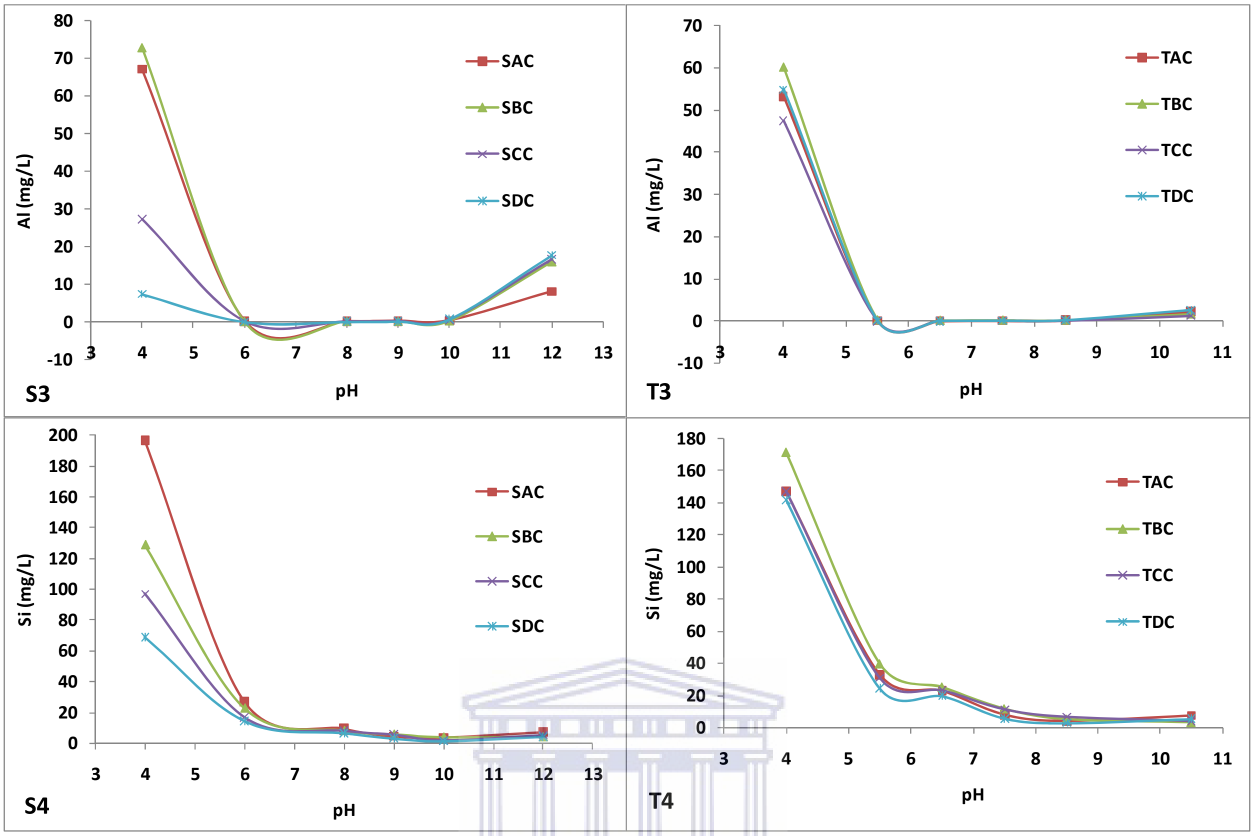

Figure 5.14: Al and Si concentrations of Secunda (S3-S4) and Tutuka (T3-T4) long-term fly ash-brine interaction residues as a function of pH.

The results of the chemical composition of the excess brine decanted from the long-term fly ash-brine interaction systems and the solid residues recovered from the interaction experiments showed that Al was leached out of the fly ashes into the brine solution even at the high pH of the systems (section 5.3.1). The concentration of Al released from Secunda solid residues (S3) into solution during the ANC tests however, was slight at the natural pH (≈12) after which the concentration of Al in the solution was reduced to the minimum between pH 6 and 10. The concentration of Al released from Tutuka solid residues (T3) was very low at the natural pH of the systems and this low concentration continued until pH ≈5.5 (Figure 5.14). The concentration of Al thereafter increased rapidly in the solutions of both Secunda and Tutuka solid residues at pH below 6. The low concentration of Al observed at the natural pH of the solid residues up to the pH between 5 and 6 showed that low concentration of Al is available for leaching after the initial leaching during the long-term interactions experiments. The increase observed at pH below 6 indicates that Al could only be released from the solid residues under extreme conditions (low pH), which might not be possible in the real disposal scenario. The rapid and continuous increase observed at pH >6 could be as a result of the dissolution of the aluminosilicate phases in the solid residues (Gitari *et al.,* 2009). The slow release of Al in the ANC systems is governed by the precipitation of amorphous phases at high pH, and the dissolution of amorphous and the crystalline phases at lower pH. Studies (Fruchter *et al.* 1990; Garavaglia and Caramuscio, 1994; Roy and Griffin, 1984; Dijkstra *et al.,* 2006, Meima and Comans, 1997) have shown that at pH below the natural pH of fly ash (ranging between 6 and 8), the release of Al is controlled by the precipitation of Al (hydr)oxides such as $Al(OH)_3$ from solution. The lower concentration of Al at pH between 6 and 10 could be attributed to the precipitation of amorphous Al-bearing phases in the systems. This indicates that the mobility of Al contained in the solid residues is low unless the pH should change significantly.

Similar to what was observed in the behavior of Al in the solid residues, the results of the chemical composition of the excess brine decanted from the long-term fly ash-brine interaction systems and the solid residues recovered from the interaction experiments showed that Si was leached out of the fly ashes into the brine solution (section 5.3.1). The release of Si from the solid residues followed the same trend with that of Al. The concentration of Si in the solutions of both Secunda and Tutuka solid residues was very low at higher pH (9-12) [Figure 5.14 (S4 and T4)] indicating that low concentration of Si is available for leaching in the solid residues after the initial leaching observed during the long-term interactions experiments. After pH below 8, the concentration of Si in the solutions of both Secunda and Tutuka solid residues increased significantly. Si is mainly contained in the silicate phases of fly ash. The increase observed at pH lower than 8 could be as a result of the dissolution of the silicate phases such as quartz (SiO_2) (Tiruta-Barna *et al.,* 2006) in the solid residues.

The effect of the longer interactions period was evident on the release of Al and Si, as the solid residues recovered after 12 months (SDC and TDC) had the lowest concentrations of Al and Si in the ANC leachates. This implies that longer period of interactions could reduce the dissolution of Al and Si-bearing phases in the solid residues.

5.3.2.2.2 Calcium and Strontium

The release of Ca and Sr from the residues of Secunda and Tutuka fly ash-brine interactions experiments is shown in Figure 5.15.

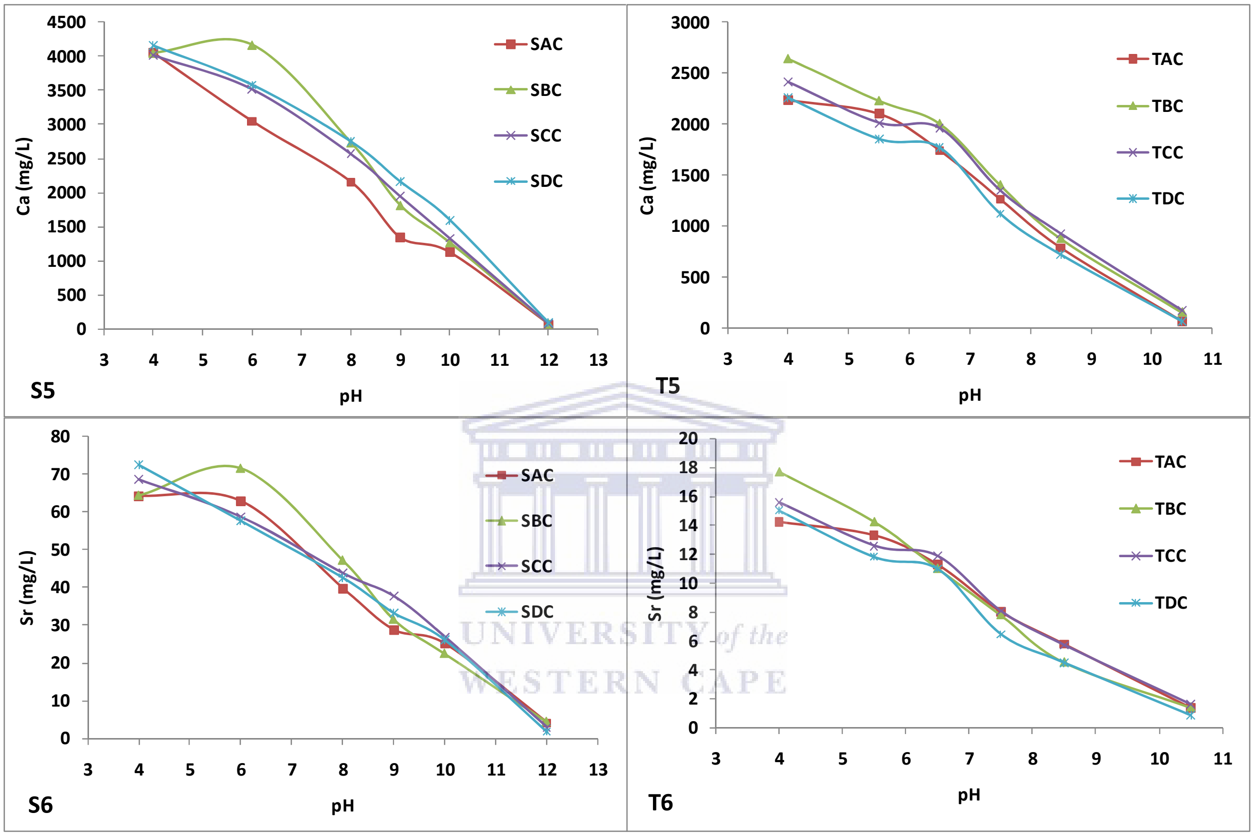

Figure 5.15: Ca and Sr concentrations of Secunda (S5-S6) and Tutuka (T5-T6) long-term fly ash-brine interaction reaction residues as a function of pH.

The results of the chemical composition of the excess brine decanted and the solid residues recovered from the long-term fly ash-brine interaction experiments showed slight difference in the concentration of Ca after the experiments [section 5.3.1 (Tables 5.1 and 5.2; Figures 5.3 and 5.6)]. This indicates that the Ca leached from the fly ash could have interacted with other species and formed new solid phases. The concentration of Ca in the leachates from the ANC tests of both Secunda and Tutuka solid residues was very low at the natural high pH of the solid residues [Figure 5.15 (S5 and T5)]. A steady increase in Ca concentration in leachates was observed with a decrease in the pH of the systems. The low concentration of Ca at the natural high pH of the ANC systems could be as a result of the significant concentration of Ca that was leached into the brine solution (Tables 5.1 and 5.2) during the long-term interactions experiments, which could have reduced the concentration of easily soluble Ca in the solid residues. The low concentrations of Ca at the natural high pH of the ANC systems could also indicate the stability of the Ca-rich mineral phases form in the residues during the interaction experiments. Apart from these, the high natural pH (>11) of the ANC systems at the beginning of the tests could favour the precipitation of Ca-rich phases thereby reducing the concentration of Ca in the solid residues solution at natural pH. However, a rapid and continuous increase in the concentrations of Ca was observed as the pH of the systems decreased. The continuous increase observed in the release of Ca as the pH decreased could be attributed to the dissolution of the Ca-rich mineral phases in the solid residues. The dissolution of gypsum has been observed to govern the solubility of Ca between pH 4 and 8 (Dijkstra *et al.,* 2006). Johnson *et al.* (1995) and Berner, (1992) observed non-stoichiometric release of Ca at high pH ranges after which a congruent dissolution of calcium silicate followed at lower pH. At low pH, there could be competitive replacement of Ca ions with the H^+ in solution thereby leading to the release of more Ca ions. The dissolution of mineral phases such as $CaCO_3$ which may have precipitated out during the long-term fly ash-brine interactions experiments could lead to an increase in Ca concentrations in the ANC leachates at low pH (Iwashita *et al.,* 2005). The ANC results showed that low amount of Ca in the solid residues were mobile when in contact with water (at high pH) only.

The trend of release of Sr in the solutions of Secunda and Tutuka solid residues was similar to that of Ca [Figure 5.15 (S6 and T6)]. Sr concentrations in the solutions of the solid residues in the ANC systems increased rapidly with decrease in pH after the lowest concentration was observed at the natural pH of the solid residues. The steady increase observed in the concentration of Sr at pH between 9 and 12 (possible pH in real disposal scenario) indicates that Sr could continuously leach from the residues despite the leaching observed during the long-term interactions experiments. The trend of the release of Sr indicates its dependence on the pH of the leachants added. The increase in the release of Sr at low pH could indicate that the low pH did not favour the formation of Sr-rich mineral phases but rather enhanced dissolution of Sr-containing phases.

5.3.2.2.3 Magnesium, Barium and Boron

Figure 5.16 presents the release of Mg, Ba and B from Secunda (SAC, SBC, SCC and SDC) and Tutuka (TAC, TBC, TCC and TDC) solid residues when in contact with leachants of different pH values.

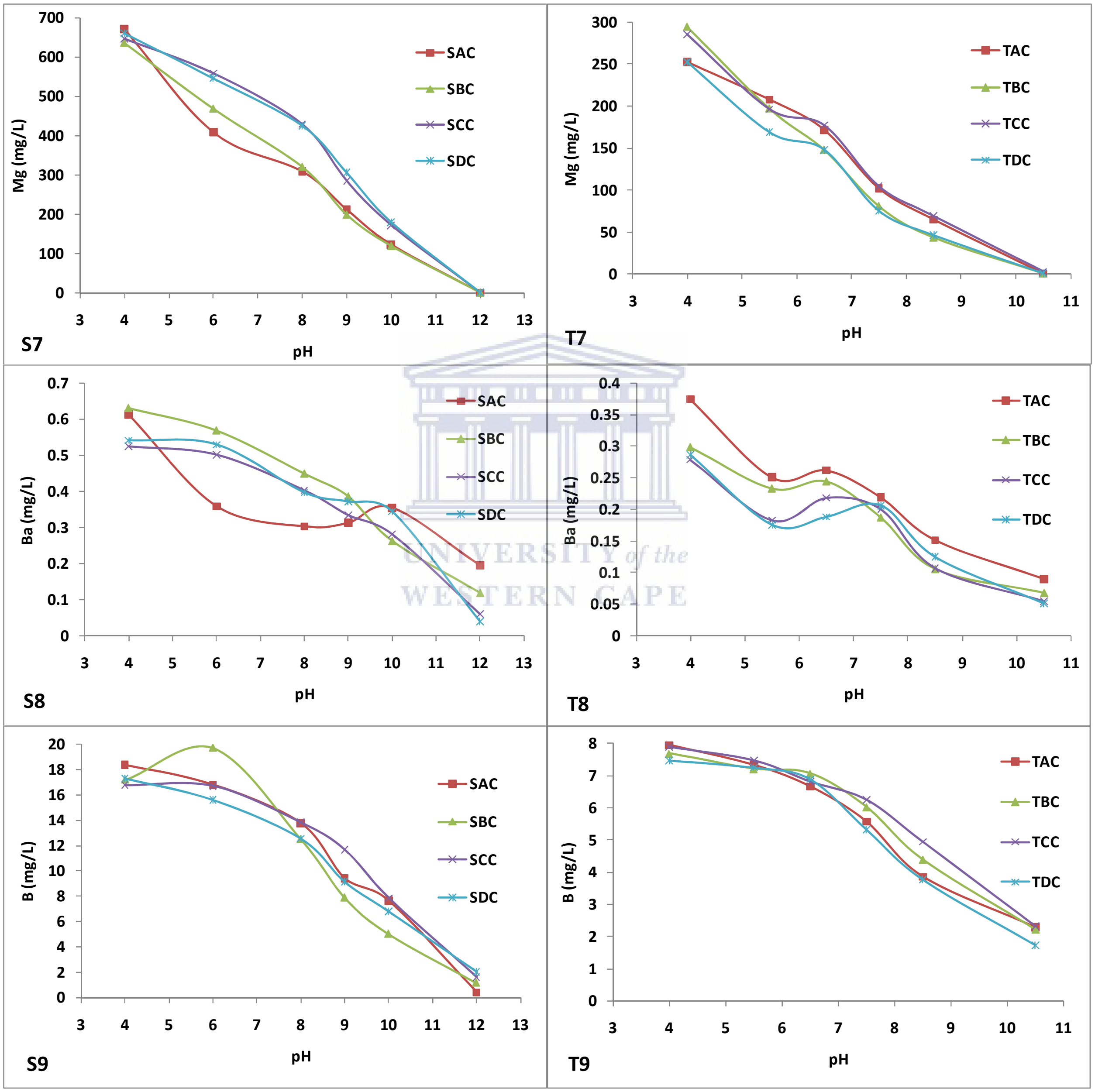

Figure 5.16: Mg, Ba and B concentrations of Secunda (S7-S9) and Tutuka (T7-T9) long-term fly ash-brine interaction reaction residues as a function of pH.

The results of the chemical composition of the excess brine decanted from the solid residues after the long-term fly ash-brine interaction experiments showed that Mg and B were significantly removed by the fly ashes at high pH of the long-term fly ash-brine interaction tests while the concentration of Ba after the initial leaching into the brine solution was observed to gradually reduce (Table 5.1 and 5.2). This indicates that these species were removed by the fly ash under static conditions over 12 months to possibly form new phases in the solid residues.

The concentration of Mg in the solutions of Secunda and Tutuka solid residues was very low at the natural high pH of the ANC tests whereafter a rapid increase in Mg concentration was observed with decrease in pH [Figure 5.16 (S7 and T7)]. The results of the long-term interactions experiments (Tables 5.1 and 5.2) showed that Mg was removed from the brine solution under the conditions applied, which could be attributed to the formation of new mineral phases such as $Mg(OH)_2$. The low concentration of Mg at the natural pH of the solid residues when in contact with ultrapure water at the start of the ANC tests could indicate that the probable Mg-rich mineral phases precipitated during the long-term interactions experiments are not mobile at high pH (when in contact with ultrapure water). At high pH, the solubility of Mg is controlled by the formation of either $Mg(OH)_2$ (Gitari *et al*., 2009; Dijkstra *et al.*, 2006; Meima and Comans, 1997) or by the more stable Mg layered double hydroxide (LDH) phase ($Mg_2Al(OH)_6(-CO_3)_{0.5}.H_2O$ (Johnson and Glasser, 2003). Mg was found to be a less readily soluble component of fly ash due to its incorporation mostly in the glass phases of the fly ash (Ugurlu, 2004). The continuous increase in the concentration of Mg in solution as the pH decreased upon acidification suggests the dissolution of Mg-rich phases and those incorporated in the glass phases in the solid residues.

The concentration of Ba released at the beginning (natural pH of the fly ash systems) of the ANC tests [Figure 5.16 (S8 and T8)] was slightly higher than what was observed in the case of Mg. The results of the long-term interactions experiments showed that Ba was leached from the fly ashes into the brine solution at the beginning of the tests but later reduced with an increase in the interactions periods (Tables 5.1 and 5.2). The release of Ba into solution at the beginning of the ANC tests could indicate the dissolution of the likely transient mineral phases formed in the solid residues or due to the continuous leaching of Ba despite the leaching observed during the long-term interactions experiments. A consistent increase in Ba concentration was observed as the pH decreased. A slight fluctuation occurred in the solution of Tutuka solid residues at pH range of 5–8. The possible formation of secondary Ba-rich mineral phases or co-precipitation of Ba in the ANC systems could account for the fluctuation in Ba concentration despite the steady decrease in the pH. Fruchter *et al.* (1988) suggested that the concentration of Ba in acidic to mildly alkaline fly ash leachates is likely to be controlled by $BaSO_4$. The concentrations of Ba released from each of the solid residues differ slightly as the concentration in the solid residues at 1 week (SAC and TAC) were found to have the highest concentrations of Ba at the beginning of the ANC tests. This showed the effect of contact time on the mobility of Ba in the solid residues.

The results of the excess brine decanted from the long-term interactions experiments (Tables 5.1 and 5.2) showed that B was removed from the brine solution, which could be due to its entrapment in new mineral phases such as ettringite that may have been formed in the long-term interactions systems. The concentration of B in the ANC leachates of Secunda solid residues was very low at the natural pH (≈12) while the B concentration in the ANC leachates of Tutuka residues was a bit higher [Figure 5.16 (S9 and T9)]. This shows the effect of final pH of the systems on the release of B from the solid residues. At high pH, B exists in aqueous solution as oxy-anion (Iwashita *et al.,* 2005; Jankowski *et al.,* 2006) such as borate. Studies (Lecuyer *et al.,* 1996; Iwashita *et al.,* 2005; Hassett, 1994; Solem-Tichmack *et al.,* 1995) have shown that the formation of ettringite [$Ca_6Al_2(SO_4)_3.26H_2O$] phase in highly alkaline solution could reduce the concentration of B. The ettringite formed could entrap the oxy-anion form of B by replacing its sulphate component with the oxy-anions. Co-precipitation of B with $CaCO_3$ was also suggested to contribute to the low concentration of B in alkaline solution (Hollis *et al.,* 1988). The initial low concentration of B in the leachate solution of Secunda at the start of the ANC tests could indicate non-dissolution of the B-containing/entraping phases when in contact with ultrapure water at high pH. The increase observed in the concentration of B as the pH decreased could be attributed to the dissolution of the B-containing phases. The rapid and continuous increase observed in the concentration of B in Tutuka solid residues as the pH decreased could be attributed to the dissolution of B from the matrix of the solid residues.

Although, the concentration of B released from each of the solid residues during the ANC tests was almost the same at each specific pH, the release of B from the solid residues generated at 12 months (SDC and TDC) was lower when compared to other solid residues. This observation revealed the effect of the contact time on the mobility of B in the solid residues when in contact with solutions of different pH values.

5.3.2.2.4 Sodium and Potassium

The release of Na and K from Secunda (SAC, SBC, SCC and SDC) and Tutuka (TAC, TBC, TCC and TDC) solid residues during the ANC tests are shown in Figure 5.17.

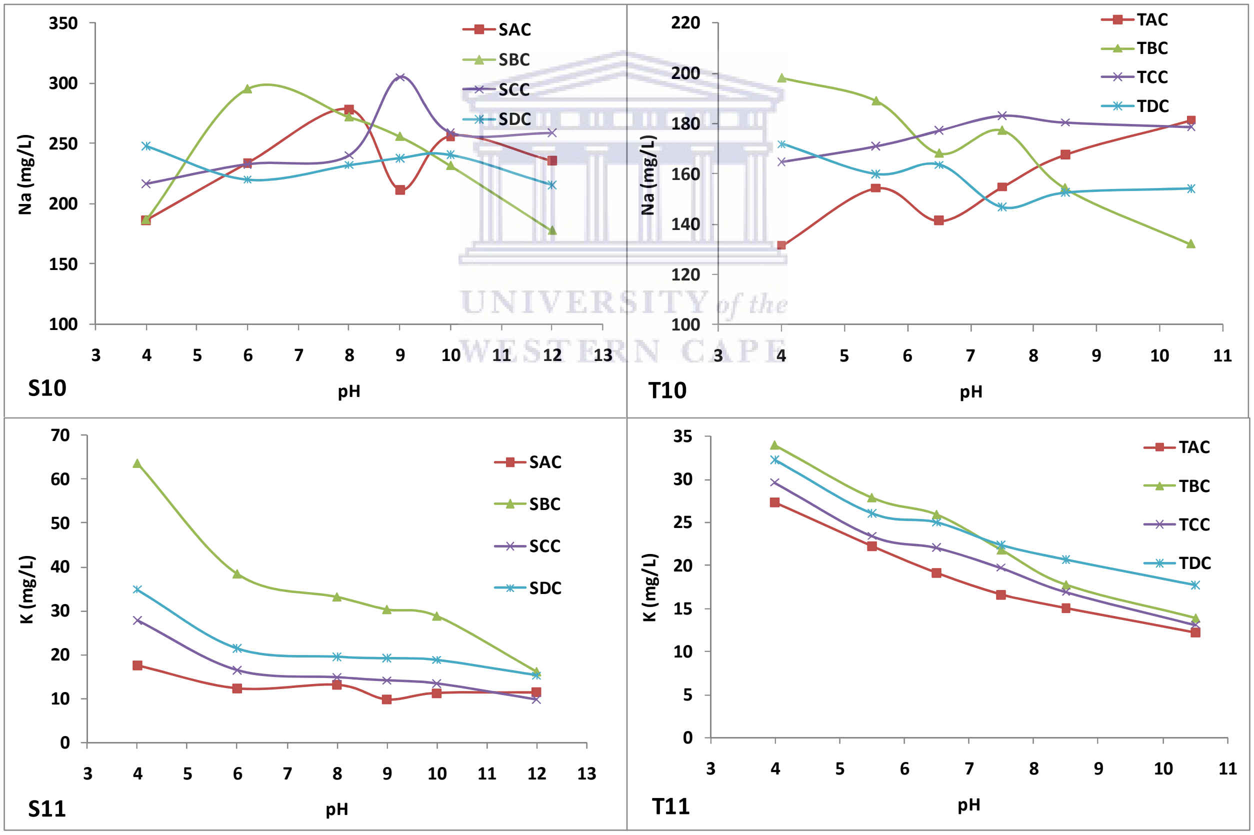

Figure 5.17: Na and K concentrations of Secunda (S10-S11) and Tutuka (T10-T11) long-term fly ash-brine interaction reaction residues as a function of pH.

The chemical composition of the excess brine decanted and the solid residues recovered from the long-term fly ash-brine interaction experiments showed that Na was significantly removed from the brine solution by the fly ashes under long-term static conditions at high pH (Tables 5.1 and 5.2; Figures 5.4 and 5.7). The release of Na into solution during the ANC tests carried out on both Secunda and Tutuka solid residues exhibits leaching behaviour that was independent of pH [Figure 5.17 (S10 and T10)]. The concentration of Na in leachates was high at the natural high pH of the ANC systems showing the solubility of Na in solid residues, and this high concentration was maintained irrespective of the pH of the systems. The trends of release of Na in the ANC systems suggest the rapid dissolution of the transient Na-rich soluble salts such as halite (NaCl) or Na_2SO_4 (Meima and Comans, 1997; Tiruta-Barna *et al.,* 2004) that may have formed in the solid residues during the long-term fly ash-brine interactions experiments. The release of significant amounts of Na at natural high pH of the ANC systems is an indication that the Na removed from the brine solution by the fly ashes during the long-term fly ash-brine interaction experiments is highly mobile immediately on contact with water.

The release of K was found to be slightly different to that of Na as a gradual increase was observed with decrease in the pH values upon acidification [Figure 5.17 (S11 and T11)]. The results of the brine decanted after the long-term interactions experiments showed that K was leached from the fly ashes into the brine solution (Tables 5.1 and 5.2). The increase observed in the concentration of K at the natural high pH of the solid residues during the ANC tests is an indication that more K could leach from the fly ashes despite the initial leaching observed during the long-term interactions experiments. This suggests that, apart from the soluble salts of K in the fly ashes, K could also be present in the matrix of the fly ash residues. The slow release of K observed in Secunda and Tutuka solid residues as the pH decreased could be attributed to the dissolution of less soluble phases in the solid residues. The concentration of K released from each of the solid residues (SAC, SBC, SCC, SDC and TAC, TBC, TCC, TDC) during the ANC tests at specific pH differed.

5.3.2.2.5 Chloride and Sulphate

The concentrations of Cl and SO_4 released from Secunda and Tutuka solid residues during the ANC tests are shown in Figure 5.18.

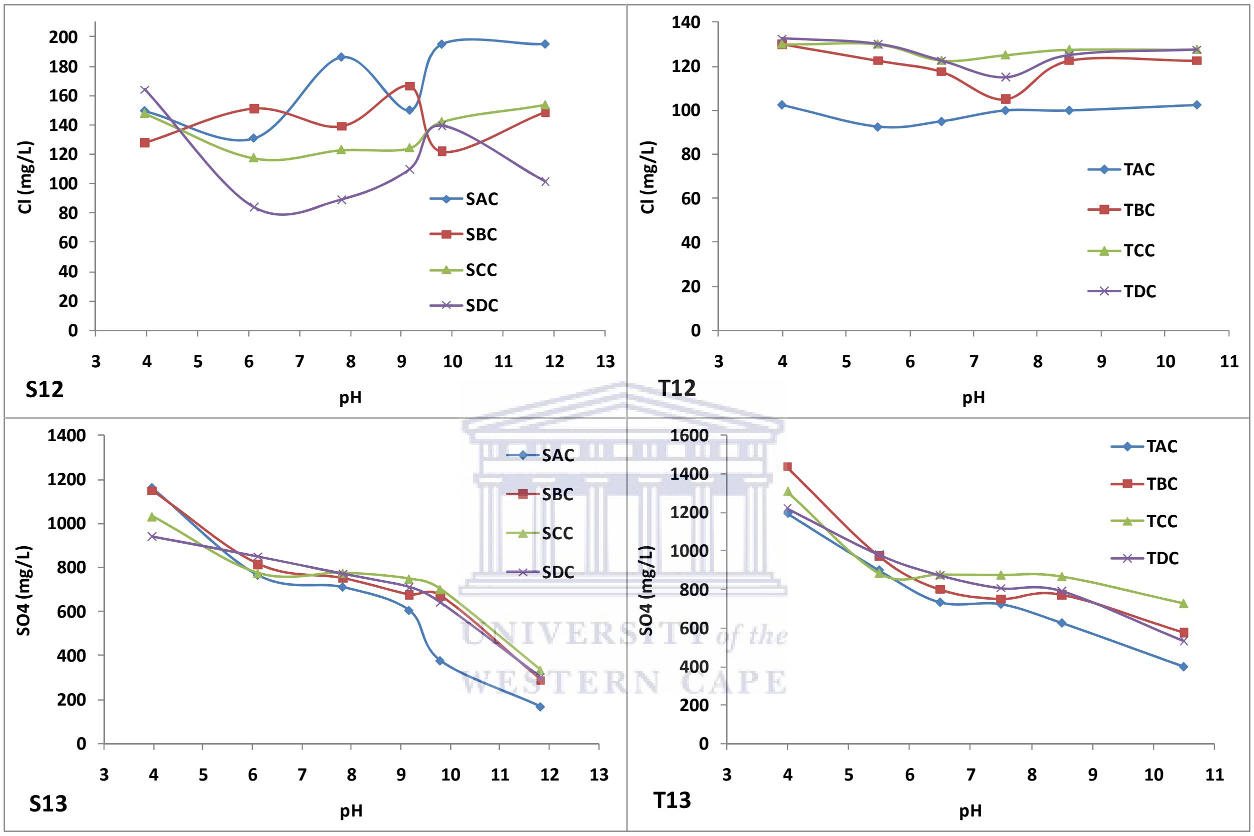

Figure 5.18: Cl and SO_4 concentrations of Secunda (S12-S13) and Tutuka (T12-T13) long-term fly ash-brine interaction reaction residues as a function of pH.

The release of Cl in the solution of Secunda and Tutuka solid residues followed the same pH independent trend as that of Na. The concentration of Cl released from both Secunda and Tutuka solid residues was high in the leachates of the ANC tests at the natural high pH of the solid residues [Figure 5.18 (S12 and T12)]. The release continued and was fluctuating throughout the ANC tests irrespective of the pH of the leaching solution. The results showing the chemical composition of the brine decanted and the solid residues after the long-term interactions experiments showed (Tables 5.1 and 5.2; Figures 5.4 and 5.7) that the fly ashes removed significant amounts of the Cl in the brine solution under the static conditions applied. The high concentration of Cl in the ANC tests irrespective of the pH showed that the Cl removed by the fly ashes during the long-term interactions experiments was highly mobile. This is an indication that the mineral phase(s) in which Cl exists in the solid residues is transient.

The concentration of SO_4 in the leachates of the ANC tests from Secunda and Tutuka solid residues was already high at natural pH of the ANC systems [Figure 5.18 (S13 and T13)]. The concentration of SO_4 significantly increased with a decrease in the pH of the ANC systems. The results presented in Tables 5.1 and 5.2; Figures 5.4 and 5.7 showed that SO_4 was significantly removed from the brine solution by the fly ashes during the long-term fly ash-brine interaction experiments. The increase observed in the concentration of SO_4 when the fly ashes contacted water (natural pH) at the start of the ANC tests could indicate the release of soluble SO_4 species that was removed from the brine by interating with the fly ashes while the continuous increase could be attributed to the dissolution of the SO_4-rich phases in the solid residues as the pH decreased showing the instability of the mineral phases that captured sulphate. The trend of release of Cl and SO_4 from the solid residues indicates that these species that were removed from the brine solution by the fly ashes are mobile even at high pH upon contact with water, which is possible to be attained in the real ash disposal scenario. Thus the removal observed in the long-term fly ash-brine interaction experiments would not be maintained and dissolution would occur upon water ingress or pH changes. The rapid release of SO_4 from the solid residues has significant implications on the environment, and would account for increasing SO_4 level in the water bodies in the catchment area where the ash dumps are located.

5.3.2.2.6 Manganese and Iron

Figure 5.19 shows the release of Mn and Fe as a function of pH during the ANC tests from the solid residues recovered from the long-term fly ash-brine interactions experiments.

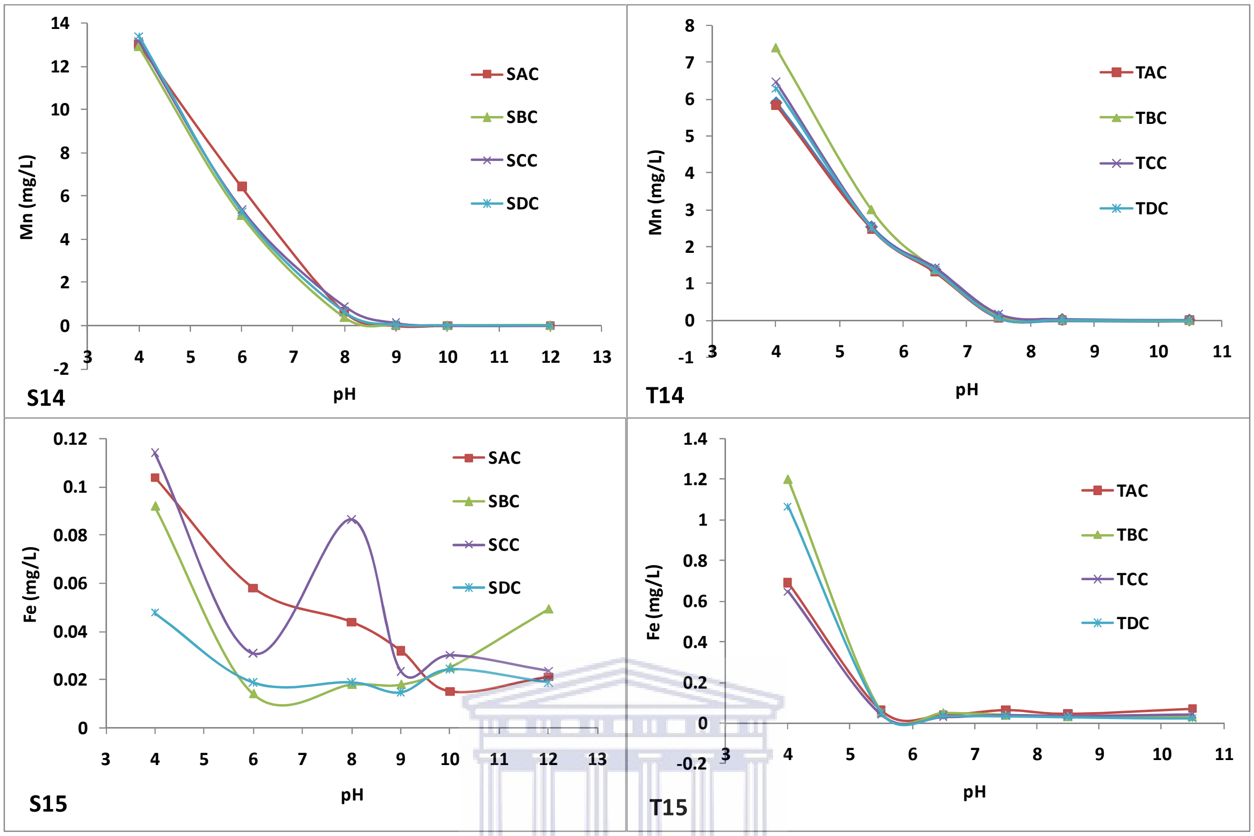

Figure 5.19: Mn and Fe concentrations of Secunda (S14-S15) and Tutuka (T14-T15) long-term fly ash-brine interaction reaction residues as a function of pH.

The results of the ANC tests showed that the concentration of Mn in the leachate solution of Secunda and Tutuka solid residues was very low from the natural high starting pH of the ANC tests to pH of around 8 [Figure 5.19 (S14 and T14)]. Almost the same trend was observed for the concentration of Fe in the ANC systems as its concentration was very low between pH 6 to the natural pH in the Tutuka case whereas in the case of Secunda, the trend was inconsistent [Figure 5.19 (S15 and T15)]. A rapid increase in the concentration of Mn was observed in the solutions of the solid residues at pH <8 while a rapid increase was observed in the concentration of Fe at pH <6. The chemical composition of the excess brine decanted from the solid residues after the long-term interactions experiments showed that Mn was removed from the brine solution while more Fe was leached into the brine solution (Tables 5.1 and 5.2). At alkaline pH, Mn and Fe in solution form oxy-hydroxides which occur as coatings around the silicate grains of fly ash particles. The possible formation of insoluble Mn and Fe oxy-hydroxides during the long-term fly ash-brine interactions experiments could account for the low concentrations of these species in the solution of the solid residues at alkaline pH. The lower concentration of Mn and Fe in the ANC leachates showed that the Mn and Fe removed from the brine solution is not mobile at high pH. The increase observed in the concentrations of Mn and Fe in the solution of the ANC systems at lower (acidic) pH (4-8) for Mn and pH 4-6 for Fe could be attributed to the dissolution of the oxy-hydroxides of these elements at different acidic pH levels. Drever, (1997) suggested that at low pH, reduction of the oxy-hydroxides leads to dissolution of their oxides thereby resulting in the increase in concentrations of Mn and Fe in the ANC test leachate solutions.

5.3.2.2.7 Cobalt, Nickel and Lead

The concentrations of Co, Ni and Pb released from Secunda and Tutuka solid residues into the leachates during the ANC tests are shown in Figure 5.20.

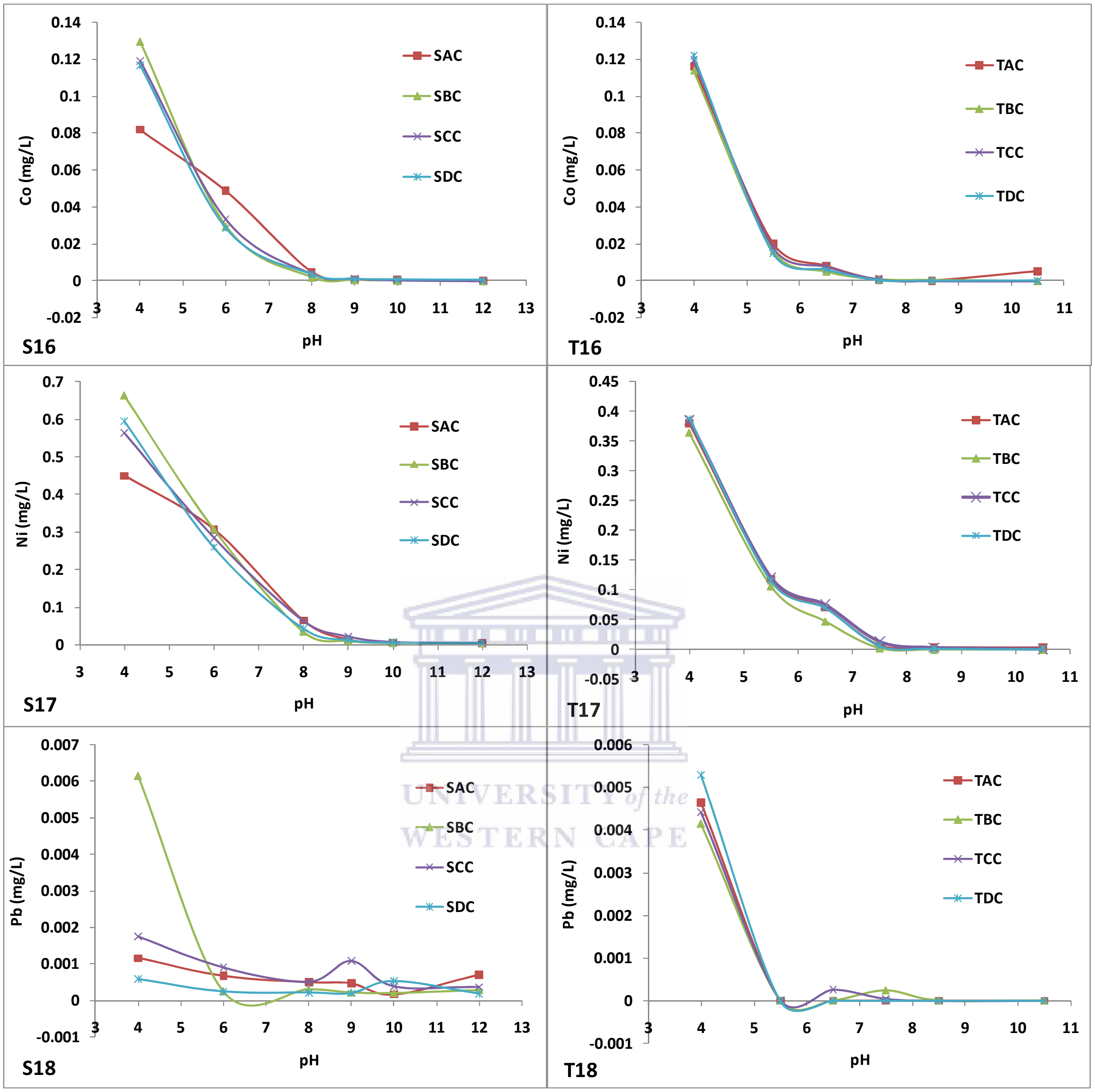

Figure 5.20: Co, Ni and Pb concentrations of Secunda (S16-S18) and Tutuka (T16-T18) long-term fly ash-brine interaction reaction residues as a function of pH.

The concentrations of Co, Ni and Pb were low in the leachate solutions of the ANC tests at alkaline pH. Co concentration was observed to be low between pH ≈8 and the natural high pH in Secunda and Tutuka ANC solutions; Ni was at its lowest concentration between pH 7.5 and the natural high pH while the concentration of Pb was low between pH 6 and the natural high pH of the respective solid residues [Figure 5.20 (S16-S18 and T16-T18)]. These species were removed from the brine solution (Tables 5.1 and 5.2) which indicates that they are enriched in the solid residues. The release of these species in the ANC systems as the pH decreased corresponds to the release of Mn and Fe which is an indication that the formation and dissolution of Fe and Mn oxy-hydroxides control the presence of Co, Ni and Pb in the ANC systems. Due to the negative charge of the Mn and Fe oxy-hydroxides, heavy metals (such as Co, Ni, Cu, Zn, Pb and Cd) are strongly adsorbed to the surface of the oxy-hydroxides thereby decreasing the availability of these trace elements in solution at high pH (Drever, 1997). In the case of Ni, Yan *et al.* (2008) and Quina *et al.* (2009) suggested the formation of $Ni(OH)_2$ as the phase controlling the release of Ni at alkaline pH 7-14 while at pH 6-9 the release of Ni was suggested to be controlled by adsorption on Fe oxy-hydroxides. At low pH, it was suggested that the increase in concentration of Co, Ni and Pb could be attributed to it slow desorption from the oxy-hydroxides (Dijkstra *et al.,* 2006; 2008). The low concentration of Ni observed at alkaline pH in the ANC tests carried out on Secunda and Tutuka solid residues could be accounted for by either sorption processes on the Fe-Mn oxy-hydroxides or as a result of the precipitation of $Ni(OH)_2$ (Quina *et al.*, 2009). The increase observed at lower pH (<8) in the ANC leachate solution suggest desorption of Ni from the oxy-hydroxides.

According the studies carried out by Van der Bruggen *et al.* (1998); Yan *et al.* (2008); Van der Bruggen *et al.* (2000); Zhang *et al.* (2008a), the release of Pb was suggested to be controlled by the precipitation of $Pb(OH)_2$ at alkaline pH (>9). Hyks *et al.* (2009) argued that Pb is a sorption/complexation-controlled element, thereby suggesting that the release of Pb under alkaline condition may be governed by sorption processes. Therefore low concentration of Pb observed in the ANC solutions at high pH could be attributed to either the precipitation of $Pb(OH)_2$ or sorption on the hydrous iron oxy-hydroxides, whereas gradual dissolution of Pb-rich phases or slow desorption of the adsorbed Pb could be responsible for the increase in Pb concentration at low pH.

Generally, the results of the ANC tests showed that Co, Ni and Pb in the solid residues are not mobile under alkaline condition but once the pH decreases they are mobilized. The effect of longer interactions period (1 week to 12 months) was not significant in the release of these species from the solid residues in the ANC tests as the concentration of species released at each specific pH was almost the same except for Pb in Secunda ANC system.

5.3.2.2.8 Copper and Zinc

The concentrations of Cu and Zn released from the solid residues of Secunda and Tutuka long-term fly ash-brine interaction during the ANC tests are shown in Figure 5.21.

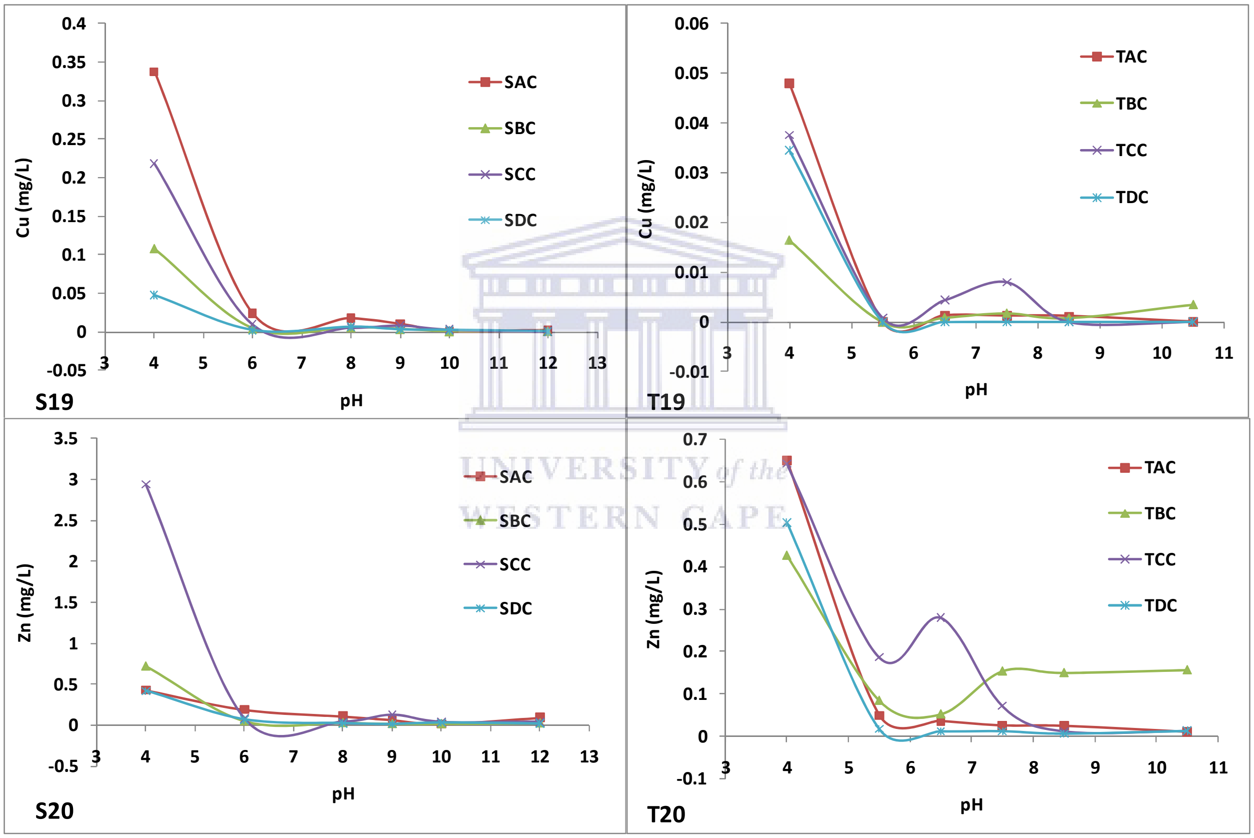

Figure 5.21: Cu and Zn concentrations of Secunda (S19-S20) and Tutuka (T19-T20) long-term fly ash-brine interaction reaction residues as a function of pH.

The trends of Cu and Zn released from Secunda and Tutuka solid residues were similar to what was observed for Mn and Fe (Figure 5.19) and for Co, Ni and Pb (Figure 5.20) in the ANC systems. This is an indication that the release of Cu and Zn is also being controlled by sorption on the reactive surfaces of hydrous Fe or Al oxy-hydroxides (Quina *et al.*, 2009). Dijkstra *et al.*

(2006) observed that the leaching of Cu into solution at alkaline pH is controlled by surface complexation to Fe- and Al (hydr)oxides. Apart from adsorption on Fe oxy-hydroxides, the release of Zn and Cu has been observed to be controlled by the formation of hydroxide complexes at alkaline pH (Van Herck *et al.,* 2000; Hyks *et al.,* 2009). The concentrations of Cu and Zn released from the solid residues were very low between pH 6 and the natural high pH of the respective solid residues at the start of the ANC tests [Figure 5.21 (S19-S20 and T19-T20)]. Surface complexation to Fe- and Al (hydr)oxides or formation of hydroxide complexes could account for the initially low concentration of Cu and Zn at high pH in the ANC leachates while their increase in the leachates at low pH could be as a result of the dissolution or desorption of the complexes. Comparing the release of species into the leachates from each of the solid residues, it was observed that the release of Cu from the solid residues at 1 week was higher than the concentration of Cu released from other residues (1-12 months) at specific pH. This could indicate the effect of the longer interactions period on the stability of the possible mineral phases formed and the mobility of this species from the solid residues. The results of the ANC tests showed that Cu and Zn in the solid residues are not mobile under alkaline condition but are mobilized when the pH is reduced below 6.

5.3.2.2.9 Arsenic, Chromium and Molybdenum

The concentrations of As, Cr and Mo released into the leachates of the ANC tests from the solid residues of Secunda and Tutuka long-term fly ash-brine interaction experiments are presented in Figure 5.22.

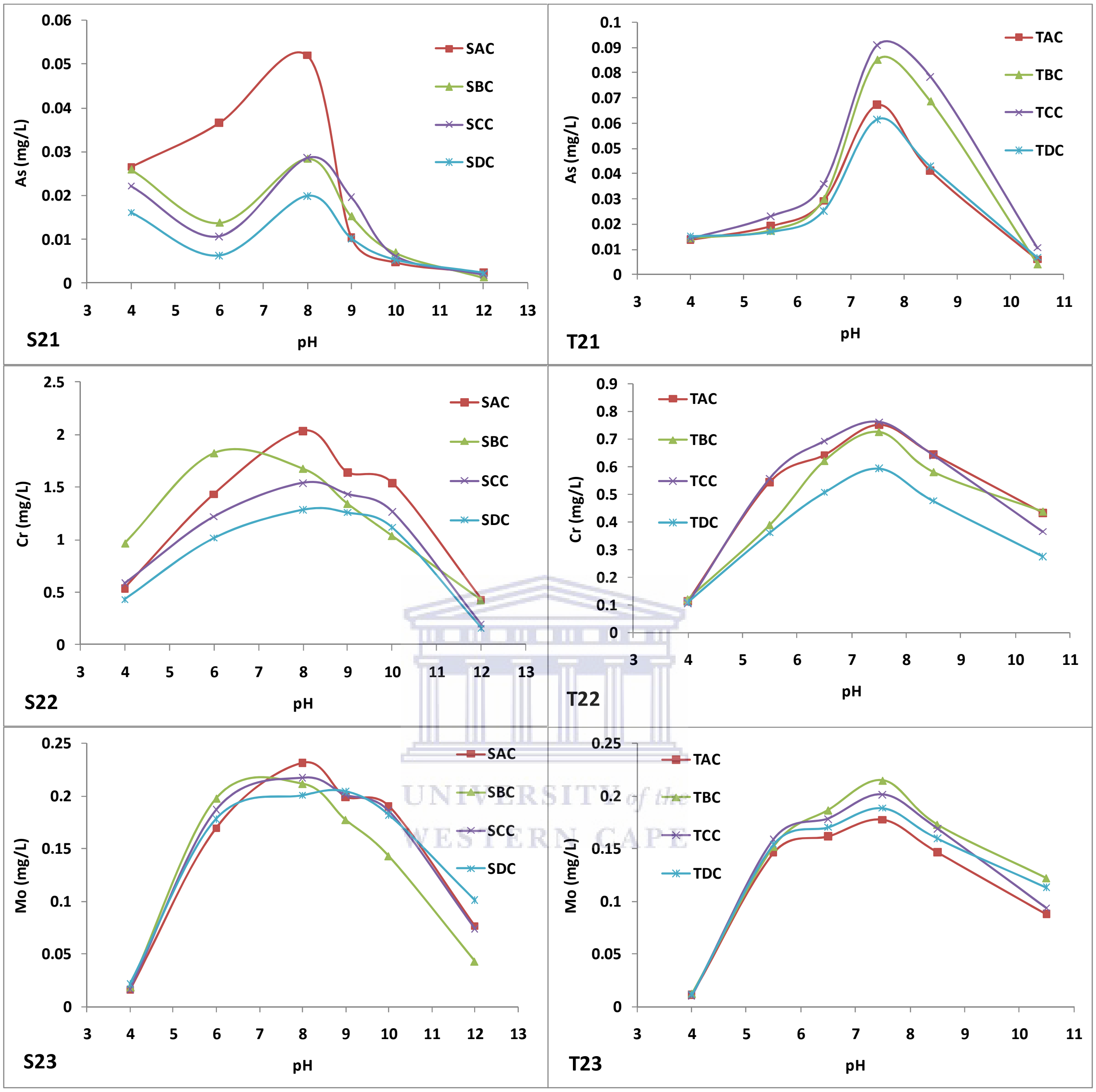

Figure 5.22: As, Cr and Mo concentrations of Secunda (S21-S23) and Tutuka (T21-T23) long-term fly ash-brine interaction reaction residues as a function of pH.

The concentration of As in the ANC leachates of both Secunda and Tutuka solid residues was very low at natural high pH at the start of the ANC tests. The concentration of As in the ANC leachates after the low concentration at natural high pH of 12 increased significantly until a maximum concentration was reached at pH 8 and 7.5 for Secunda and Tutuka residues respectively. Thereafter, the concentration of As decreased at pH below 7 [Figure 5.22 (S21 and T21)]. The release of As depended upon the pH of the systems and was governed by both adsorption and precipitation reactions. According to Goh and Lim, (2004); Jankowski *et al.* (2006), the leaching of As in fly ash solution is controlled by adsorption and precipitation processes depending on the quantity present in the fly ash samples. In the presence of considerable amounts of Ca in solution at alkaline pH, the precipitation of $Ca_3(AsO_4)_2$ can reduce the concentration of As in solution (Lee and Saunders, 2003). The presence of ettringite $[Ca_6[Al(OH)_6]_2(SO_4)_3\cdot26(H_2O)]$ in solution at pH >10 may reduce the concentration of As by substituting the SO_4 with the oxy-anion form of As. The low concentration of As in the ANC systems at pH >10 could be due to precipitation of $Ca_3(AsO_4)_2$ or as a result of its entrapment in the ettringite phase in the systems. The increase in the concentration of As in the leachates between pH 8 and 10 could be due to the dissolution of ettringite phase in the ANC systems. The decrease observed in the concentration of As at pH lower than 7 could be controlled by adsorption processes as the low pH does not favour the precipitation of either ettringite or $Ca_3(AsO_4)_2$.

The leaching pattern of Cr shows that its release from the Secunda and Tutuka solid residues is strongly dependent on the pH of the ANC systems. The concentration of Cr was very low at natural high pH of the ANC tests with the leachates of Secunda fly ash-brine solid residues having the lower values [Figure 5.22 (S22 and T22)]. A rapid increase in Cr concentration was observed in the ANC systems until a maximum concentration was reached at pH 8 and 7.5 for Secunda and Tutuka fly ash-brine residues respectively. At pH below 7, a rapid decrease in Cr concentration was observed in the leachates and this persisted till the end of the experiment at pH 4. The concentration of Cr in the ANC systems represents total Cr as ICP-MS used for the analysis did not separately analyze Cr based on their oxidation states [Cr(III) and Cr(VI)]. However, compounds of Cr(III) has been observed to be sparingly soluble while Cr(VI) is highly soluble (Cornelis *et al.,* 2008; Tiruta-Barna *et al.,* 2006; Drever 1997). Therefore, in the ANC systems, Cr(VI) could be the dominating form of Cr. Quina *et al.* (2009) suggested that the formation of ettringite phase at alkaline pH could reduce Cr concentration by entrapping the oxy-anion form of Cr in solution. They also suggested that, at low pH, sorption controls the release of Cr(IV) which is present in solution as an anion. At pH 3–7, Zhang *et al.* (2008a) suggested surface complexation as the process controlling the leaching of Cr in solution. Due to the alkaline pH (>10) that favours the formation of ettringite, low concentration of Cr observed in the ANC systems at pH >10 could be attributed to either its uptake on ettringite or surface adsorption while the low concentrations at low pH could be as a result of surface complexation. The increase in Cr concentration in the ANC leachates at pH 7-8 could be due to of the dissolution of the ettringite which had entrapped the leached oxyanion or due to desorption of the adsorbed Cr.

The release pattern of Mo was similar to that of Cr as shown in Figure 5.22. The leaching of Mo and its mobility has been observed to depend on the alkalinity or acidity of the leachate, and the availability of Mo in the matrix of fly ash (Dijkstra *et al.,* 2006). The concentration of Mo was very low at natural high pH of the ANC tests but a rapid and steady increase was observed as the pH of the solution was reduced [Figure 5.22 (S23 and T23)]. A maximum concentration was reached at pH 8 and 7.5 for leachates of Secunda and Tutuka fly ash-brine residues respectively, and thereafter, a rapid decrease in Mo concentration was observed in the leachates at pH <7. Mo has been observed to precipitate as MoO_3 at high pH (Jankowski *et al.,* 2006), which could account for the low concentration of Mo observed at the beginning of the ANC test when the pH was greater than 10. At pH 8-10, Meima and Comans, (1999) suggested that the solubility of phases such as powellite ($CaMoO_4$) controls the leaching of Mo. The increase observed in Mo concentration with decrease in the pH (8-10) could be attributed to the dissolution of highly soluble Cr-containing phases in the residues of the fly ash-brine interaction tests. According to Comans *et al.* (2000) and Kukier *et al.* (2003), the concentration of Mo at low pH is controlled by adsorption of the oxyanion (MoO_4^{2-}) on Fe and Al in solution. The low concentration of Mo at low pH could be accounted for by the adsorption process on Al or Fe as significant concentrations of Al and Fe [Figure 5.14 (S3 and T3) and Figure 5.19 (S15 and T15)] are present in the ANC leachate solutions at low pH.

The results of the ANC tests revealed that As in the solid residues are not mobile at alkaline pH but at near-neutral pH. The release of Cr and Mo in the ANC systems showed that these species are mobile at alkaline pH but immobile when the pH of the systems is reduced. The lower pH attained in the ANC tests by the addition of acid to the leachants may take a longer time to be attained in the real ash disposal scenario.

5.3.2.2.10 Percentage of species released from the solid residues at different pH

Figures 5.23 to 5.30 present the percentage of selected species released into the leachates from the solid residues at different pH during the ANC tests. This extraction percentage calculation was done on the species observed to have been removed from the brine solution during the long-term fly ash-brine interactions experiments. This is to determine the percentage of the "removed species" that are mobile under different pH conditions. Some species that leached from the fly ashes into the brine solution during the long-term fly ash-brine interaction experiments were also considered in this calculation in order to determine if the species will be continuously released and what percentage will be leached at different pH despite its initial leaching during the long-term interactions experiments.

The extraction percentage (E*p*) was calculated using the total chemical composition of the solid residues and the concentration of species in the leachates from the ANC tests. The extraction percentage value was calculated according to the formula adapted from Baba *et al.* 2008.

$$Ep = (Cl/Cs)\ X\ 100$$

Where E*p* is the extraction percentage of each species (%), C*l* is the concentration of the species in the leachate (mg/L), and C*s* the concentration of the species in solid residue (mg/L).

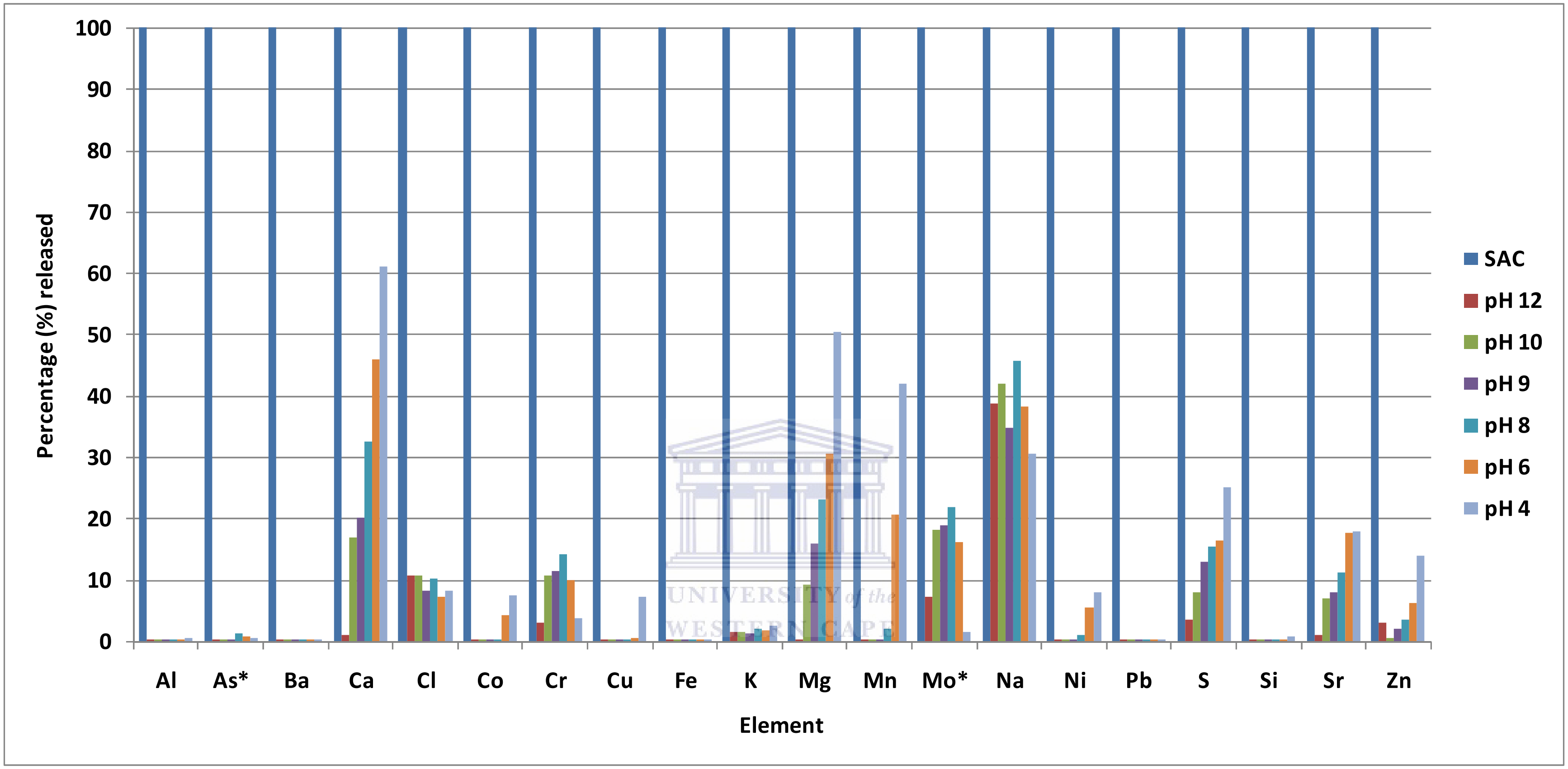

Figure 5.23: Percentage (%) of species released from Secunda solid residue at 1 week (SAC) as a function of pH (*data from total acid digestion tests)

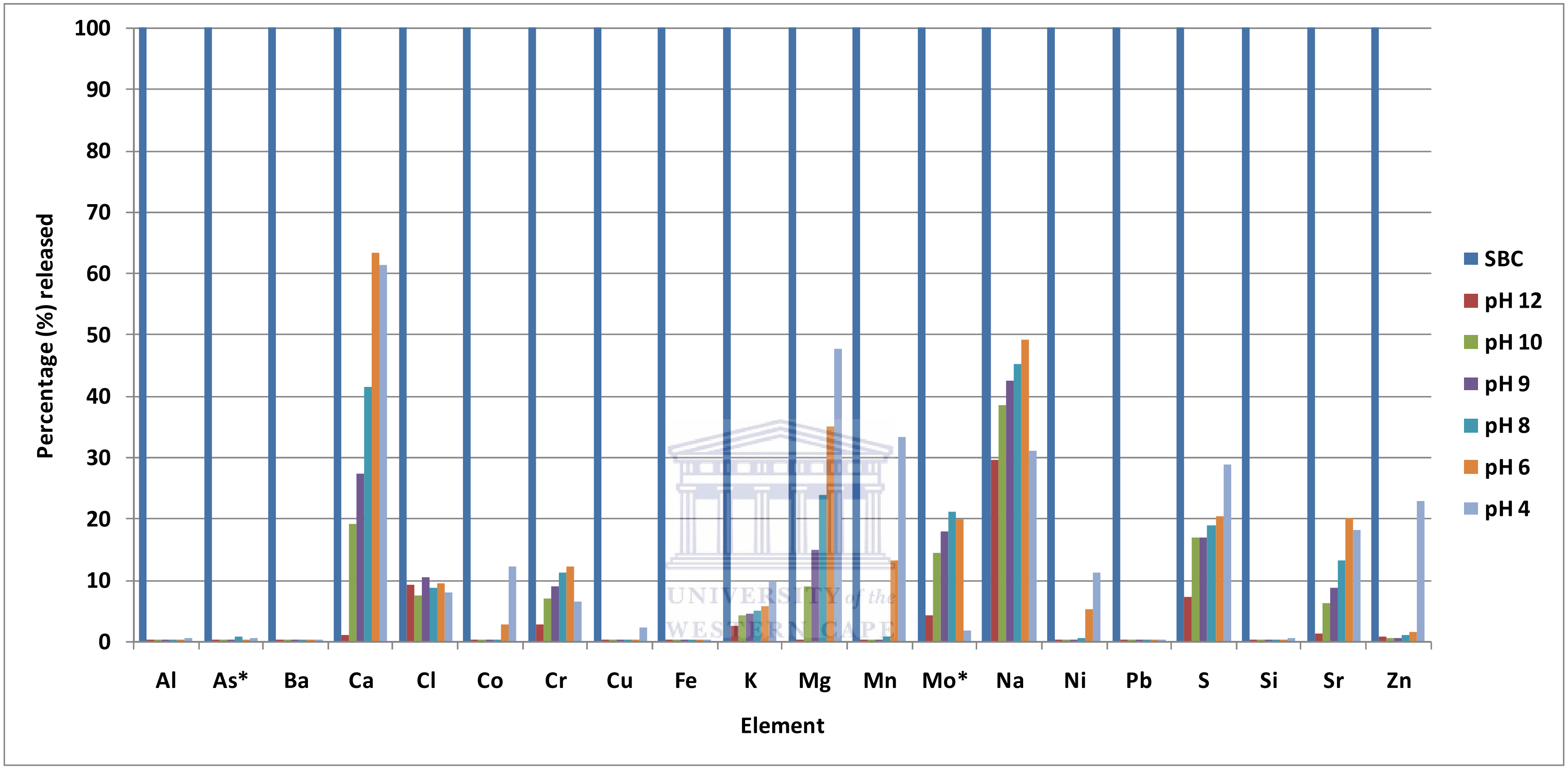

Figure 5.24: Percentage (%) of species released from Secunda solid residue at 1 month (SBC) as a function of pH (*data from total acid digestion tests)

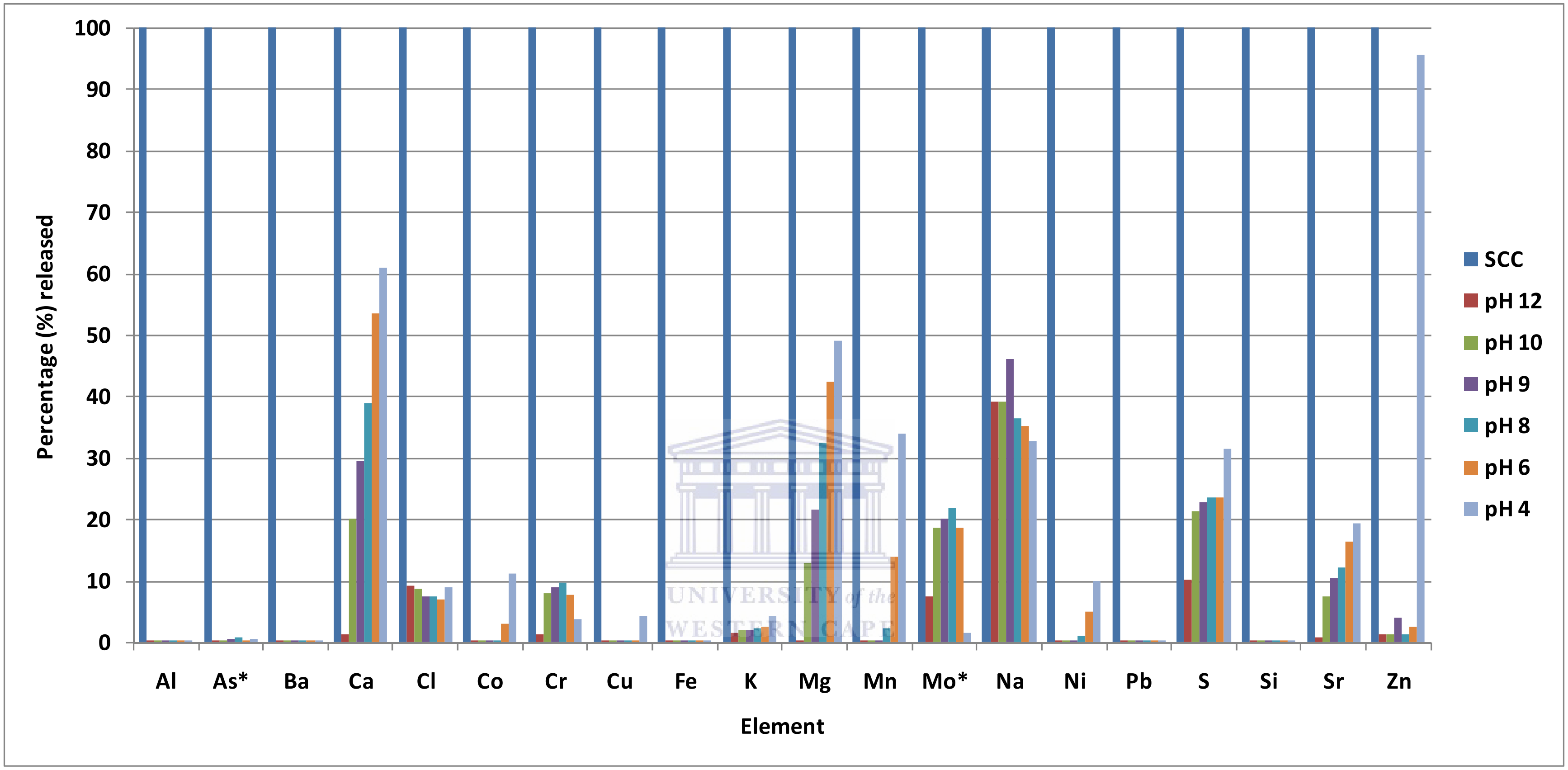

Figure 5.25: Percentage (%) of species released from Secunda solid residue at 6 months (SCC) as a function of pH (*data from total acid digestion tests)

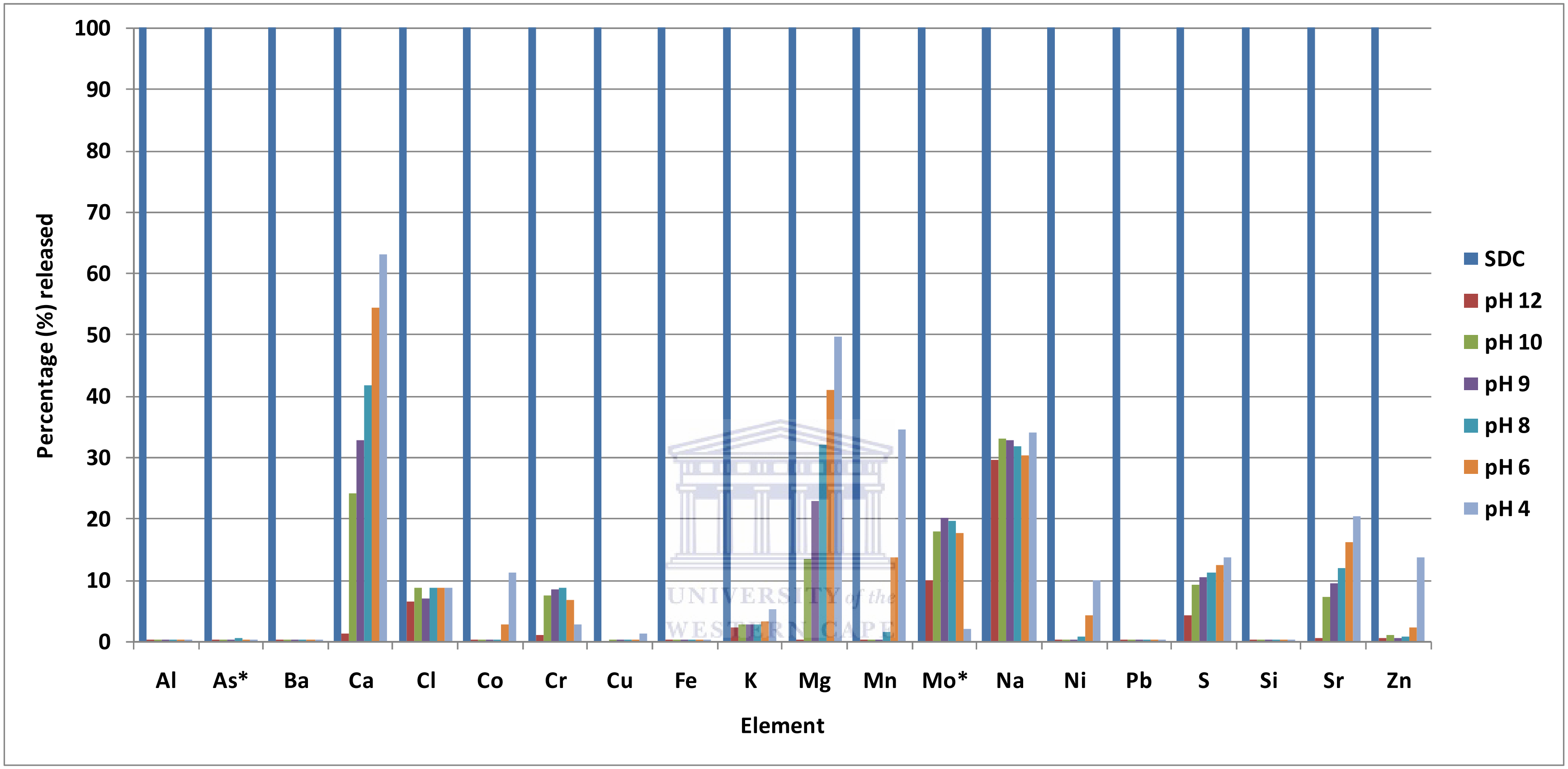

Figure 5.26: Percentage (%) of species released from Secunda solid residue at 12 months (SDC) as a function of pH (*data from total acid digestion tests)

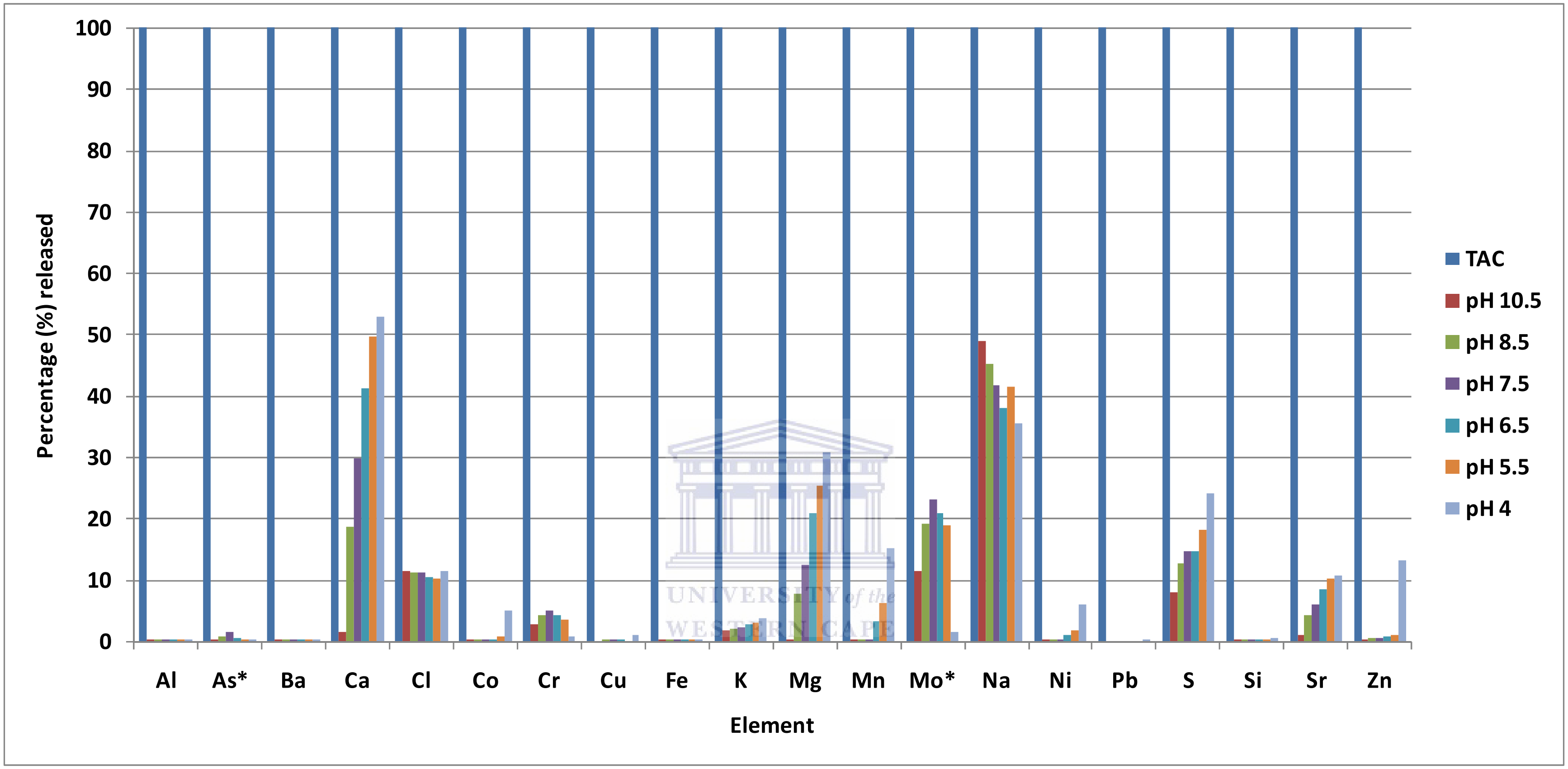

Figure 5.27: Percentage (%) of species released from Tutuka solid residue at 1 week (TAC) as a function of pH (*data from total acid digestion tests)

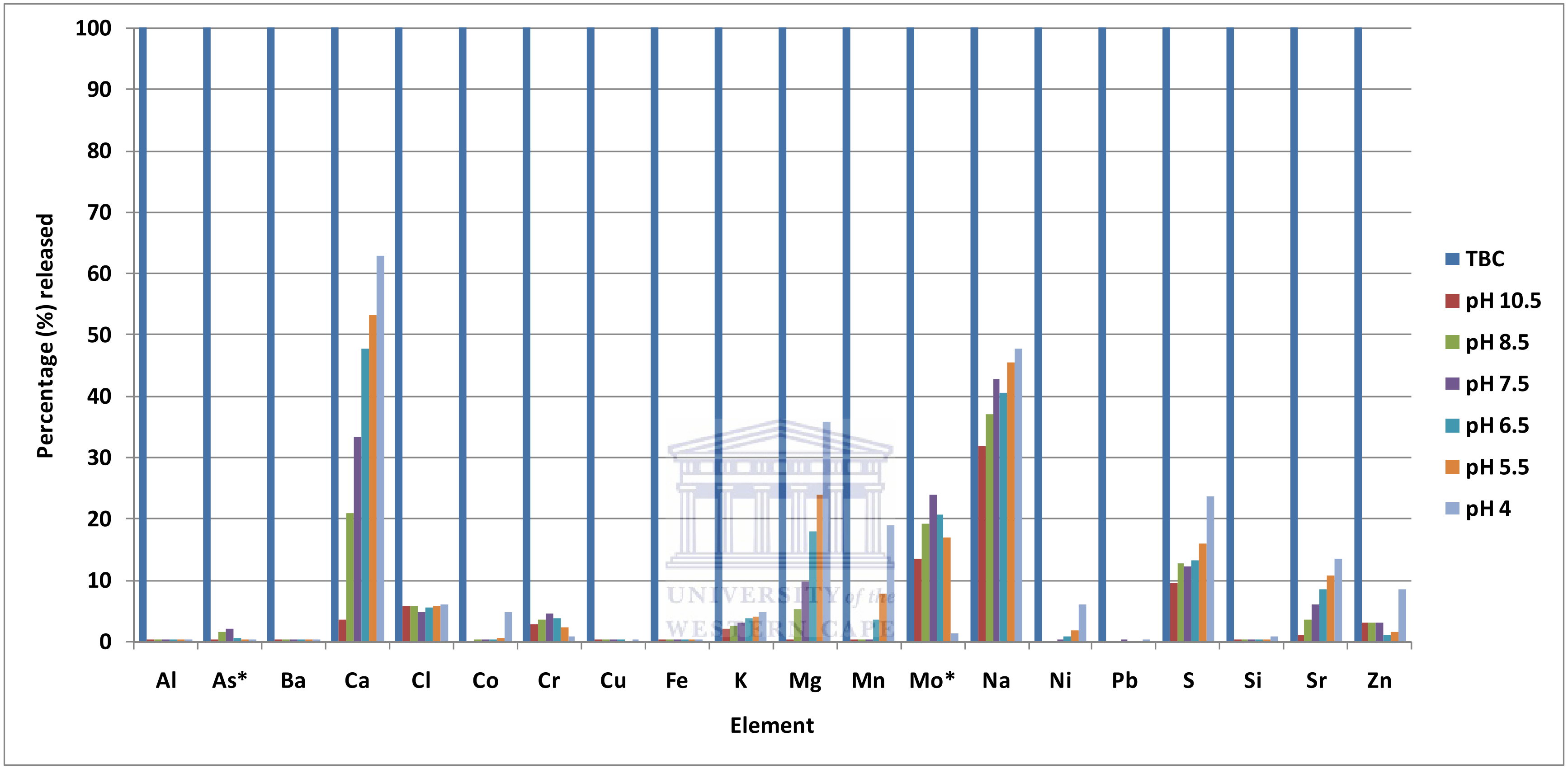

Figure 5.28: Percentage (%) of species released from Tutuka solid residue at 1 month (TBC) as a function of pH (*data from total acid digestion tests)

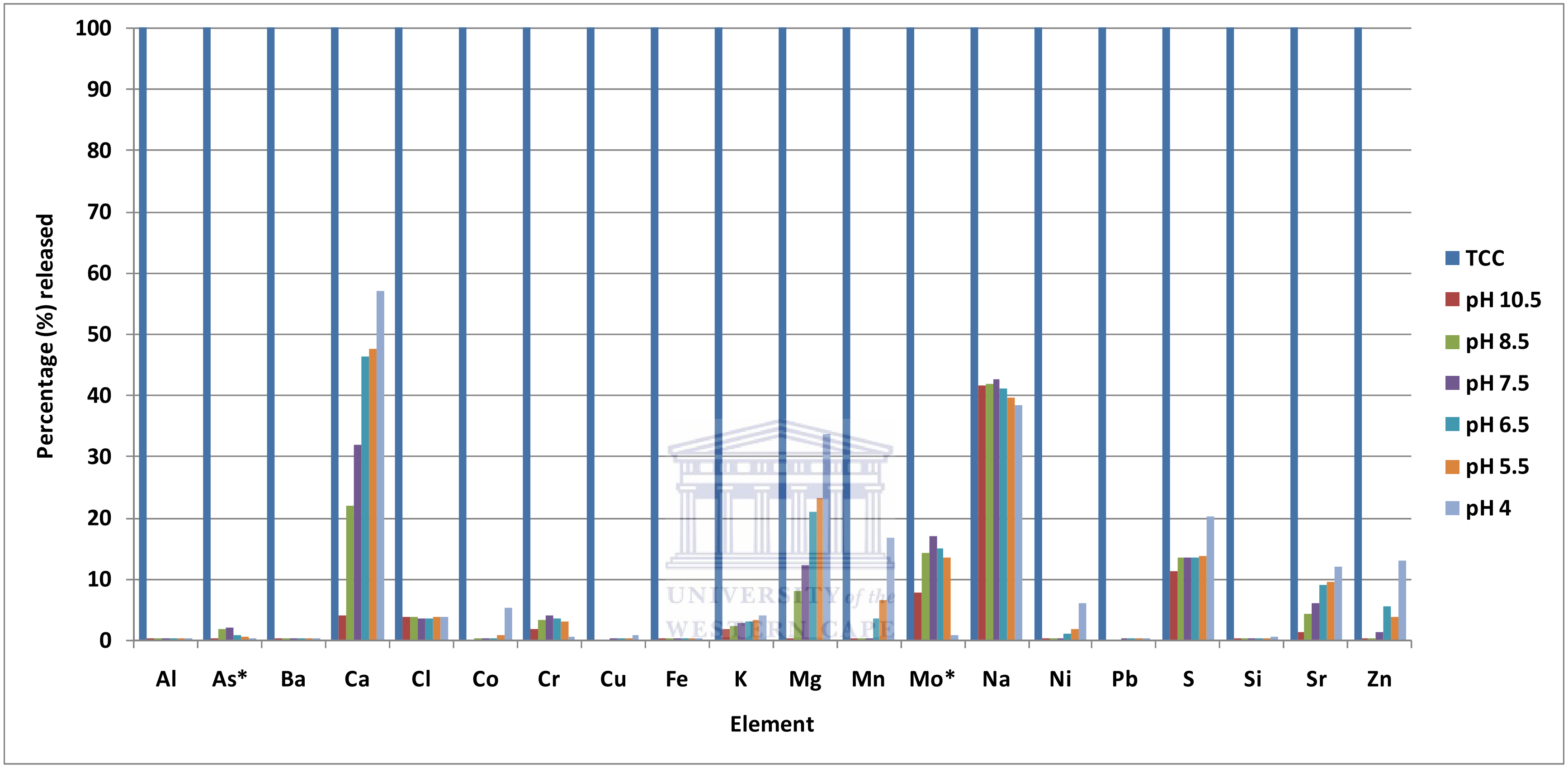

Figure 5.29: Percentage (%) of species released from Tutuka solid residue at 6 months (TCC) as a function of pH (*data from total acid digestion tests)

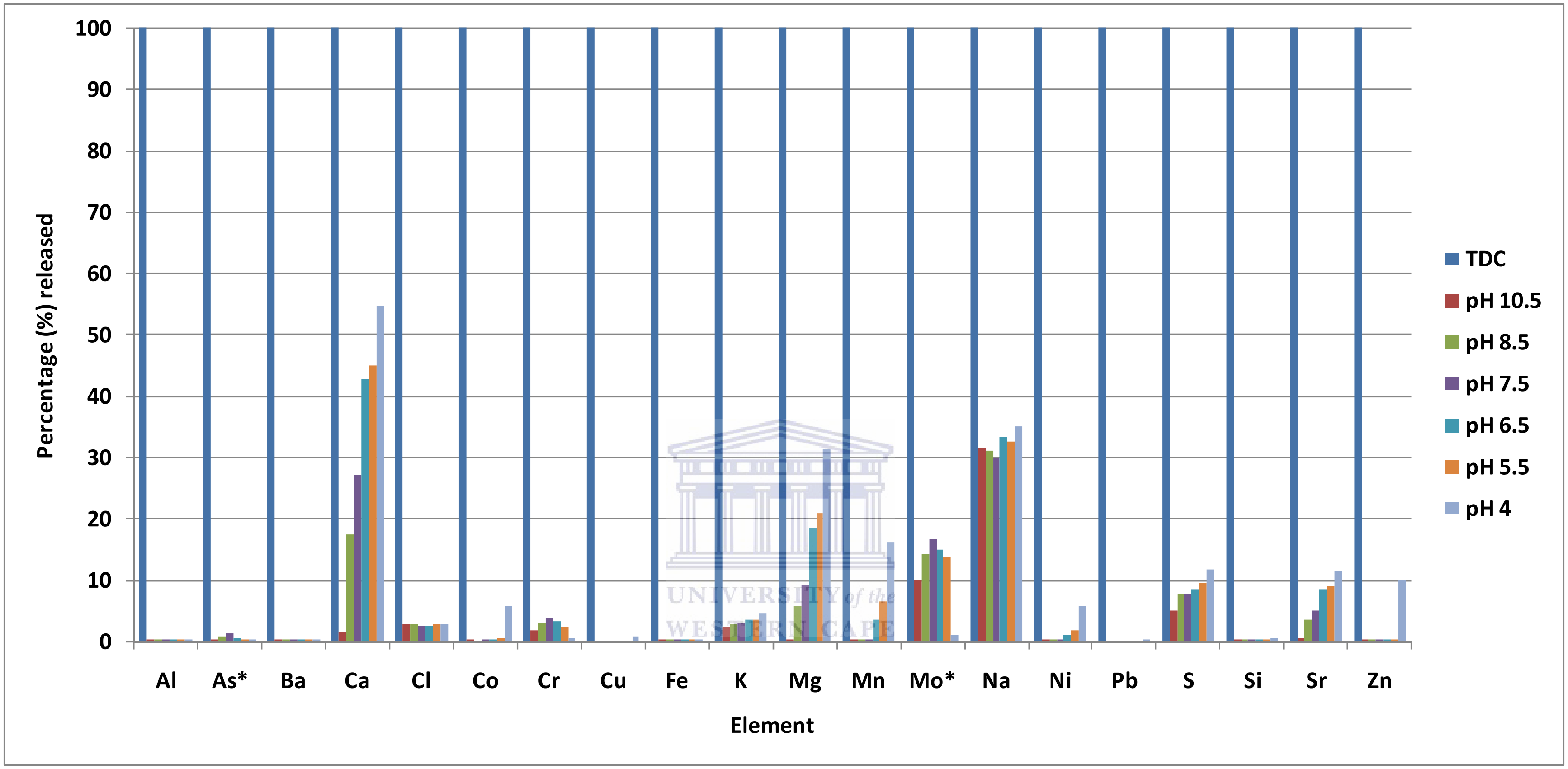

Figure 5.30: Percentage (%) of species released from Tutuka solid residue at 12 months (TDC) as a function of pH (*data from total acid digestion tests)

The percentages (mass-balance) of both major and minor species released from the solid residues after contacting solutions of different pH are shown in Figures 5.23 to 5.30. The extraction percentage of all the species released from the solid residues into the leachates initially at natural high pH of the ANC tests (pH 12 for Secunda and pH 10.5 for Tutuka) was very low except for Ca, Cr, Cl, K, Mo, S, Na and Zn (in some cases) which concentrations in the leachates were observed to be high with Na and Cl having the highest extraction percentage (29.7-39.2 % in Secunda leachates and 31.5-48.9 % in Tutuka leachates). The low solubility of most of these species at natural high pH (>10) could be as a result of precipitation and adsorption processes (Manahan, 1994; Bozkurt *et al.,* 2000). Low retention observed for Na and Cl in the solid residues at high pH indicates their presence as easily soluble salts in the residues. As the pH decreased, the extraction percentage of some species such as Ca, Mg, Mn, Ni, Co, S, Sr and Zn increased significantly especially at pH 4. The increase in the concentrations of these species could be attributed to the dissolution of mineral phases containing the species and the inability of these species in the leachates to form secondary mineral phases due to the low pH. Generally, the results indicating the percentages of species released from the solid residues showed that the mobility of Mg, Al, Si, Fe, Pb, Co and Ni is low and these species would only be released from the solid residues at extreme conditions such as very low pH. On the other hand, the results showed that a significant amount of Na, Cl and S (SO_4) removed from the brine solution during the long-term interaction experiments are immediately mobile when in contact with water. Despite the observed leaching of Cr and Mo from the fly ashes during the long-term interaction experiments, these species in the solid residues are mobile when in contact with water.

5.3.2.2.11 Summary

With the exception of Na and Cl, the release of species from the solid residues generated from the fly ash-brine interaction experiments depended on the pH of the solution in contact with the solid residues. The concentrations of major species such as Al, Si, Ca, Ba, Sr, Mg and B released into the ANC leachates were observed to be very low at alkaline pH. The decrease in the concentrations of these species at the natural high pH of the ANC tests may not only be as a result of the precipitation of new mineral phases during the ANC tests but could also be associated with the previously observed high initial dissolution of the soluble salts of these species during the long-term fly ash-brine interactions experiments. The dissolution of the soluble salts or oxides of these species as observed in Tables 5.1 and 5.2 during the long-term fly ash-brine interactions experiments may reduce the concentrations available for leaching in the solid residues at natural pH during the ANC tests.

The concentrations of minor species such as Fe, Mn, Co, Ni, Pb, Cu and Zn were observed to be very low at alkaline pH. The results of the characterization of the long-term fly ash-brine interactions solid residues (Figures 5.3 to 5.8) showed that most of these minor species were removed from the brine solution by the fly ashes. Therefore, the low concentrations of species such as Fe, Mn, Co, Ni, Pb, Cu and Zn at alkaline pH may not be as results of their low concentrations in the solid residues as argued in the case of the major species. The low concentrations of these minor species could be attributed to their existence in less soluble phases due to the chemical interactions during the long-term fly ash-brine interactions experiments. The results of the characterizations of the solid residues showed the removal of these species by the fly ashes (Figures 5.3 to 5.8), and the removal was suggested to be controlled by dissolution/precipitation and adsorption/desorption processes. The results of the ANC tests agree with the suggestion that the release of Co, Ni, Pb, Cu and Zn seems to be controlled by the release of Fe and Mn. Heavy metals strongly adsorb to insoluble Fe and Mn oxy-hydroxides formed in alkaline solution. The ANC tests revealed that most of the heavy metals removed from the brine solution by the fly ashes are not mobile under natural conditions.

The release of most of the species in the ANC systems increased with decrease in the pH of the leaching solution except species such as Na, Cl, As, Cr and Mo. The release of Na and Cl showed their independence of pH. Na and Cl concentrations were very high at the natural high pH and these high concentrations continued throughout the ANC tests. This phenomenon shows that the Na and Cl-rich solid phase(s) formed during the long-term fly ash-brine interactions experiments are highly soluble and could easily dissolve when in contact with solution irrespective of the pH of the solution. The ANC results showed that significant amounts of SO_4 removed from the brine solution by the fly ashes during the long-term fly ash-brine interaction experiments are mobile when in contact with water. The ANC tests showed that the release of As, Cr and Mo is controlled by the pH. These species could be released at pH 7-11, while low pH favours their retention in the fly ash-brine interactions solid residues. The high extraction percentage of Cr and Mo observed at pH 7-8 (Figures 5.23 to 5.30) could be a major concern as it is possible to attain this pH range in the real co-disposal scenario.

The results presented and discussed in this chapter (5) showed the effect of the long-term fly ash-brine interactions on the leaching and removal of species from the brine solution under static and closed conditions. The formation of transient secondary mineral phases was observed as a result of the interactions of the species in the long-term fly ash-brine interaction systems. The application of the ANC tests to determine the stability of the secondary mineral phases formed in the solid residues and the mobility of the species when in contact with solutions of different pH values revealed that some species such as Na, Cl and SO_4 are easily soluble and mobile while some species especially the trace heavy metals could not be easily released under the expected environmental conditions for ash disposal scenarios.

Having studied and understood the effects of the long-term fly ash-brine interactions under static and closed conditions (an experiment that simulates the co-disposal scenario of Tutuka power station) on the release of major and minor species, it is necessary to understand the effect of the fly ash-brine interactions under a continuous flow-through condition on the release of major and minor species. The next chapter (6) deals with the chemical interactions of species in the fly ash-brine systems under a flow-through condition. This is to simulate the co-disposal technique practice by Secunda power utility, a situation where fly ash and brine are mixed together and the brine solution is introduced into the fly ash-brine systems on a continuous basis.

Chapter 6

Removal of major and minor species from fly ash-brine systems: Up-flow percolation test

6 Introduction

This chapter presents the results and discussion of the up-flow percolation (column leaching) test carried out on Secunda and Tutuka fly ashes with brine or brine-antiscalant solution as the leachants. The up-flow percolation test was employed to simulate a condition where fly ash and brine are co-disposed as slurry after which brine continuously percolates through the disposed fly ash. The up-flow percolation test was carried out according to European standard method prEN14405 (prEN14405, 2003). This method involves packing the material to be tested (fly ash) in columns in a standardized manner (detailed description in section 3.3.5), and the brine solution is percolated in an up-flow direction through the columns at a specified flow-rate to attain fixed liquid/solid (L/S) ratios. This approach was used to determine the capacity of the fly ash to remove both major and minor constituents from the brine solution under continous renewal of leachant and to study the release of major and minor constituents from the fly ash packed in a column after a specific volume of brine had percolated through the fly ash. A continuous vertical up-flow was used in this study so that the column would be properly saturated with the brine and to prevent preferential percolation of the brine during the percolation test. The dry mass of fly ash in the column, volume of brine percolated through the column as well as the time taken for collection of leachate were used to calculate the L/S ratios used in the graphs. This system extended the applied L/S ratio range to L/S 80 hence a fixed mass of ash was exposed to a significant active flow of brine over a period of 173 days (see experimental details in chapter 3 section 3.3.5).

Apart from the results and discussion of the up-flow percolation tests, the solid residues recovered from the up-flow percolation tests were characterized and the results and discussion of the characterization are presented in this chapter. The characterization was carried out using different techniques such as SEM-EDS, XRF and XRD to determine the morphology, chemical and mineralogical composition of the solid residues respectively. This chapter also contains the results and discussion of the sequential extraction tests carried out on the solid residues from the up-flow percolation tests. The constituents in the leachates of the up-flow percolation tests are expected to give an insight into the species removed or leached during the up-flow percolation tests. The chemical composition of the solid residues coupled with the results of the sequential extractions tests are expected to give an insight into the association of elements with specific secondary mineral phase that may form over time in the column during the fly ash-brine interactions and the mobility of the species in the solid residues.

The objectives of the study carried out in this chapter include; 1) understanding the release and removal of species from fly ash-brine interactions in a column system under a controlled flow rate, 2) understanding the influence of anti-scalant on the interactions and the release of species in the fly ash-brine column systems, and 4) understanding the mobility of species in fly ash-brine column systems.

The results and discussion presented in this chapter are divided into three (3) sections namely; sections 6.3.1, 6.3.2 and 6.3.3. Section 6.3.1 presents and discusses the release and removal of species from fly ash-brine interactions systems during the up-flow percolation tests. Section 6.3.2 presents and discusses the results of the characterization carried out on the solid residues, which include the results of pH and EC profiles of the solid residues, the morphology (SEM-EDS), mineralogy (XRD) and chemical composition (XRF) of the solid residues from the up-flow percolation tests, and section 6.3.3 presents the results and discussion of the sequential extraction tests carried out to determine the physicochemical form and the mobility of the species in the solid residues recovered from the up-flow percolation tests.

6.1 Overview

Up-flow percolation tests are designed to evaluate the release of constituents under either local equilibrium or advection conditions as a function of time. This method involves the flow of liquid through a fixed bed of solid material and the percolated liquid is collected as a function of

L/S ratio, which is used as a surrogate for leaching time. The up-flow percolation test has been considered a better leaching procedure for assessing field impact data than any other available batch test because it provides a fundamental basis from which to estimate constituent release under a variety of field conditions (Fatoba, 2008). Leachate generated by the column method is reportedly more representative of leachate derived from a disposal site than is the leachate from the batch method.

6.2 Materials and Methods

The description of the samples, the experimental protocols and the analytical techniques used in this chapter are presented in chapter 3. The XRD, XRF and SEM-EDS are presented in section 3.4.7, 3.4.8 and 3.4.9 respectively. The experimental procedures for the up-flow percolation tests and the sequential extraction tests are presented in sections 3.3.5 and 3.3.8 respectively. The preparation of the solid residues generated from the up-flow percolation tests for further analyses and the experimental procedures for the determination of pH, EC and TDS of the solid residues are presented in sections 3.3.6 and 3.3.7 respectively. The anion and cation analysis of the leachates from the experiments were done using IC and ICP-MS respectively (see sections 3.4.5 and 3.4.6 respectively).

6.3 Results and discussion

This section presents and discusses the results of the up-flow percolation tests carried out to determine the extent of the release of species from fly ash and the degree of removal of species from the brine solution during the fly ash-brine interactions, and to determine the influence of antiscalant on the removal and the release of species in the up-flow percolation systems. The up-flow percolation test was employed to simulate a condition where fly ash and brine are co-disposed as slurry after which brine continuously percolates through the disposed fly ash. The concentrations of species released from the fly ash-brine interactions systems were compared with the concentrations of species released from the fly ash-brine-antiscalant interactions systems in order to understand the effect of the antiscalant on the degree of release of species in the systems.

For easy identification of the figures and graphs in this section, SC represents parameters from Secunda column leachates and TC represents parameters from Tutuka column leachates.

6.3.1 The release and removal of species in fly ash-brine and fly ash-brine-antiscalant interactions

The results and discussion in the section will be presented in the following order; the pH and the electrical conductivity (EC) trends of the up-flow percolation leachates will be discussed whereafter the major and then the minor elements removed or released in the up-flow percolation systems, and the solubility controlling their removal or release will be discussed. All the results will be integrated to give a conclusion.

6.3.1.1 pH and Electrical Conductivity

Figure 6.1 presents the pH and EC profiles of the up-flow percolation tests involving fly ash-brine and fly ash-brine-antiscalant interactions as a function of L/S ratio. As stated in section 6.2.3.2, the up-flow percolation test was equilibrated for a period of 3 days and the first eluate collected after the equilibration was at L/S 0.1.

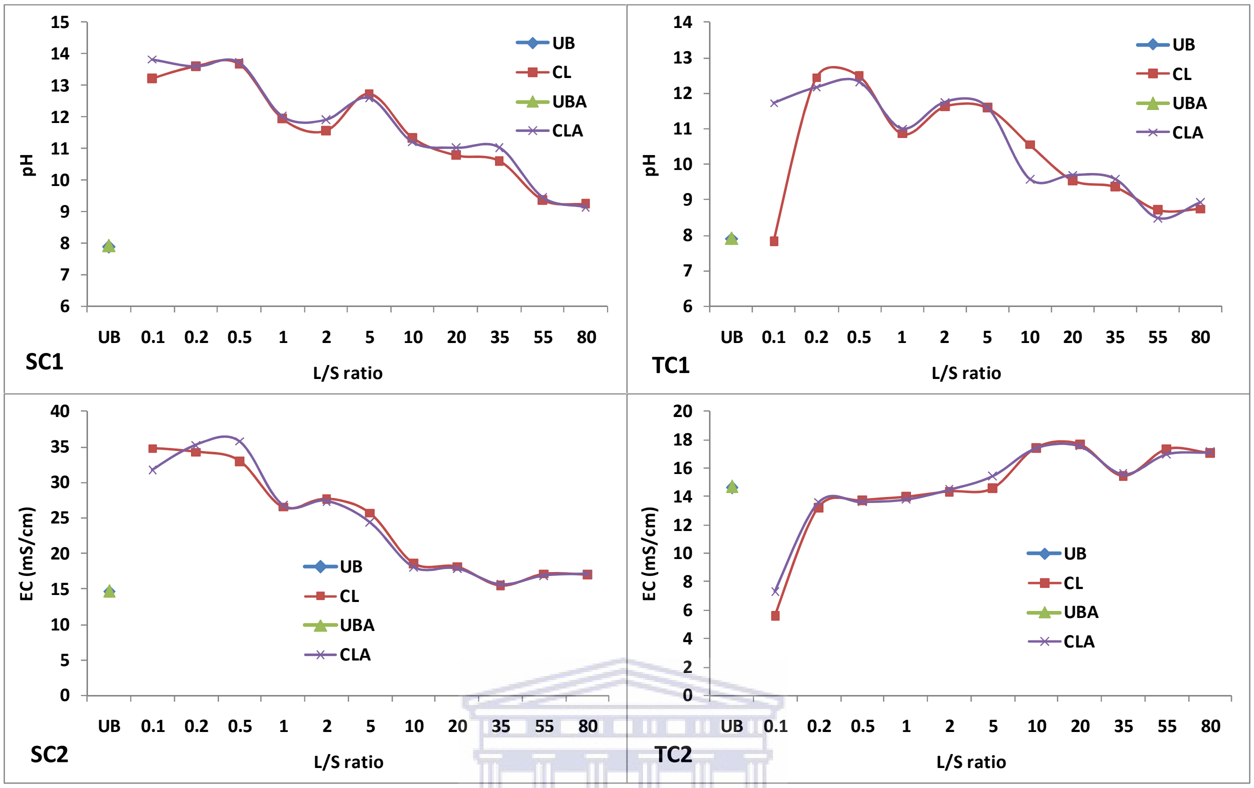

Figure 6.1: pH (SC1 and TC1) and EC (SC2 and TC2) profiles of up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine-antiscalant leaching trend

The pH (SC1 and TC1) and EC (SC2 and TC2) profiles of Secunda and Tutuka fly ash-brine and fly ash-brine-antiscalant interactions in the up-flow percolation tests are shown in Figure 6.1. The pH of the UB and the UBA was ≈8. The pH of the fly ash-brine and fly ash-brine-antiscalant systems was very high at the beginning of the tests except for CL in Figure 6.1 (TC1) where the pH value at the beginning of the test was almost the same as the pH of the leachant. The pH of Secunda systems (SC1) was found to be greater than 13 immediately after the equilibration. In the case of Tutuka systems (TC1), the pH of the fly ash-brine system without antiscalant was found to be in the range of 7 and 12 at the beginning of the interaction tests whereas the Tutuka fly ash-brine with antiscalant behaved in the same way as the Secunda system with pH of ≈12. The variation observed in the pH values of the systems could be attributed to the variation in the concentrations of the basic oxides such as CaO and MgO in Secunda fly ash when compared to Tutuka fly ash (as reported in chapter 4; Table 4.2). The pH of Secunda systems (SC1) was at the highest at the beginning of the experiments with pH of ≈13 while the pH of Tutuka systems (TC1) increased slowly reaching the maximum pH above 12 at L/S 0.5. The high pH values observed in the leachates of the up-flow percolation systems during the first few volumes of flow could be attributed to the dissolution and hydrolysis of alkalinity-contributing oxides such as CaO on the surface of the fly ash particles during the three days equilibration period (Fatoba 2008; Iwashita *et al.,* 2005; Reardon *et al.,* 1995). After the initial increase, the pH of the systems (SC1 and TC1) gradually decreased over several bed volumes of flow. The gradual decrease in the pH of the systems after the maximum pH was reached at L/S 0.5 could be due to the slow release and continuous flushing-out of the dissolved alkalinity-contributing components as a result of the low flow rate (12 mL/h) applied in the systems. At L/S 5 in SC1, an increase in the pH was observed while such increase was observed in TC1 between L/S 2 and 5. The increase in pH observed between L/S 2 and 5 in the systems could be attributed to the further dissolution of the fly ash matrix after the readily soluble components were released. The effect of the antiscalant on the pH of the fly ash-brine systems was not significant as the pH trends of the fly ash-brine systems (CL) were similar to the fly ash-brine-antiscalant systems (CLA) except at the beginning of the test in Tutuka systems. At the beginning of the up-flow percolation tests, the pH of the fly ash-brine-antiscalant system (CLA) was slightly higher in Secunda system (SC1) and significantly higher in Tutuka system (TC1) when compared to the pH of the fly ash-brine system (CL). This effect could be attributed to the three days equilibration period during which the antiscalant interacted with the species in the systems. The interactions of the antiscalant apparently resulted in the increased dissolution of the alkalinity contributing phases such as CaO, as an increase was noticed in the release of Ca in the fly ash-brine-antiscalant systems at the beginning of the tests [(Figure 6.3 (TC5)].

After the three days equilibration period, the EC of Tutuka systems (TC2) was initially considerably lower (in the range of 5 and 7 mS/cm for CL and CLA respectively) than the EC of the unreacted brine solutions (UB and UBA) at the beginning of the test. Thereafter, the EC of TC2 increased rapidly to ≈12 mS/cm at L/S 0.2 after which a gradual and steady increase was observed until the end of the test except at L/S 35 where a decrease in the EC values of both fly ash-brine and fly ash-brine-antiscalant systems were observed. On the other hand, the EC of Secunda systems (SC2) increased from ≈15 mS/cm to the maximum of between 30-35 mS/cm at the beginning of the percolation test (after the equilibration) after which a gradual decrease from 35-15 mS/cm in the EC trends were observed for both fly ash-brine and fly ash-brine-antiscalant systems. The low EC values observed in Tutuka systems at the beginning of the test could be attributed to the removal of some major species such as Na, Cl and SO_4 from the fly ash-brine and fly ash-brine-antiscalant systems upon the initial contact of the fly ash with brine. The removal could be as a result of transient precipitation of some elements or mineral phases due to the super-saturation of these species in the systems. The rapid increase observed in the EC thereafter could be attributed to the dissolution of the transient phases or the dissolution of major components locked up in the matrix of the fly ash that are released over time as the pH decreased. This interpretation is based on the fact that the concentrations of Na, Cl and SO_4 in the leachates [Figure 6.3 (TC7) and Figure 6.5 (TC11 and TC13)] were also found to be very low at the same L/S ratio where the EC values of TC1 were found to be low and vice versa. This could therefore suggest that the EC values of the systems are being controlled by the concentrations of Na, Cl and SO_4 in the systems.

In contrast to the Tutuka systems where the EC increased steadily, the EC of Secunda systems decreased steadily from about 35-15 mS/cm. The high EC observed at the beginning of the test, in the case of Secunda system (SC2), could be accounted for by the dissolution of highly soluble components of the fly ash during the three days equilibration period. The gradual decrease in the EC as observed in SC2 could indicate the removal of the dissolved species either by precipitation or as a result of flushing out of some of the dissolved species due to continuous and gradual flow of fresh brine solution in the systems. The almost stable EC of ≈15 mS/cm observed at the end of the tests in SC2 and TC2 could be attributed to the slow dissolution of components locked up in the aluminosilicate matrix that are released over time. Considering the effect of antiscalant on the EC values of the systems, the addition of antiscalant seems to have no effect on the EC as there was no significant difference in the EC trends of either fly ash-brine or fly ash-brine-antiscalant systems [Figure 6.1 (SC2 and TC2)].

6.3.1.2 Aluminum and Silicon

The graphs presenting the release of Al and Si in leachates from the fly ash-brine and fly ash-brine-antiscalant up-flow percolation systems are shown in Figure 6.2 below.

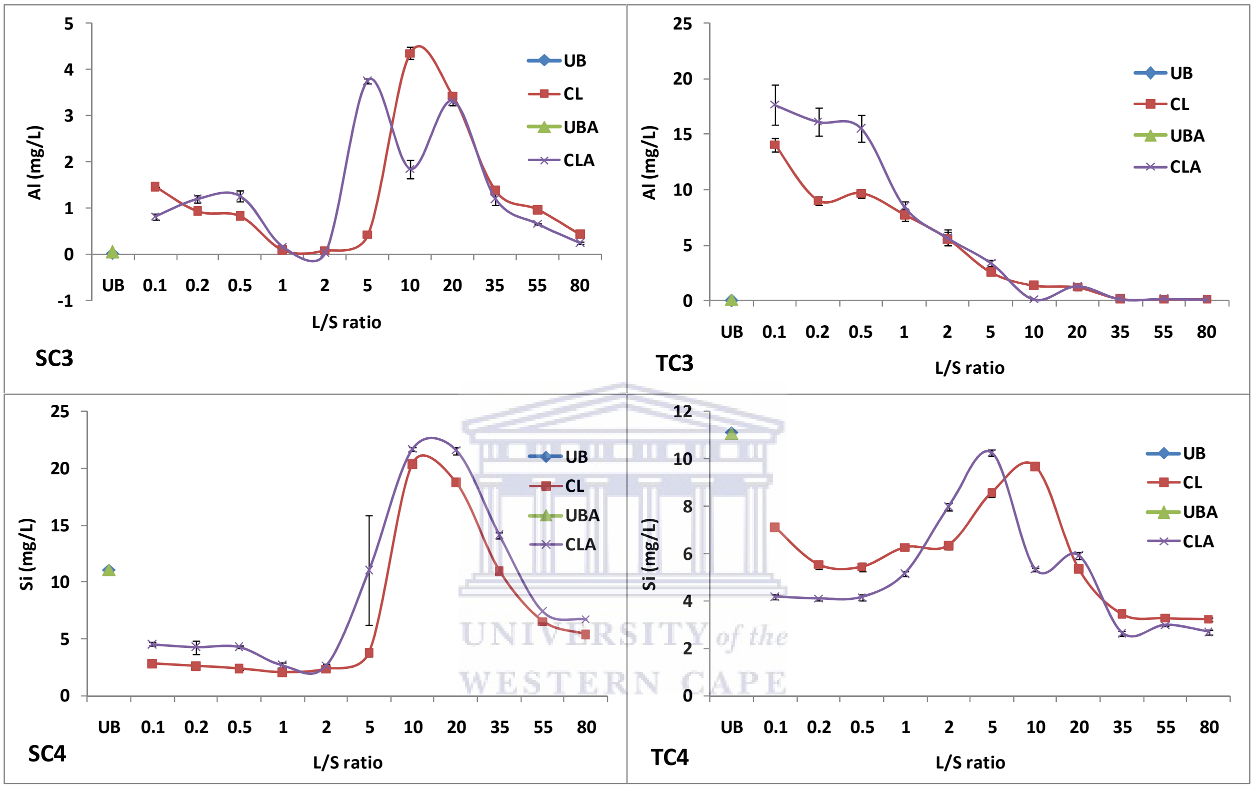

Figure 6.2: The concentration of Al (SC3 and TC3) and Si (SC4 and TC4) released from the up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine-antiscalant leaching trend

The concentration of Al in the leachate samples collected from Secunda up-flow percolation systems (SC3) was between 1-2 mg/L after the equilibration whereas the concentration of Al in the unreacted brine solutions at the beginning of the up-flow percolation tests was almost zero. This indicates that Al was released from fly ash upon equilibration with brine. The concentration of Al in SC3 leachate thereafter reduced to a minimum at L/S 1 and 2 whereafter an increase to about 4 mg/L was observed at L/S 10 and 5 for fly ash-brine systems and fly ash-brine-antiscalant [SC3 (CLA and CL)] respectively after which the concentration of Al gradually decreased in the systems for the remaining L/S ratio. The release of Al in leachates samples of Tutuka systems (TC3) was higher (about 18 mg/L) thus more Al was released from the fly ash after equilibration at the beginning of the test. After the increase observed during equilibration, a gradual decrease in Al concentration was observed in TC3 leachates and continued until the end of the percolation tests. The leaching patterns of Al could be attributed to the precipitation of its hydroxides or as a result of flushing out of Al as a result of continuous inflow of brine solution. The slight increase observed in the concentration of Al in SC3 leachates at the beginning of the tests could be attributed to the dissolution of amorphous aluminosilicates in the fly ash. In fly ash systems, it was argued that after the rapid dissolution of CaO and other soluble salts, the mineral phase most susceptible to weathering are amorphous glassy aluminosilicates and silica (Seoane and Leirós, 2001). The decrease observed at L/S 1-2 and 5 in SC3 could be as a result of formation of transient phases or amorphous Al hydroxide phases such as $Al(OH)_{3,}$ diaspore (AlOOH) and wairakite ($Ca_2Al_2Si_4O_{12}\cdot 2H_2O$) (Georgakopoulos *et al.,* 2002; Tiruta-Barna *et al.,* 2006; Hyks *et al.,* 2009) due to high pH of the up-flow percolation systems. The rapid increase observed at L/S 5 and 10 in SC3 could be accounted for by the dissolution of the transient or by further dissolution of the glassy Al phases. The difference observed in the leaching trend of Al in Tutuka systems (TC3) compared to that of Secunda systems (SC3) could be as a result of the lower pH of the former due to the dust suppression pretreatment it underwent before the sample was taken. The higher concentration of Al in Tutuka systems (TC3) at the beginning of the tests could be as a result of the greater solubility of the amorphous glassy or crystalline Al phases in the fly ash due to the lower pH of Tutuka systems.

The release of Si in both Secunda and Tutuka systems (SC4 and TC4) followed the same trend. The concentration of Si at the beginning of the tests (L/S 0.1-2) was observed to be lower than the Si concentration in UB and UBA which indicates that Si was removed from the brine solution during equilibration. The removal of Si at the beginning of the tests could be due to the formation of transient amorphous Si-bearing mineral phases. Georgakopoulos *et al.* (2002) suggested that the presence of Al and Si in solution at high pH, could lead to the formation of amorphous Al hydroxides and Si-rich mineral phases such as gehlenite ($Ca_2Al_2SiO_{73}SiO_5$) and hatrurite (Ca_3SiO_5). The formation of these phases was possible due to the significant concentration of Ca released into the up-flow percolation systems. A rapid increase in Si concentration was observed at L/S 5-20 and 2-10 in Secunda (SC4) and Tutuka (TC4) systems respectively with more Si released from Secunda fly ash (≈15 mg/L) than Tutuka fly ash (≈6 mg/L). The increase in both systems could be accounted for by the dissolution of the transient secondary mineral phases formed or as a result of the further dissolution of the silica matrix of the fly ash (Ward *et al.,* 2009) in case of Secunda systems (SC4). In the case of Tutuka systems (TC4), the dissolution of some amorphous silica containing phase formed at the beginning of the tests could account for the increase at L/S 5 and 10. This assumption was based on the fact that despite the increase in the concentration of Si at L/S 2-10 in Tutuka systems (TC4), the concentration of Si in Tutuka systems remained lower than its concentration in the UB and UBA. The addition of antiscalants to the system appeared to enhance the dissolution of the fly ash matrix in some cases.

6.3.1.3 Calcium, Strontium and Sulphate

The trends of Ca, Sr and SO_4 concentrations released from the fly ash-brine and fly ash-brine-antiscalant systems during the up-flow percolation tests are shown in Figure 6.3.

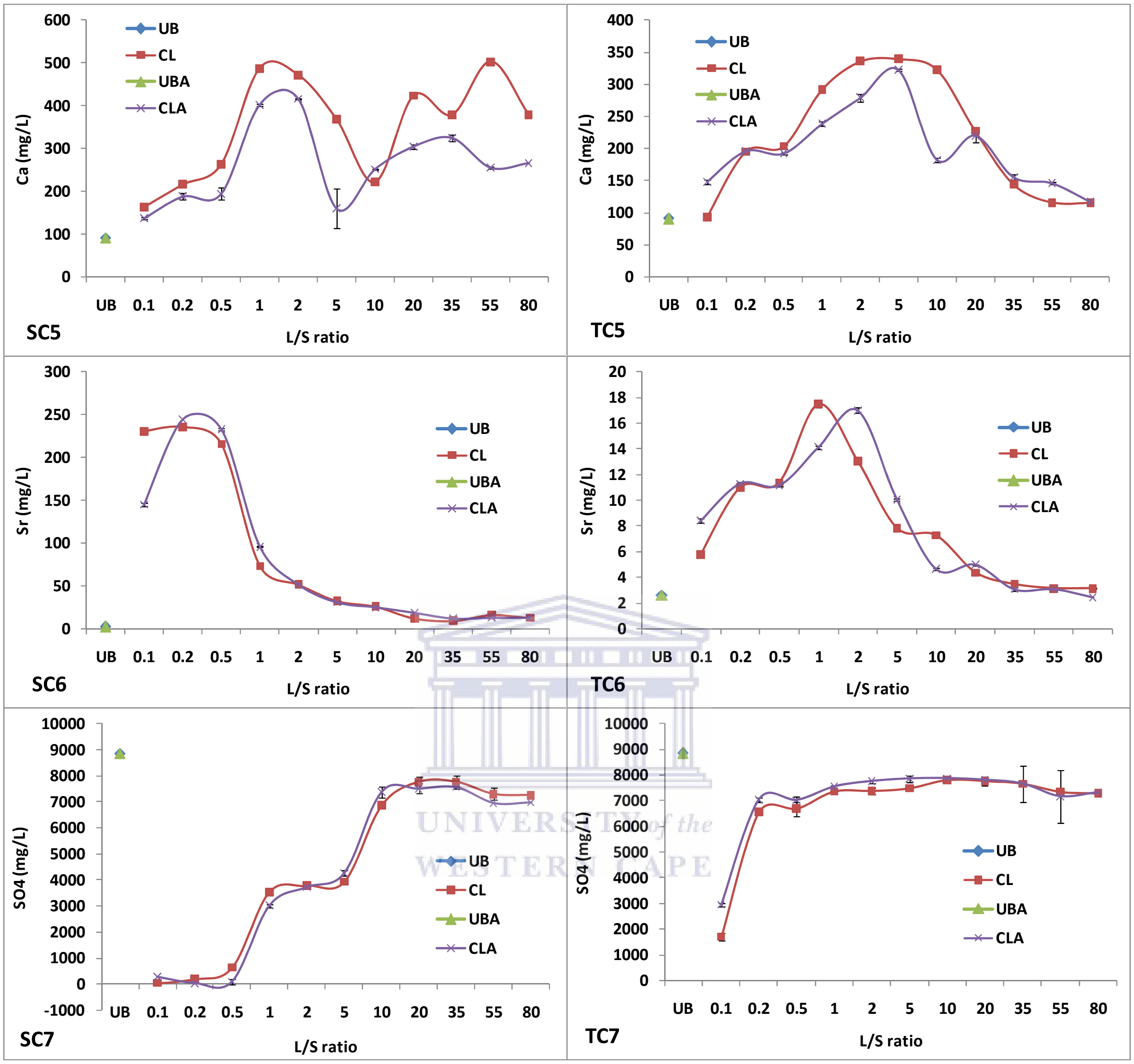

Figure 6.3: The concentration of Ca (SC5 and TC5), Sr (SC6 and TC6) and SO_4 (SC7 and TC7) released from the up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine-antiscalant leaching trend

The concentration of Ca in UB and UBA was about 100mg/L; that of Sr was about 2 mg/L while SO_4 levels were exceptionally high, being nearly 9000 mg/L (Figure 6.3). The concentration of Ca in leachates from both Secunda and Tutuka up-flow percolation systems (SC5 and TC5) slightly increased after equilibration at the beginning of the tests compared with its concentration in the unreacted brine solutions (UB and UBA). The concentration of Ca gradually increased until a maximum of about 500 mg/L and 350 mg/L was reached at L/S 1 and 5 in SC5 and TC5 respectively. A decrease in the concentration of Ca was observed at L/S 5 and 10 in SC5 for CLA and CL respectively after which a gradual increase was observed. The trend of Ca released from the fly ash-brine systems showed that apart from the initial dissolution of readily soluble Ca-rich phases such as CaO, the dissolution of Ca-rich phases locked in the fly ash matrix contributed to the gradual increase in Ca concentration. The fluctuation in the concentration of Ca in the Secunda systems and the gradual decrease observed in Tutuka systems (TC5) after the maximum was reached at L/S 5 could be as a result of depletion of Ca-bearing phases by flushing with brine (more likely as it is a flow-through system) or due to precipitation and dissolution of transient Ca-rich mineral phases in the fly ash-brine and fly ash-brine-antiscalant systems (Georgakopoulos *et al.,* 2002; Hjelmar, 1990). Steenari *et al.* (1999) suggested that the presence of other species such as SO_4 in alkaline fly ash systems could produce Ca-hydrated mineral phases such as gypsum and calcite. Ca in fly ash occurs mainly as lime (CaO), anhydrite ($CaSO_4$) and in the glass matrix, and these anhydrous phases are very reactive when exposed to aqueous solution. Therefore the solubility and reactivity of Ca with other species could responsible for the trend of Ca observed in leachates in the up-flow percolation systems. The trends of Ca in the systems showed a slight influence of the antiscalant on the release of Ca as the concentration of Ca released from the fly ash-brine-antiscalant (CLA) systems was slightly lower than that of the fly ash-brine systems (CL). This indicates that the antiscalant could slow down the dissolution of the Ca-rich phases in the systems and on the other hand may facilitate the precipitation of new Ca-rich mineral phases. This observation was contrary to the expectation that the addition of antiscalant to brine could inhibit the formation of scales such as $CaSO_4$ in the brine solution (Al-Shammiri *et al.,* 2000). The pH or the dosage of antiscalant (50 mg per litre of brine) of the systems may limit the effect of the anti-scalant.

The leachates from both Secunda and Tutuka systems showed an increase in Sr concentration at the beginning of the tests after equilibration compared with Sr levels in the brine solutions (UB and UBA). The increase rapidly reached a maximum of about 250 mg/L at L/S 0.2 in the case of leachates from Secunda systems (SC6) while the maximum concentration of Sr (≈16 mg/L) in the Tutuka systems (TC6) was attained at L/S 1 and 2 (Figure 6.3). The concentration of Sr thereafter decreased gradually until the end of the percolation tests. There was a significant difference in the concentration of Sr released from Secunda fly ash compared to Tutuka fly ash, which could be attributed to the difference in the concentration of Sr in the fresh fly ashes (Table 4.2). The initial increase in concentrations of Sr could be due to the dissolution of its oxide in the fly ashes. Reardon *et al.* (1995) observed that the oxide of Sr, when in contact with aqueous solutions, is readily soluble leading to high concentration of Sr in the leachates of the fly ash systems. The gradual decrease in the concentration of Sr after the maximum was reached in the systems could be due to the formation of new Sr-rich mineral phases or as a result of the flushing out of the dissolved Sr species due to the continuous inflow of the brine solutions. The effect of antiscalant on the release of Sr in the systems showed that antiscalant retarded the release of Sr slightly in the Tutuka systems and also in the Secunda systems but did not affect the overall amount of Sr released.

The concentration of SO_4 in the leachates [Figure 6.3 (SC7 and TC7)] from both Secunda and Tutuka systems showed a very significant decrease in concentration after equilibration at the beginning of the up-flow percolation tests compared with the concentration of SO_4 in unreacted brine solutions (UB and UBA). This indicates that SO_4 was removed from the brine during and after the equilibration. The concentration of SO_4 removed from the brine solution by the fly ashes during equilibration was between 6000 and 9000 mg/L. After the very low concentration of SO_4 observed in the leachates at the beginning of the tests, the SO_4 concentration increased again until a maximum (7000-8000 mg/L) was observed at L/S 20 and 10 in Secunda (SC7) and Tutuka (TC7) up-flow percolation systems respectively. The trends of SO_4 showed that SO_4 was removed from the brine solutions by the fly ashes as a result of precipitation of SO_4 bearing phases. According to Bock (1961), in a systems containing considerable concentration of Ca and SO_4, the precipitation of gypsum ($CaSO_4.2H_2O$) could control the release of SO_4 but when the solution contains excess of Na or KCl, the precipitation of anhydrite is possible only at high temperature. The removal of SO_4 from the systems especially at the beginning of the tests could be attributed to the formation of Ca-SO_4-rich mineral phases such as gypsum. According to the previous study (Fatoba, 2008) on the release of species from fly ash when in contact with ultrapure water, Ca was significantly leached from fly ash into solution when in contact with water. The significant amounts of SO_4 present in the brine solution could interact with the Ca released from the fly ashes during equilibration to form new Ca-SO_4 rich mineral phases. Therefore the low concentrations of Ca [Figure 6.3 (SC5 and TC5)] and SO_4 [Figure 6.3 (SC7 and TC7)] could be attributed to the interactions between these species to form new mineral phases. Gypsum is moderately soluble in water or in aqueous solution. The gradual dissolution of the transient hydrated Ca-SO_4 rich phase formed at the beginning of the tests (during equilibration period) could be responsible for the increase in the concentration of SO_4 after the initial minimum concentration.

6.3.1.4 Magnesium, Barium and Boron

Figure 6.4 presents the concentrations of Mg (SC8 and TC8), Ba (SC9 and TC9) and B (SC10 and TC10) released in the leachates of Secunda and Tutuka systems during the up-flow percolation tests.

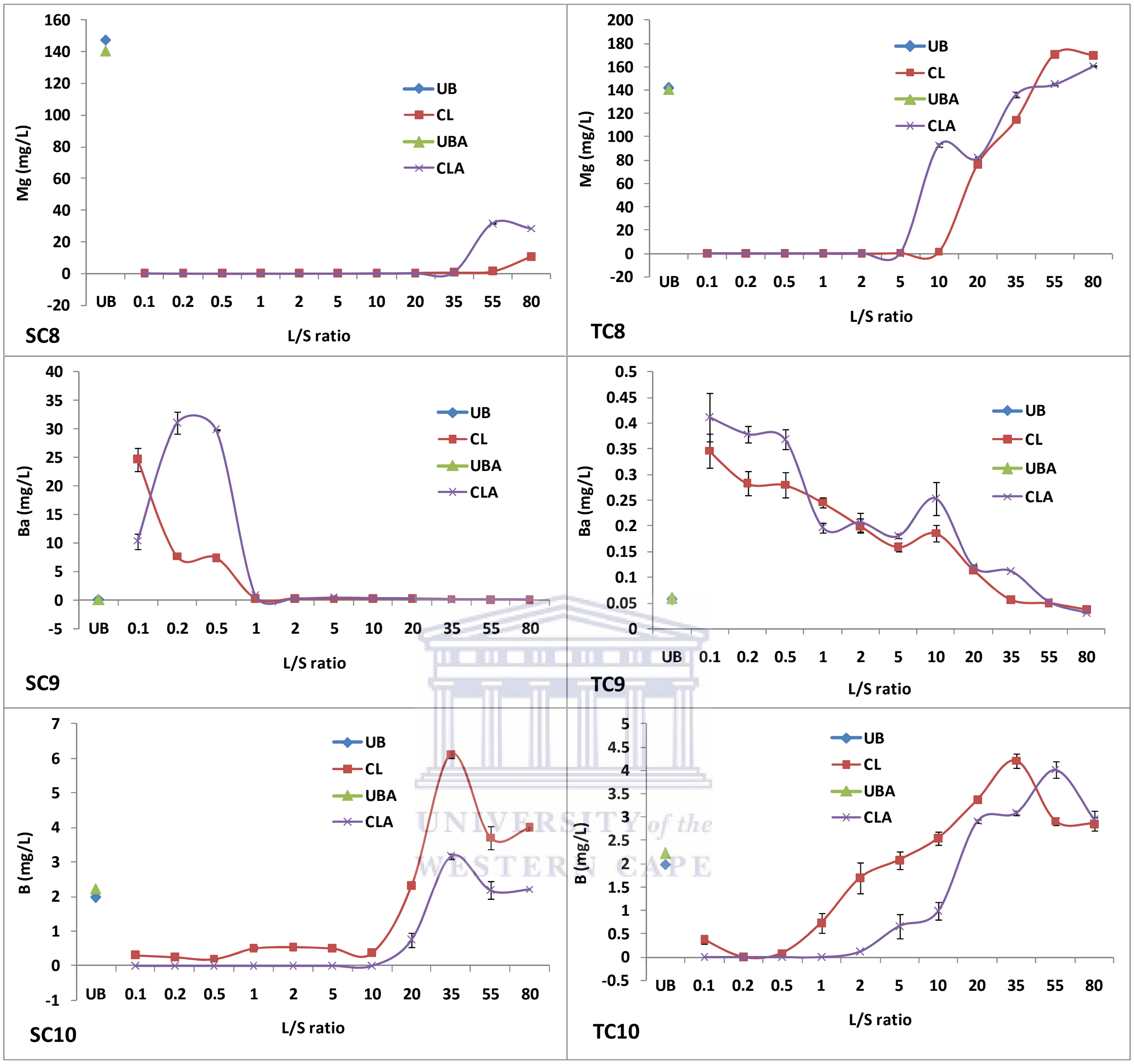

Figure 6.4: The concentration of Mg (SC8 and TC8), Ba (SC9 and TC9) and B (SC10 and TC10) released from the up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine-antiscalant leaching trend

The concentration of Mg in the UB and UBA was approximately 140 mg/L; those of Ba and B were approximately 0.05 mg/L and 2 mg/L respectively (Figure 6.4). The concentration of Mg in the leachates of the up-flow percolation systems indicates the removal of approximately 140 mg/L Mg from the brine solutions during the interactions with the fly ashes despite the continuous inflow of the fresh brine solutions [(Figure 6.4 (SC8 and TC8)]. The concentration of Mg in the leachates was very low (nearly zero) at the beginning of the tests compared with the concentrations of Mg in the unreacted brine solutions (UB and UBA). An increase in the concentration of Mg was observed at L/S 55 and 10 in Secunda (SC8) and Tutuka (TC8) up-flow percolation systems respectively. The low concentration of Mg which indicates its removal from the systems could be attributed to the formation of Mg-rich mineral phases such as $Mg(OH)_2$ due to the alkaline pH of the systems which favours the formation of these mineral phases. The hydrolysis of MgO in fly ash in alkaline condition has been observed to form sparingly soluble brucite ($Mg(OH)_2$) (Warren and Dudas, 1984; Tiruta-Barna *et al.,* 2006), and this could account for the low level of Mg in the leachates of the up-flow percolation tests. Apart from MgO present on the surface of fly ash, Mg is also present in the slowly dissolving glassy phase (Mattigod *et al.,* 1990), and this could account for the gradual increase observed in Mg concentration in the leachates above levels found in UB over time at L/S 55 in Tutuka (TC8) systems. The effect of antiscalant was not evident on the release of Mg.

The trend of Ba concentration in the leachates from the fly ash systems was different from that of Mg, as an increase of about 30 mg/L in the concentration of Ba in the case of Secunda systems and only about 0.4 mg/L in the case of Tutuka systems was observed in the systems after equilibration at the beginning of the up-flow percolation tests [Figure 6.4 (SC9 and TC9)]. A sharp decrease in Ba concentration from about 30 mg/L to 0.5 mg/L was observed in Secunda (SC9) systems at L/S 1 while the decrease from 0.4 mg/L to 0.05 mg/L observed in Tutuka (TC9) systems was more gradual. The difference in the trends observed in the two systems could be as a result of the difference in the pH values of the up-flow percolation systems. The initial increase in the concentration of Ba in the systems could be attributed to the dissolution of its soluble oxides in the fly ash during the equilibration period. The oxide of Ba in fly ash is readily soluble when in contact with aqueous solution (Reardon *et al.,* 1995) thereby increasing the concentration of Ba in the systems. The decrease observed in the concentration of Ba after attaining the maximum levels at the beginning of the tests could suggest the precipitation of secondary mineral phases such as barite. Due to the high concentration of SO_4 in the brine solutions, the precipitation of barite ($BaSO_4$) or Sr-substituted barite $(Ba,Sr)SO_4$ in the alkaline systems is highly possible. The possible precipitation of Sr-substituted barite as one of the mineral phases controlling the release of Ba in the systems was evident as the trends of Sr and Ba especially in Secunda systems were almost the same.

The concentration of B (<0.5 mg/L) in the up-flow percolation leachates was lower than its concentration in unreacted brine solutions (UB and UBA) (≈2 mg/L) at the beginning of the tests [Figure 6.4 (SC10 and TC10)]. This is an indication that B was removed from the brine solutions during equilibration at the start of the percolation tests. After the initial decrease in B concentration, there was a gradual increase in its concentration to about 6 mg/L and 4.5 mg/L at L/S 35 in Secunda (SC10) and Tutuka (TC10) systems respectively to levels above those of UB and UBA. Comparison of the L/S ratio at which B leaching increased [Figure 6.4 (SC10 and TC10)] with the pH profiles (Figure 6.1) showed that the leaching of B from the fly ashes increased when the pH of the systems had decreased to ≈11 [Figure 6.1 (SC1 and TC1)]. This observation shows the effect of gradual decreasing of pH in the fly ash-brine and fly ash-brine-antiscalant systems on the release of B. B exists as an oxyanion in alkaline solution, and can co-precipitate with $CaCO_3$ or be substituted for SO_4 in ettringite if present in the systems (Hollis *et al.,* 1988; Jankowski *et al.,* 2006). The decrease observed in concentration of B during equilibration at the beginning of the percolation tests could be as a result its entrapment in the ettringite structure. The increase observed at L/S 20 and 1 in Secunda (SC10) and Tutuka (TC10) systems respectively could be attributed to the dissolution of the amorphous and aluminosilicate glassy matrix that incorporated B (Hulett *et al.,* 1980; Querol *et al.,* 1995).

The addition of antiscalant had a negligible effect on the release of B in the systems as the concentration of B in the fly ash-brine-antiscalant systems was found to be lower than what was observed in the fly ash-brine systems at each L/S ratio. The slight retardation observed in the leaching of B in the fly ash-brine-antiscalant systems indicates that addition of antiscalant to the brine solution could slow down the release of B from the systems.

6.3.1.5 Sodium, Potassium and Chloride

The concentrations of Na (SC11 and TC11), K (SC12 and TC12) and Cl (SC13 and TC13) in the leachates of Secunda and Tutuka up-flow percolation systems are shown in Figure 6.5 below.

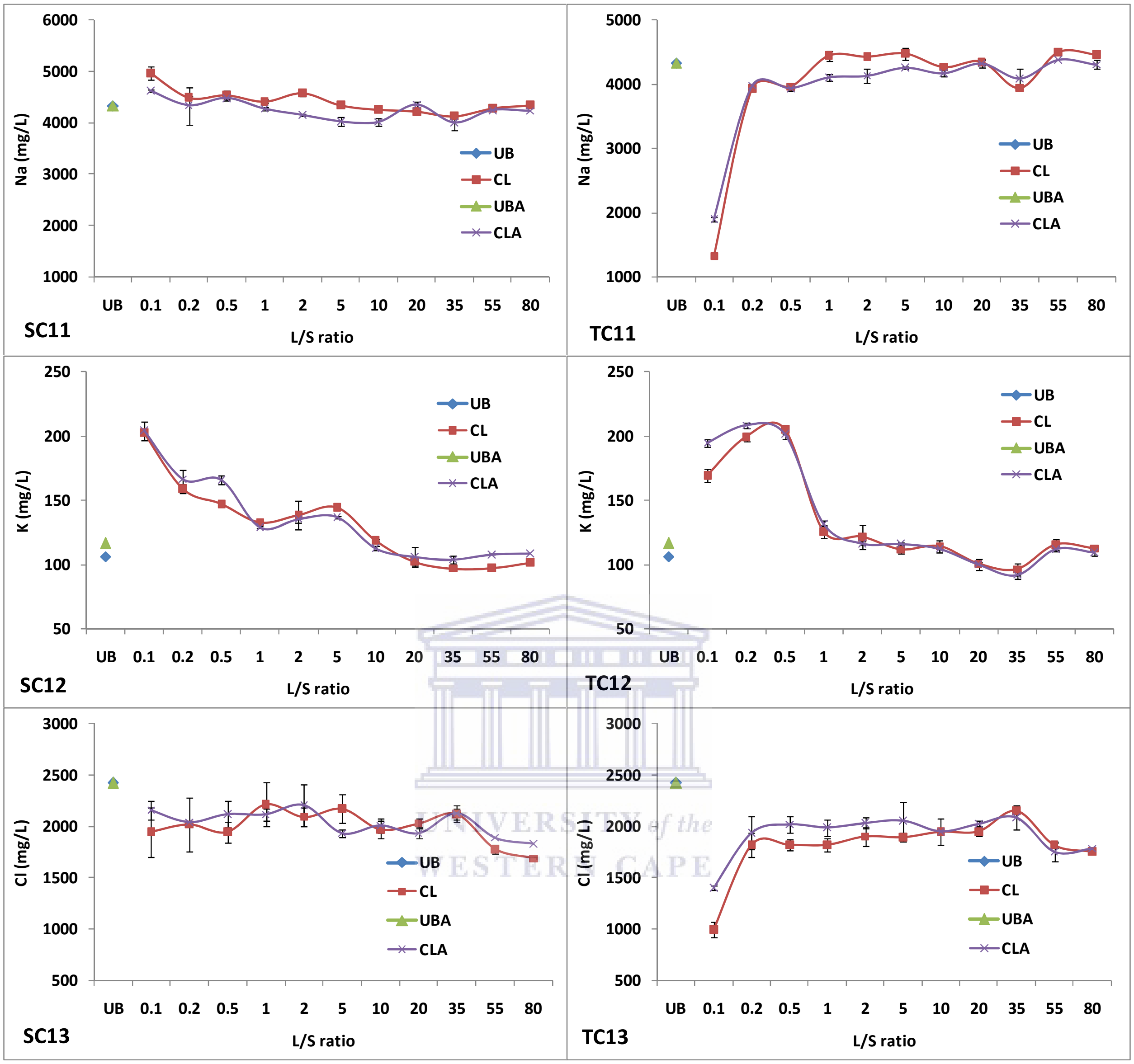

Figure 6.5: The concentration of Na (SC11 and TC11), K (SC12 and TC12) and Cl (SC13 and TC13) released from the up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine-antiscalant leaching trend

Na concentration was very high in UB and UBA, being approximately 4400 mg/L; K levels were lower at approximately 110 mg/L whereas Cl levels were high being around 2400 mg/L. Two different trends were observed for the release of Na into the leachates from Secunda (SC11) and Tutuka (TC11) up-flow percolation systems (Figure 6.5). The concentration of Na in UB and

UBA was approximately 4400 mg/L, and a slight increase in the concentration of Na (approximately 5000 mg/L) was observed in Secunda (SC11) systems after equilibration while initially, at L/S 0.1, a significant decrease to about 1000 mg/L in Na concentration was observed in Tutuka (TC11) systems immediately after equilibration and at the beginning of the up-flow percolation tests. After the initial increase in the concentration of Na in SC11, a slight and slow decrease (slightly lower than the levels in UB and UBA) was observed and this concentration (>4000 mg/L) was maintained throughout the period of the tests. On the other hand in the Tutuka systems, the concentration of Na in TC11 increased abruptly at L/S 0.2 from approximately 1000 mg/L to 4000 mg/Land was almost equal to its concentration in UB and UBA throughout the percolation tests with small fluctuation except at L/S 35 where a slight decrease in the concentration was observed. The slight increase of Na at L/S 0.1 in Secunda (SC11) systems when compared with the concentration in UB and UBA, could be attributed to the leaching of Na from the fly ash during the three days equilibration period while the initial decrease in Na concentration in Tutuka (TC11) systems immediately after the equilibration period may be as a result of the formation of transient Na-rich phase upon contact with fly ash due to the super-saturation of Na in the brine containing systems. The nearly immediate dissolution of the transient Na-rich phase or the reduction in the capacity of the fly ash to capure more Na from the brine due to continous flow of brine may account for the increase in Na concentration in TC11 at L/S 0.2. The concentration of Na in both Secunda and Tutuka up-flow percolation systems was stable after L/S 0.5, and slightly lower than the concentration in UB and UBA. These trends indicate that after the initial removal of Na, the capacity of the fly ashes to remove more Na from the brine solutions during the tests reduced as a result of continous flow of fresh brine solution. Moreover, the addition of antiscalant had no significant impact on the release of Na in the systems.

The trend of Cl was similar to that observed for Na in the leachates. However, the concentration of Cl in the leachates after contact with fly ash was lower than the concentration in UB and UBA throughout the period of the up-flow percolation tests. This indicates that some Cl was removed from the brine solution throughout the period of the up-flow percolation tests. Cl was initially removed from the brine solution in Tutuka systems after equilibration. Between L/S 0.1 and 0.2, the Cl removed from Tutuka systems was re-dissolved and the levels increased from about 1000 mg/L to about 2000 mg/L for the duration of the experiments with small fluctuation. The removal patterns of Cl in Tutuka systems (TC13) corresponded to those of Na (TC11) indicating that the removal of Cl from the systems could be controlled by the formation of a transient halite (NaCl) phase at the beginning of the tests. Due to the sufficient concentration of Ca and Al in the up-flow percolation systems as a result of matrix dissolution of fly ash, the probable formation of Friedel's salt [$Ca_4Al_2Cl_2(OH)_{12}{\cdot}4H_2O$] could also account for the reduction in the concentration of Cl after the initial stages in the systems (Suryavanshi and Swamy, 1996; Bothe and Brown, 2004; Hyks *et al.,* 2009). The addition of antiscalant appeared to inhibit Cl removal in the Tutuka systems but not in the Secunda systems.

The concentration of K in the systems increased by approximately 100 mg/L compared to UB and UBA at the beginning of the tests [Figure 6.5 (SC12 and TC12)]. The concentration in the leachates thereafter reduced until an almost stable concentration of approximately 100 mg/L (similar to UB and UBA) was observed at L/S 20 and 1 in Secunda and Tutuka up-flow percolation systems respectively. The initial increase observed after equilibration in the concentration of K in the fly ash-brine systems could be attributed to the dissolution of the soluble salts of K such as sylvite (KCl) on the surface of the fly ash particles (Hyks *et al.,* 2009). The gradual decrease in the concentration before a stable concentration of K was attained could be attributed to the flushing out of soluble K due to continuous inflow of brine solutions into the systems. The trend of K concentration showed that the interactions of the brine solutions with the fly ashes did not remove K from the brine solutions.

The addition of antiscalant to the brine solution seemed to have no significant effect on the release of Na, K and Cl in the up-flow percolation systems as generally no significant difference was observed between the concentrations of these species in fly ash-brine and fly ash-brine-antiscalant systems.

6.3.1.6 Iron and Manganese

Figure 6.6 shows the release of Fe and Mn into leachates from Secunda (SC12 and SC13) and Tutuka (TC12 and TC13) fly ash-brine up-flow percolation systems.

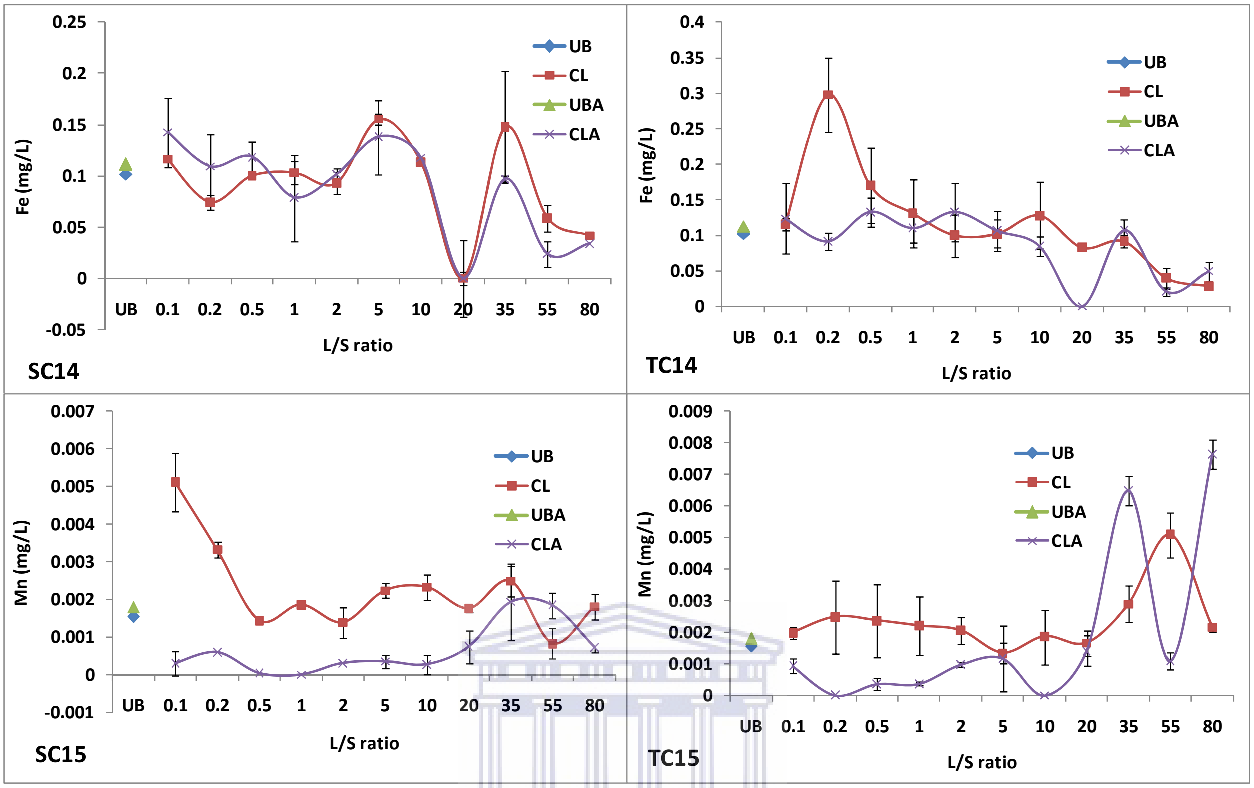

Figure 6.6: The concentrations of Fe (SC14 and TC14) and Mn (SC15 and TC15) released from the up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine- antiscalant leaching trend

Low levels of Fe and Mn were present in UB and UBA, 0.1 mg/L and 0.002 mg/L respectively. The trend of Fe and Mn released into the leachates of the up-flow percolation tests was almost the same as no significant difference was observed in the concentration of these species in the leachates when compared with their concentrations in UB and UBA [Figure 6.6 (SC14, SC15, TC14 and TC15)]. The concentration of Fe in Secunda systems at the beginning of the tests fluctuated around the levels observed in the UB and UBA except at L/S 20 where a lower concentration of Fe was observed. The slight increase in the concentrations of Fe and Mn at the beginning of the tests could be attributed to the partial dissolution of their oxides from the fly ash surface when in contact with the brine solutions. The slight fluctuation observed in the release of Fe and Mn could be attributed to the dissolution and precipitation of Fe and Mn-oxyhydroxides in the systems due to the high pH of the systems. It was suggested that the concentrations of the Fe and Mn in fly ash leachates are controlled by precipitation of their hydroxides (Roy and Griffin, 1984). The effect of the antiscalant was revealed in the release trends of Mn as the concentration of Mn in the fly ash-brine-antiscalant was found to be lower than that of fly ash-brine systems and even lower than the Mn concentration in UB and UBA. This indicates that the antiscalant in the brine solution could enhance the precipitation of the Mn-oxyhydroxides in the systems. The increase in the concentration of Mn in TC15 over time could be attributed to the decrease in the pH of the systems over time which may have caused the dissolution of Mn precipitates from the matrix of the fly ash.

6.3.1.7 Cobalt, Nickel and Lead

The concentrations of Co (SC16 and TC16), Ni (SC17 and TC17) and Pb (SC18 and TC18) in the leachates released from the up-flow percolation tests is presented in Figure 6.7 below.

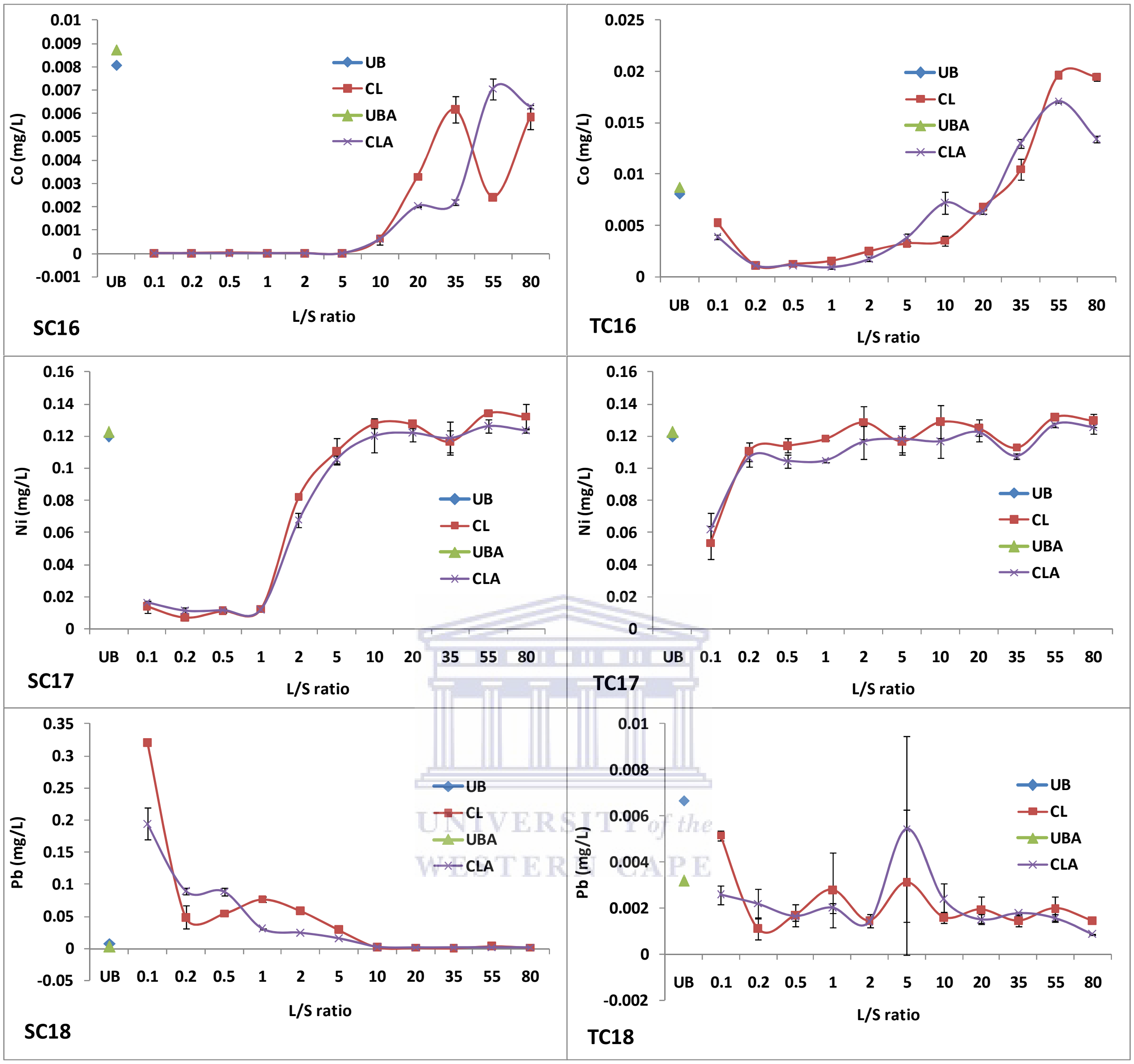

Figure 6.7: The concentration of Co (SC16 and TC16), Ni (SC17 and TC17) and Pb (SC18 and TC18) released from the up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine-antiscalant leaching trend

Although present in minor concentration, the levels of Pb and Ni were an order of magnitude higher than Co concentration in the unreacted brine. Pb being present in concentration of approximately 0.3 mg/L, Ni levels was around 0.1 mg/L but Co concentration being approximately 0.009 mg/L (Figure 6.7). Co was immediately removed from the brine solutions after contact with Secunda fly ash but increased after L/S 10 to around 0.006 mg/L. In the case of Tutuka systems, Co levels decreased from approximately 0.01 mg/L to 0.005 mg/L. Co removal in the leachates of the up-flow percolation systems (SC16 and TC16) was initially significant compared to the concentration of Co in UB and UBA. This indicates that Co was removed to levels below 0.001 mg/L from the brine solutions by interactions with the fly ashes at L/S 0.1-10 during the interactions tests. Thereafter, the concentration of Co gradually increased in the leachates of Secunda systems (SC16) at L/S 10, and at L/S 2 in the case of Tutuka systems (TC16). The gradual and fluctuating increase continued until the end of the percolation tests with the concentration of Co in Tutuka systems (TC16) increasing to above 0.02 mg/L, double the amount that was observed in UB and UBA from L/S 35. The initial removal of Co from the brine solutions during the percolation tests despite the continuous inflow of brine solution indicates that Co was removed as a result of transient precipitation of Co-containing phases or co-precipitated with other phases in the systems. The gradual increase observed in SC16 from L/S 10 may not necessarily be due to the dissolution of the Co-containing mineral phase(s) formed at the beginning of the tests, but could be due to the inability of the fly ash to cause precipitation of more Co-containing phases due to continuous inflow of brine solutions. While the gradual increase in Co concentration in TC16 could be associated with the dissolution of Co-containing phases in the fly ash due to decrease in the pH of the systems from alkaline to circum-neutral. The addition of antiscalant delayed the release of Co at some stage in the Secunda systems but not in the Tutuka systems.

Ni was removed from the brine solution during the initial stages of the up-flow percolation systems. The concentration of Ni in the leachates was lower than what was observed in the unreacted brine solutions (UB and UBA) from the beginning of the tests until L/S 10 in the case of Secunda systems and until L/S 0.2 in the case of Tutuka systems. This implies that Ni was initially removed from the brine solutions by the fly ashes. The concentration of Ni in the leachates was below 0.02 mg/L from L/S 0.1 to 1 in the case of Secunda systems (SC17) after which a rapid increase was observed in the concentration of Ni up to approximately 0.13 mg/L. In the case of Tutuka systems (TC17), the concentration of Ni was below 0.06 mg/L at L/S 0.1 and increased thereafter to approximately 0.12 mg/L at L/S 0.2. Ni has been observed not to be easily hydrolyzed (Rio *et al.,* 2002) which could suggest that its removal at the beginning of the tests may not be as a result of precipitation of transient Ni-containing mineral phases in the systems. However, the removal of Ni from the systems at the beginning of the test could be due to adsorption of Ni on the negatively charged surface of the fly ash particles (Ram *et al.,* 2007). The fact that Ni is weakly adsorbed on the surface of fly ash particles (Rio *et al.,* 2002) could lead to easy desorption of Ni over time thereby increasing its concentration in the leachates. The lowering of the pH (≈9) of the up-flow percolation systems towards the end of the tests could lead to the leaching of adsorbed Ni into the systems. The removal or release of Ni in the systems was not significantly affected by the addition of antiscalant as only a slight difference was observed in the concentration of Ni in the leachates of fly ash-brine and fly ash-brine-antiscalant systems.

The trends of Pb concentration in the leachates of Secunda and Tutuka up-flow percolation systems [Figure 6.7 (SC18 and TC18)] were different from those of Ni and Co. The concentration of Pb in Secunda systems increased immediately to 0.3 mg/L and was two order of magnitude higher than that observed in UB and UBA indicating that Pb was immediately released from the Secunda fly ash during the equilibration period whereas in Tutuka systems, Pb decreased to below 0.002 mg/L. In contrast to the weak hydrolysis of Ni in solution, Pb is one of the more easily hydrolyzed ions (Rio *et al.*, 2002). The rapid dissolution and hydrolysis at high pH may account for the increasing trend of Pb ions in the Secunda systems at the beginning of the tests. The levels of Pb in Secunda systems ranged between zero and 0.3 mg/L whereas the Tutuka systems was two order of magnitude lower, ranging between 0.001 and 0.005 mg/L. The differences observed in the concentration of Pb during the tests when comparing the two fly ash-brine systems could be attributed to the pretreatment and conditioning of Tutuka fly ash with brine before the sample was collected for this study, (see chapter 3, section 3.2) during which part of the hydrolysable Pb ions in the fly ash may have leached out. After the initial increase, the concentration of Pb in the leachates of Secunda systems reduced sharply (SC18) which could be due to the flushing out of the hydrolyzed Pb during the first few volumes of brine passed through between L/S 0.1 0.2. The concentration of Pb thereafter in SC18 and TC18 remained relatively steady with minor fluctuation that could be as a result of its adsorption or desorption on the surface of the fly ash particles. Due to the high pH of the systems, the surfaces of the fly ash particles were negatively charged thereby adsorbing the positively charged Pb ions in the systems (Alinnor, 2007). The effect of the antiscalant upon the release of Pb was negligible as the concentration of Pb in the fly ash-brine and fly ash-brine-antiscalant systems was almost the same except at L/S 0.1 where variation in the concentration was observed.

6.3.1.8 Copper and Zinc

Figure 6.8 below presents the release of Cu (SC19 and TC19) and Zn (SC20 and TC20) from the fly ash-brine and fly ash-brine-antiscalant systems of Secunda and Tutuka up-flow percolation tests.

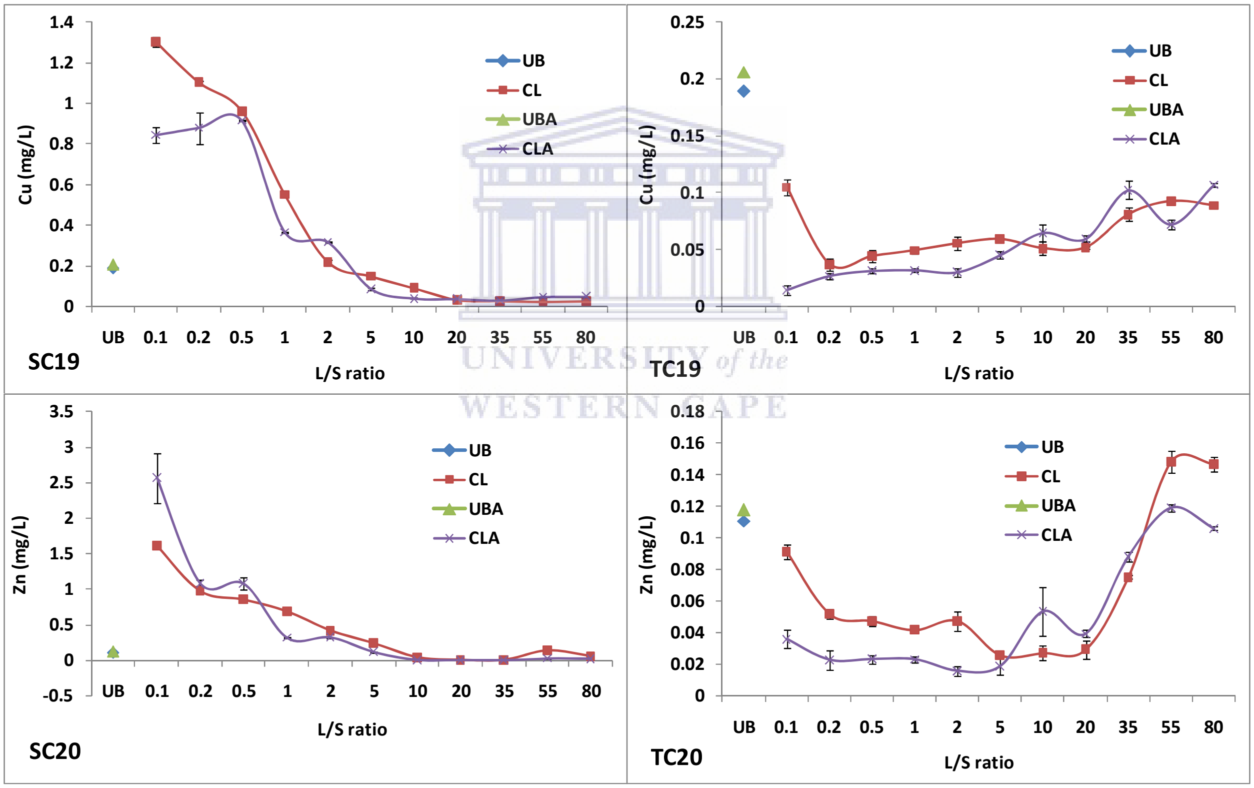

Figure 6.8: The concentration of Cu (SC19 and TC19) and Zn (SC20 and TC20) released from the up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine-antiscalant leaching trend

The levels of Cu in the UB and UBA were around 0.2 mg/L, whereas Zn levels were approximately 0.12 mg/L. The release of Cu and Zn in the leachates of both Secunda and Tutuka up-flow percolation systems followed similar trends (Figure 6.8). It was observed that the concentrations of Cu and Zn in Secunda (SC19 and SC20) systems increased after equilibration to around 1 mg/L or 2 mg/L respectively at the beginning of the experiment, and were considerably higher than what was observed in unreacted brine solutions (UB and UBA) indicating leaching from Secunda fly ash. After the initial increase, the concentrations of Cu and Zn gradually decreased in the Secunda systems until concentrations lower than the Cu and Zn concentrations in UB and UBA was attained at L/S 20 and 10 for Cu (SC19) and Zn (SC20) respectively. In contrast to what was observed in the Secunda systems, the concentrations of Cu and Zn in Tutuka systems (TC19 and TC20) were initially lower than the concentrations of Cu and Zn in the UB and UBA indicating their removal upon contact of the brine solutions with Tutuka fly ash. A gradual increase was observed in the concentrations of Cu and Zn thereafter in the leachates from Tutuka systems but not up to the concentrations in unreacted brine solutions except at L/S 55 and 80 where a higher concentration was observed for Zn in TC20. The lower concentration of Cu and Zn in Tutuka systems when compared with their concentrations in UB and UBA indicates that these species were removed from the brine solutions as a result of interactions with the fly ash. But the increase in the concentrations of Cu and Zn at the beginning of the tests in the case of Secunda systems could indicate the rapid dissolution of soluble Cu and Zn species that were present on the surfaces of Secunda fly ash. The pretreatment of Tutuka fly ash before the sample was taken may have led to the leaching of these species from the surfaces of the fly ash particles before the experiment, and this could account for their initial lower concentrations in Tutuka systems after equilibration at the beginning of the tests. However, the behaviour of Cu and Zn is considered to be governed by adsorption process due to the high pH of the fly ash-brine and fly ash-brine-antiscalant systems. At high pH, adsorption of species such as Cu, Zn and Pb on the surfaces of the fly ash particles are very high as the surfaces of the fly ash particles become negatively charged thereby attracting the positively charged ions of Cu and Zn (Hequet *et al.,* 2001; Rao *et al.,* 2002; Alinnor, 2007; Pan *et al.,* 2003) in the systems.

The effect of antiscalant was slightly evident in the removal of Cu and Zn from the up-flow percolation systems as the concentrations of leachable Cu and Zn observed in Secunda fly ash-brine-antiscalant systems were slightly lower that what were observed in the Secunda fly ash-brine systems.

6.3.1.9 Arsenic, Chromium and Molybdenum

The concentrations of As, Cr and Mo released from the up-flow percolation tests carried out on Secunda and Tutuka fly ashes and brine solutions are presented in Figure 6.9 (SC21-SC23 and TC21-TC23).

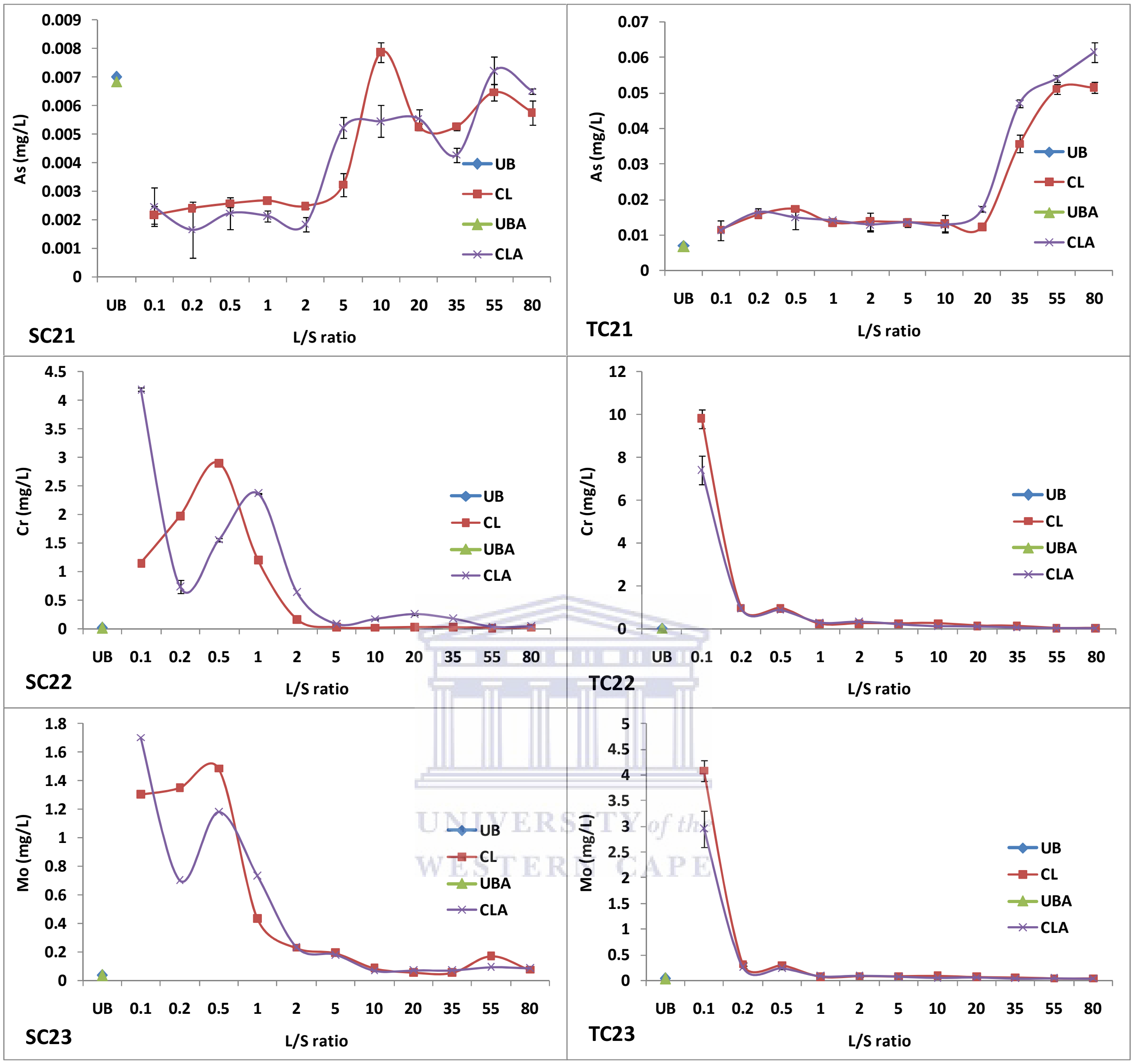

Figure 6.9: The concentration of As (SC21 and TC21), Cr (SC22 and TC22) and Mo (SC23 and TC23) released from the up-flow percolation tests as a function of L/S ratio: UB = unreacted brine, UBA = unreacted brine and antiscalant, CL = fly ash-brine leaching trend, CLA = fly ash-brine-antiscalant leaching trend

The concentration of As in UB and UBA was around 0.007 mg/L whereas that of Cr and Mo was 0.02 mg/L and 0.04 mg/L respectively. The concentration of As in the Secunda systems (SC21) after the contact of brine with the fly ash was initially lower than its concentration in UB and UBA throughout the interactions period except at L/S 10 where a slightly higher concentration

(0.008 mg/L) was observed in Secunda fly ash-brine leachate (CL) [Figure 6.9 (SC21 and TC21)]. In the case of Tutuka systems (TC21), the concentration of As in the leachates was initially slightly higher (between 0.01 and 0.02 mg/L) than the concentration in UB and UBA after the beginning of the tests whereafter the concentration increased significantly to 0.06 mg/L at L/S 35. The lower concentration of As in Secunda systems (SC21) at the beginning of the tests compared with the As in UB and UBA showed that As was removed from the brine solutions by Secunda fly ash. The removal of As from the Secunda fly ash-brine and fly ash-brine-antiscalant systems could be governed by the precipitation of transient As-containing phases such as $Ba_3(AsO_4)_2$. The concentration of As in solution can also be reduced by the precipitation of $Ca_3(AsO_4)_2$ at alkaline pH when a considerable amount of Ca is present in the solution such as the case in this study (see Figure 6.3) (Goh and Lim, 2004; Jankowski *et al.*, 2006). It was also suggested by Eary *et al.* (1990) and Wagemann, (1978) in their studies that the precipitation of $Ba_3(AsO_4)_2$ is the likely controlling solid phase for As in solutions where Ba concentrations are at equilibrium with $BaSO_4$. Although the oxidation state of As was not considered in this study, Essington (1988) suggested that the formation of $Ba_3(AsO_4)_2$ is more dependent on high concentration of As(V) in solution. The variation observed in the release of As from Secunda and Tutuka up-flow percolation systems could be due to the difference in the pH of the two systems. The pH of a system is a very important factor for the precipitation or adsorption of species (Ahmaruzzaman, 2010). In a certain pH range, precipitation of some species increases with increase in pH, and then decreases with decrease in pH. The slight lower pH of Tutuka systems may not favour the precipitation of As. Instead, the dissolution of As in the silicates of fly ash may occur (Martinez-Tarazona and Spears, 1996) thereby increasing its concentration in Tutuka up-flow percolation leachates (TC21).

The release of Cr in the leachates of Secunda and Tutuka up-flow percolation systems were different for each fly ash type trends. In both cases, an increase in the concentrations of Cr was observed after equilibration at the beginning of the tests, after which the concentrations of Cr reduced rapidly. In the case of the Tutuka systems, much higher amounts of Cr were released in the leachates where up to 10 mg/L was measured after equilibration, whereas in Secunda systems without antiscalant only 1 mg/L was released. The concentration of Cr in the leachates was reduced to a minimum at L/S 2 and 1 for Cr in SC22 and TC22 respectively. In the case of Mo, the concentrations were reduced from 1.6 mg/L and 4 mg/L to the minimum at L/S 20 and 1 in SC23 and TC23 respectively. The increase observed at the beginning of the tests indicates the leaching of both Cr and Mo species into the systems from the fly ashes with far higher solubility of Cr species in Tutuka fly ash. Potentially toxic species such as Cr and Mo have been observed to be commonly associated with the nonmagnetic fraction of fly ash in the glass phase, and are distributed on the surface of the ash particles therefore having higher dissolution characteristics (Smith *et al.,* 1979; Meserole *et al.,* 1979; Tiruta-Barna *et al.,* 2006; Jankowski *et al.*, 2006). The rapid dissolution of these soluble species from the surfaces of the fly ash particles during the equilibration period may explain the increase observed in the concentrations of Cr and Mo in the leachates. The rapid decrease in the concentrations of Cr and Mo thereafter could be attributed to the flushing out of these soluble species due to continuous inflow of brine into the systems. Mo and Cr especially Cr(IV) are highly soluble and mobile under alkaline conditions (Jankowski *et al.,* 2006) but could precipitate at low pH.

The effect of antiscalant on the leaching of Cr and Mo in Secunda fly ash was noticeable with antiscalant mobilizing Cr and Mo upon first contact with the fly ash. In Tutuka systems (TC22 and TC23), the effect was negligible.

6.3.1.10 Mass balance

The percentage of species leached from the fly ashes or removed from the brine solution (UB) at selected L/S ratios during the up-flow percolation tests are presented in Tables 6.1 and 6.2. The % leached or removal of the species was calculated using the following equation;

$$\%\, Removal/Leaching \ = \frac{CUB - CL}{CUB}\, X\, 100$$

Where; CUB is the concentration of species in unreacted brine (UB)

CL is the concentration of species in the leachate

Table 6.1: Percentage of species leached from fly ash or removed from brine during the up-flow percolation tests on Secunda fly ash and brine at selected L/S ratios (All values are in % except UB = mg/L, EC = mS/cm and pH)

		L/S ratio					
Parameter	UB	0.1	1	5	20	55	80
Al	0.01	-13016.31	-742.73	-3698.77	-30671.77	-8634.90	-3803.81
As	0.01	69.00	61.85	53.96	24.94	7.74	17.76
B	1.98	84.34	74.40	74.29	-17.01	-86.37	-101.52
Ba	0.06	-42576.43	-456.20	-231.78	-402.79	-103.59	-27.99
Ca	91.01	-79.74	-435.13	-304.62	-365.20	-452.34	-315.12
Co	0.01	100	100	100	59.22	69.95	27.45
Cr	0.02	-7529.40	-7856.20	-59.52	-108.59	15.35	-6.18
Cu	0.19	-587.97	-190.47	21.65	82.83	87.77	86.33
Fe	0.10	-14.39	-1.32	-52.55	99.00	41.94	59.11
K	106.20	-90.75	-25.16	-36.04	3.56	8.24	4.40
Mg	147.50	99.86	99.95	99.94	99.76	100	92.77
Mn	0.00	-229.21	-19.73	-43.63	-13.23	46.46	-16.13
Mo	0.04	-3332.63	-1036.37	-408.52	-54.61	-354.68	-98.41
Na	4323.22	-14.88	-2.14	-0.46	2.27	0.91	-0.44
Ni	0.12	88.40	89.79	7.80	-6.49	-12.11	-10.30
Pb	0.01	-4722.53	-1050.81	-335.92	84.13	44.34	78.86
Si	11.10	74.64	81.55	65.71	-68.88	41.15	51.60
Sr	2.59	-8796.45	-2728.71	-1151.25	-370.71	-521.96	-390.26
Zn	0.11	-1366.70	-524.06	-116.82	95.04	-25.53	45.46
Cl	2424.00	19.73	8.52	10.34	16.33	26.62	30.34
SO4	8858.00	99.44	60.01	55.65	12.34	17.60	18.08
pH	7.89	13.21	11.95	12.73	10.79	9.38	9.24
EC (mS/cm)	14.63	34.75	26.50	25.65	18.13	17.10	17.01

Table 6.2: Percentage of species leached from fly ash or removed from brine during the up-flow percolation tests on Tutuka fly ash and brine at selected L/S ratios (All values are in % except UB = mg/L, EC = mS/cm and pH)

		L/S ratio					
Parameter	UB	0.1	1	5	20	55	80
Al	0.01	-126062.36	-69417.12	-22863.07	-10734.62	-1080.38	-1186.00
As	0.01	-64.02	-92.42	-93.89	-75.24	-628.57	-635.59
B	1.98	80.97	63.05	-4.89	-69.56	-46.92	-43.90
Ba	0.06	-498.32	-324.16	-175.13	-97.76	13.37	34.61
Ca	91.01	-2.18	-220.57	-273.30	-150.23	-27.39	-26.37
Co	0.01	34.26	80.69	59.51	15.93	-144.06	-141.76
Cr	0.02	-65106.81	-1317.72	-1419.46	-734.77	12.53	12.67
Cu	0.19	44.66	74.01	68.82	72.64	51.25	53.15
Fe	0.10	-13.31	-28.53	-0.32	18.90	61.04	72.22
K	106.20	-59.38	-18.47	-5.10	5.33	-8.66	-5.83
Mg	147.50	99.78	99.93	99.65	100	100	100
Mn	0.00	-27.63	-41.65	13.85	-6.47	-227.88	-38.61
Mo	0.04	-10637.69	-98.44	-122.27	-77.15	-11.28	-7.99
Na	4323.22	69.41	-2.83	-3.59	-0.58	-4.07	-3.23
Ni	0.12	55.35	1.18	2.34	-4.52	-10.21	-8.36
Pb	0.01	22.61	58.08	53.25	70.99	70.18	78.36
Si	11.10	35.87	43.55	22.72	51.77	70.48	70.84
Sr	2.59	-121.87	-575.16	-202.44	-68.75	-21.29	-20.98
Zn	0.11	17.28	62.18	76.64	73.41	-34.36	-33.04
Cl	2424.00	58.80	24.88	21.85	19.49	25.03	27.66
SO4	8858.00	80.73	16.93	15.52	12.31	17.05	17.78
pH	7.89	7.83	10.86	11.59	9.55	8.71	8.74
EC (mS/cm)	14.63	5.60	13.97	14.57	17.67	17.33	17.05

The percentage of species leached from the fly ashes or removed from the brine solutions at selected L/S ratios are shown in Tables 6.1 and 6.2. The negative (-) sign indicates the percentage leached from the fly ash into the brine solution while the positive values indicates the percentage removed from the brine during the up-flow percolation tests. The calculated mass balance revealed that significant percentage of species such as As (17.76-69 %), B (74.29-84.34 %), Co (27.45-100 %), Cu (21.65-86.33 %), Fe (59.11-99 %), K (3.56-4.4 %), Na (2.27 %), Ni

(7.8-89.79 %), Pb (78.86-84.13 %), Si (51.6-81.55 %), Zn (45.46-95.04 %), Cl (8.52-30.34 %) and SO_4 (12.34-99.44 %) were removed from the brine solution at some stage (L/S ratio) by Secunda fly ash while species such as Ba, Ca, Cr, Mo and Sr were leached from Secunda fly ash into the brine solution in significant quantities (Table 6.1). In the case of Tutuka up-flow percolation systems (Table 6.2), some species such as B (63.05-80.97 %), Co (15.93-80.69 %), Cu (44.66-74.01 %), Fe (18.9-72.22 %), K (5.33 %), Mg (46.36-99.93 %), Mn (13.85 %), Na (69.41 %), Ni (7.8-89.79 %), Pb (78.86-84.13 %), Si (51.6-81.55 %), Zn (45.46-95.04 %), Cl (8.52-30.34 %) and SO_4 (12.34-99.44 %) were observed to be removed significantly from the brine solution by the fly ash. The significant removal of some species from the brine solution at specific L/S ratio could be attributed to the either precipitation or adsorption process in the up-flow percolation systems.

The removal capacity of the two fly ashes varied slightly. The percentage of some species such as As, B, Co, Cu, Mg, Si and SO_4 removed from the brine solution by Secunda fly ash was higher than the percentage removed by Tutuka fly ash in most cases. The observed difference in the removal capacity of the fly ashes could be attributed to the leaching of some species such as Ca, Ba and Sr from Secunda fly ash in higher amounts that could interact with these species to form secondary mineral phases. The increase in the removal capacity of Secunda fly ash could also be due to the slightly higher pH than Tutuka fly ash. The Tutuka fly ash removed more Na and Cl from the brine solution than Secunda fly ash.

6.3.1.11 Summary

The up-flow percolation test was employed to simulate a co-disposal scenario where fly ash and brine are mixed to form a slurry after which brine solution was percolated through on a continuous basis. This was aimed at determining the effect of continuous flow of brine on fly ash and brine interactions and its impact on the release of major and minor species from the co-disposal systems. This scenario simulates the case of Secunda power station where ash is slurried and ponded in a wet ash handling system. This is in contrast to the static and closed systems presented in chapter 5.

The results of the up-flow percolation tests showed that some species such as B and Ni were removed from the brine solutions by both Secunda and Tutuka fly ashes at the beginning of the tests but started leaching out after L/S 5 (after 11 days of up-flow percolation tests). Significant concentrations of Mg, Cl, SO_4, Si, As and Co were removed from the brine solution by Secunda fly ash throughout the period of the up-flow percolation tests. Species such as Al, Ba, Ca, Sr, Na (except at L/S 20-55), Cr, Mn and Mo showed a continuous leaching from Secunda fly ash throughout the percolation tests, which indicates that these species were continuously leached from the fly ash by contact with brine flows. Cu, Fe, K, Pb and Zn were leached from Secunda fly ash at the beginning of the up-flow percolation tests but were later removed significantly from the brine solution by the fly ash after L/S 5 (after 11 days). The species that were removed by Tutuka fly ash was similar. Apart from Mg, Cl, SO_4, Si and Co, Cu and Pb were removed from the brine solution by Tutuka fly ash throughout the percolation tests. Al, Ba, Ca, Na (except at L/S 0.1), K, Sr, As, Cr, Mn and Mo were leached from Tutuka fly ash into the systems during the up-flow percolation tests. Fe was leached from Tutuka fly ash at the beginning of the percolation tests up to L/S 5 but was removed from the brine solution between L/S 20-80.

The removal and subsequent release of some species in the systems could be as a result of precipitation followed by dissolution of the transient secondary mineral phases formed during the interactions. Ca, Ba, Sr, Cr and Mo showed a continuous leaching throughout the percolation tests, which indicates that these species leached continuously from the fly ashes by contact with brine flows. Generally, the trends observed in the release of species from the up-flow percolation systems showed that the removal capacity of the fly ashes could be exhausted at a stage due to continuous inflow of brine thereby overwhelming the removal capacity of the fly ashes. Apart from the reduction in the capacity of the fly ash to remove species from brine, metals held in the fly ash matrix could be released over time by brine flowing continuously through the ash system. For instance, the capacity of the fly ashes to remove the major species such as Cl and SO_4 contained in the brine was very high at L/S 0.1 (immediately after equilibration), thereafter the removal capacity of the fly ashes reduced continuously throughout the percolation tests. Unlike in the long-term interactions tests (chapter 5, section 5.4.1) where Na, Cl and SO_4 were removed significantly from the brine solution with an increase in the interactions period, the concentration of Na in the brine solution was not significantly reduced during the up-flow percolation tests except at L/S 0.1 in Tutuka up-flow percolation systems. This observation could give the fly ash-brine co-disposal techniques simulated in chapter 5 an advantage over the wet ashing practice simulated by the up-flow percolation tests.

The effect of antiscalant in the removal of species from the brine solution and the release of species from the fly ashes was generally not significant. The addition of the antiscalant into the systems in some cases retarded the leaching of some species while in some case the leaching of species was enhanced. For instance, some species such as B, Al, Si, Ca, Sr, Cu and Zn showed slight enhanced leaching effects of anticalant on their release in the up-flow percolation systems.

Generally, the results of the up-flow percolation tests showed that some were removed from the brine solution throughout the percolation period while some were removed from the brine solution by the fly ashes at the beginning of the tests and were released over time (Tables 6.1 and 6.2). Having observed the removal of some species from the brine solution as a result of its interactions with fly ash during the up-flow percolation tests, it was necessary to substantiate the removal of species by characterizing the solid residues generated from the fly ash-brine interactions during the up-flow percolation tests. The characterization of the solid residues was expected to give more insight into the species removed from the brine solutions by the fly ashes. The results of the characterization of the solid residues using different techniques such as XRD, SEM-EDS and XRF will be presented in the next section (6.3.2).

6.3.2 Characterization of the solid residues recovered from the up-flow percolation tests

The section presents and discusses the results of the characterization carried out on the solid residues recovered from the up-flow percolation tests. This section is divided into sub-sections 6.3.2.1, 6.3.2.2, 6.3.2.3 and 6.3.2.4. Sub-section 6.3.2.1 deals with the pH and EC profiles of the solid residues. The pH and EC profiles of the solid residues were done in order to determine the effect of the fly ash-brine interactions on the pH and the EC during the up-flow percolation tests, and to give an insight into the mobility of species in the fly ash-brine systems during the up-flow percolation tests. Sub-section 6.3.2.2 presents and discusses the XRF results showing the chemical composition of the solid residues. This was done to determine whether some species from the brine solution were captured by the fly ashes. The results of the XRF is expected to corroborate the ICP-MS and IC results presented in section 6.3.1 which showed that some species were removed from the brine solution by the fly ashes. Sub-section 6.3.2.3 deals with the mineralogical composition of the solid residues. The XRD analysis is expected to identify the secondary crystalline mineral phases formed as a result of the fly ash-brine interactions during the up-flow percolation tests. Finally on this section, sub-section 6.3.2.4 deals with the results of the SEM-EDS showing the effect of the fly ash-brine interactions on the morphology of the fly ashes after the up-flow percolation tests. The EDS analysis is expected to semi-quantitatively identify most of the species associated with some mineral phases that could not be identified by XRD in the solid residues.

6.3.2.1 pH and EC profiles of the up-flow percolation solid residues

The pH and EC profiles of the solid residues were done (experimental details in section 3.3.7) in order to determine the effect of the fly ash-brine interactions on the pH and the EC during the up-flow percolation tests. The pH and the EC of the Secunda and Tutuka fresh fly ashes were compared with pH and EC of the solid residues recovered after the percolation tests. The pH and the EC profiles are expected to give an insight into the mobility of species down the columns during the percolation tests.

The pH and EC profiles of the solid residues generated from the interactions of brine and fly ashes during the up-flow percolation tests are presented in Figure 6.10 below.

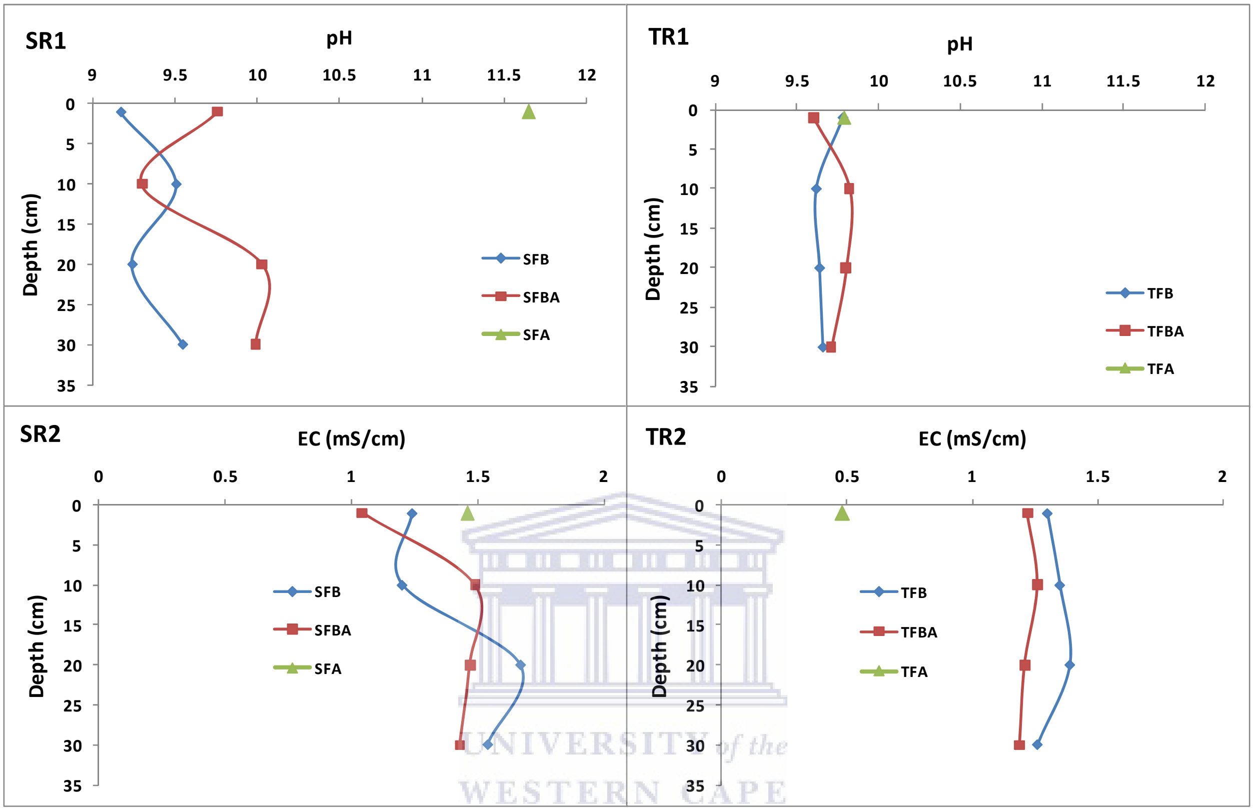

Figure 6.10: pH and EC profiles of Secunda (SR1 and SR2) and Tutuka (TR1 and TR2) up-flow percolation residues as a function of depth. SFA = Secunda fresh fly ash, SFB = Secunda fly ash-brine residues, SFBA = Secunda fly ash-brine-antiscalant residues, TFA = Tutuka fresh fly ash, TFB = Tutuka fly ash-brine residues, TFBA = Tutuka fly ash-brine-antiscalant residues

The pH profiles (Figure 6.10) for Secunda solid residues (SR1) (experimental details in section 3.3.7) showed a lower pH (between 9.2 and 9.7) compared with the pH of the Secunda fresh fly ash (SFA) (11.6) irrespective of the section of the columns analyzed. The overall decrease in the pH of the Secunda solid residues could be attributed to the dissolution of the alkalinity contributing oxides such as CaO and MgO during the up-flow percolation tests. A slightly higher pH was observed in Secunda solid residue, SFBA, at 20 and 30 cm depth. This could be as a result of incomplete dissolution of the soluble alkalinity-contributing phases at these sections of the column during the test period of 173 days. It is possible that had the tests been extended, the alkalinity contributing phase(s) would have been exhausted throughout the ash column. The dissolution of the precipitated Ca-rich phases such as gypsum ($CaSO_4.2H_2O$) and portlandite [$CaOH)_2$] (Hyks *et al.,* 2009) could lead to the slight increase in the pH at 20 cm depth. This is supported by the data presented in Tables 6.8 and 6.9 where the concentration of Ca and S at 20 and 30 cm depth were higher indicating the presence of Ca-S-rich mineral phase(s). The pH profiles of Tutuka solid residues (TR1) were slightly lower than the pH of the fresh fly ash (TFA) especially at 1 cm depth (at point of contact with brine inflow). The slight difference in the pH of Tutuka solid residues (pH 9.6) and that of the fresh fly ash (pH 9.8) could be attributed to the decrease in the CaO and MgO contents of Tutuka fresh ash (Table 4.2) (Mattigod *et al.,* 1990; Querol *et al.,* 2000). The lower CaO and MgO content of Tutuka fresh fly ash compared to Secunda fresh ash (Table 4.2) may be attributed to the pretreatment of the fly ash with brine before sampling. Similar to what was observed in the solid residue of Secunda fly ash-brine-antiscalant (SFBA), the pH of the solid residue of Tutuka fly ash-brine-antiscalant (TFBA) was slightly higher at 10 and 20 cm depth.

The decrease observed in the pH profiles of both Secunda and Tutuka solid residues compared to the fresh fly ashes gives a clear indication that the interactions of fly ash and brine leads to the significant decrease in the pH of fly ash-brine systems over time. The decrease in the pH of the systems favours the dissolution and the mobility of species locked in the ash matrix. Therefore, a continuous dissolution of more mineral phases, including the aluminosilicates, from the solid residue when in contact with brine or aqueous solution is inevitable thereby increasing the mobility of contaminant species into the environment over time.

The EC trends of Secunda solid residues (SR2) (see section 3.3.7 for the experimental details) showed lower values (1.2 mS/cm) in comparison with the EC value of Secunda fresh fly ash (≈1.5 mS/cm) at 1 cm depth. The EC thereafter increased to the original value and above down the column. The decrease observed in the EC values of the residues at 1 cm depth and its increase down the ash column could be attributed to the mobilization of most of the dissolved species through the column because of the continuous inflow of brine solution during the up-flow percolation tests. The increase observed at 20 cm to about 1.6 mS/cm could be attributed to the mobility of some species as a result of the dissolution of the transient phase(s) formed in the solid residues during the up-flow percolation tests. The EC trends of Tutuka solid residues (TR2) were higher (≈1.3 mS/cm) than that of the fresh ash (0.5 mS/cm) irrespective of the depth of the columns. The increase in the EC of the solid residues when compared with the EC value of Tutuka fresh fly ash (TFA) is an indication that some of the species originating from the brine were captured by the fly ash. The dissolution of the transient soluble phases formed during the up-flow percolation tests could be responsible for the increase in the EC values. Generally, the EC trends observed give an indication that most of the species removed from the brine solution by the fly ashes during the up-flow percolation tests are not stable and can be release over time. Having shown by the EC results that some species from the brine solution were captured by the fly ashes, the need to support this observation necessitated the chemical analysis of the solid residues. The XRF results showing the chemical composition of the solid residues in order to determine the degree of removal of species from the brine solution by the fly ashes is presented in the sub-section 6.3.2.2.

6.3.2.2 Chemical composition of the up-flow percolation solid residues: XRF analysis

As presented and discussed in section 6.3.1 of this chapter, coupled with the EC profile of the solid residues, some species were removed from the brine solutions by the fly ashes while some were leached from the fly ashes into the fly ash-brine systems during the up-flow percolation tests. The XRF analysis showing the chemical composition of the solid residues was carried out to give more insight into the species remaining in the solid residues after leaching and the species removed from the brine solution by the fly ashes during the up-flow percolation tests. Although the XRF analysis is not the best method to be used in determining the mineral phase(s) responsible for the removal of a particular species from the brine solution, the abundance of some species in the solid residues when compared with their concentrations in the fresh fly ashes could predict the formation of new mineral phases in the solid residues. The concentrations of As, Mo and Ni in the solid residues are not presented because these species were not analyzed by the XRF technique.

The chemical composition (measured by XRF) of major and minor species (mg/kg) in the fresh fly ashes and in the solid residues are presented in Tables 6.3 and 6.4.

Table 6.3: Mean concentration of Secunda fresh ash (SFA) and solid residues of the up-flow percolation tests (SR = Secunda fly ash-brine solid residue; SRA = Secunda fly ash-brine-antiscalant solid residue)

Element (mg/kg)	SFA	SR	Concentration leached/ retained	SRA	Concentration leached/ retained
Al	137751	129710.8	-8040.2	129030.3	-8720.7
Ba	2292	1670.9	-621.1	1642.5	-649.5
Ca	66467	51399.5	-15067.5	57367.5	-9099.5
Cl	73.9	1278.4	1204.5	1168.2	1094.3
Fe	16506	16317.8	-188.2	16116.5	-389.5
K	6724	6398.5	-325.5	6338.3	-385.7
Mg	13572	17819.3	4247.3	15222	1650
Na	4525	6985.8	2460.8	6813.3	2288.3
S	1378.4	9602.5	8224.2	11567	10188.6
Si	231787	212373	-19414	211261.8	-20525.2
Sr	3268.1	2788.6	-479.5	2902.8	-365.3
Co	10.5	10	-0.5	10.2	-0.3
Cr	129.8	128	-1.8	127.8	-2
Cu	37	28.5	-8.5	38.2	1.2
Mn	387	350.3	-36.7	374.8	-12.2
Ni	58.5	54.6	-3.9	54.5	-4
Pb	41	46.4	5.4	45.7	4.7
Zn	32.1	88.9	56.8	60.8	28.7

Table 6.4: Mean concentration of Tutuka fresh ash (TFA) and solid residues of the up-flow percolation tests (TR = Tutuka fly ash-brine solid residue; TRA = Tutuka fly ash-brine-antiscalant solid residue)

Element (mg/kg)	TFA	TR	Concentration leached/ retained	TRA	Concentration leached/ retained
Al	129495	125925	-3570	126077.3	-3417.7
Ba	983.7	852.9	-130.8	855.3	-128.5
Ca	42096	35121.3	-6974.7	35776.5	-6319.5
Cl	730.3	1940.6	1210.3	1544.9	814.6
Fe	37907	37172	-735	36831.5	-1075.5
K	6890	6888	-2	6915	25
Mg	8204	11141.5	2937.5	10602.3	2398.3
Na	2151	5323.8	3172.8	5960.3	3809.3
S	7025.1	7874.1	849	9210.6	2185.6
Si	242352	230648.3	-11703.7	230359	-11993
Sr	1164.4	1120.9	-43.5	1144.1	-20.3
Co	21	21.6	0.6	20.9	-0.1
Cr	145.3	135.7	-9.6	157.5	12.2
Cu	32.8	36.4	3.6	42.1	9.3
Mn	387	407	20	393	6
Ni	62.2	59.2	-3	58.8	-3.4
Pb	50.3	58	7.6	59.7	9.4
Zn	48.5	104.3	55.8	73.8	25.3

The concentrations of the some species such as Na, Mg, Cl, S, Cu, Pb and Zn in the solid residues recovered from both Secunda and Tutuka up-flow percolation tests showed an increase compared with their concentrations in the fresh fly ashes from Secunda and Tutuka (Tables 6.3 and 6.4). The increase was as a result of the interactions of the fly ashes with the brine solution. This clearly shown that some of the species in the brine solution were captured in significant quantities by the fly ashes during the up-flow percolation tests. The removal capacity of Tutuka fly ash on Na was higher than that of Secunda fly ash while the capacity of Secunda fly ash to remove Mg (4247.3 mg/kg), S (8224.2 mg/kg) and Zn (56.8 mg/kg) from brine was higher than that of Tutuka fly ash (2937.5 mg/kg, 849 mg/kg and 55.8 mg/kg respectively). The amount of

Cl removed by the two fly ashes from the brine was almost the same. Despite the high removal capacity of the fly ashes in the case of some species, the concentrations of species such as Al, Ba, Ca, Si, Sr, K, Fe and Cr were observed to be reduced in the solid residues compared to their concentrations in the fresh fly ashes. This indicates that these species were leached from the fly ashes into the brine solution during the up-flow percolation tests. The results of the analysis of the leachates from the up-flow percolation tests (section 6.3.1) showed an increase in the concentrations of Al, Ba, Ca, Si, Sr, K, Fe and Cr in the leachates, and this supports the decrease observed in the concentrations of these species in the solid residues. Higher concentrations of Al, Ba, Ca, K, Si and Sr were leached from Secunda fly ash than the concentrations of these species leached from Tutuka fly ash. This could be attributed to the higher concentrations of these species in Secunda fly ash (SFA) (Tables 6.3 and 6.4). The effect of antiscalant was shown on the concentrations of species such as Mg, S, Cl and Zn as the concentrations of Mg, Cl and Zn were lower in the solid residues of the systems containing antiscalant (SRA and TRA). On the other hand, the concentration of S in SRA and TRA was higher than what was observed in the SR and TR. The effect of antiscalant varied in the two fly ash solid residues, as the concentration of Na in SRA was lower than its concentration in SR while the Na concentration in TRA was found to be higher than in TR. Detailed discussion of the species removed from the brine solution by the fly ashes and the species leached from the fly ashes are presented below considering the concentrations at different section (depth) of the columns.

Tables 6.5 to 6.8 present the concentrations of species in the solid residues at different section (depth) of the column. Detailed discussions on the major and minor species such as Al, Si, Ca, Sr, S, Mg, Ba, Na, K, Cl, Fe, Mn, Co, Ni, Pb, Cu, Cr and Zn in the solid residues are presented below.

Table 6.5: Chemical composition of the Secunda solid residues from the up-flow percolation tests at different depth (SR 1 cm, SR 10 cm, SR 20 cm and SR 30 cm) n=3

	Major element (mg/kg)										
Depth (cm)	Al	Ba	Ca	Cl	Fe	K	Mg	Na	S	Si	Sr
SFA	137751	2292	66467	73.9	16506	6724	13572	4525	1378.4	231787	3268.1
1 cm	138556	1771.8	39276	1791.4	17490	6993	16041	7478	5396.3	227291	2934.1
10 cm	131870	1735.4	46574	1027.7	16636	6490	22024	7178	4300.3	215326	2791.2
20 cm	123446	1570.5	57440	1154	15653	6043	18928	6840	15557.2	202956	2556.9
30 cm	124971	1606.1	62308	1140.6	15492	6068	14284	6447	13156.1	203919	2872.1
Mean	129710.8	1670.9	51399.5	1278.4	16317.8	6398.5	17819.3	6985.8	9602.5	212373	2788.6

	Minor element (mg/kg)						
Depth (cm)	Co	Cr	Cu	Mn	Ni	Pb	Zn
SFA	10.5	129.8	37	387	58.5	41	32.1
1 cm	10.43	127.2	35.1	391	56.28	42.5	253
10 cm	10.6	127.3	28.1	352	59.19	49.2	41.7
20 cm	8.86	127.6	15.7	333	50.99	45.3	30.3
30 cm	10.05	129.9	35.1	325	52.03	48.6	30.4
Mean	10	128	28.5	350.3	54.6	46.4	88.9

Table 6.6: Chemical composition of the Secunda solid residues (fly ash-brine-antiscalant) from the up-flow percolation tests at different depth (SRA 1 cm, SRA 10 cm, SRA 20 cm and SRA 30 cm) n=3

	Major element (mg/kg)										
Depth (cm)	Al	Ba	Ca	Cl	Fe	K	Mg	Na	S	Si	Sr
SFA	137751	2292	66467	73.9	16506	6724	13572	4525	1378.4	231787	3268.1
1 cm	136787	1770.8	42733	1307.8	17285	6884	16876	7500	4879.8	225341	3099.8
10 cm	127872	1632.4	55099	1089.9	16134	6238	17960	6714	10235.9	209174	2679.1
20 cm	124595	1542.6	65481	1092.4	15485	6085	13301	6573	17263.9	203535	2774.6
30 cm	126867	1624.1	66157	1182.7	15562	6146	12751	6466	13888.6	206997	3057.9
Mean	129030.3	1642.5	57367.5	1168.2	16116.5	6338.3	15222	6813.3	11567	211261.8	2902.8

	Minor element (mg/kg)						
Depth (cm)	Co	Cr	Cu	Mn	Ni	Pb	Zn
SFA	10.5	129.8	37	387	58.5	41	32.1
1 cm	10.9	130.9	39.5	407	57.8	46.98	149.3
10 cm	9.5	130.1	30.5	391	53.9	46.28	33.3
20 cm	9.7	119.2	47.9	349	51.9	44.01	29.7
30 cm	10.5	130.9	34.7	352	54.5	45.4	31.2
Mean	10.2	127.8	38.2	374.8	54.5	45.7	60.8

Table 6.7: Chemical composition of the Tutuka solid residues from the up-flow percolation tests at different depth (TR 1 cm, TR 10 cm, TR 20 cm and TR 30 cm) n=3

	Major element (mg/kg)										
Depth (cm)	Al	Ba	Ca	Cl	Fe	K	Mg	Na	S	Si	Sr
TFA	129495	983.7	42096	730.3	37907	6890	8204	2151	7025.1	242352	1164.4
1 cm	128487	858.3	33977	1724.2	37566	7060	8085	5417	6660.8	234525	1169.6
10 cm	125739	859.2	35168	2202.8	36683	6859	12166	5335	10168.2	228245	1108.9
20 cm	124686	843.2	35435	2075.9	37163	6808	12508	5380	7034.7	228585	1103.3
30 cm	124788	850.9	35905	1759.3	37276	6825	11807	5163	7632.7	231238	1101.6
Mean	125925	852.9	35121.3	1940.6	37172	6888	11141.5	5323.8	7874.1	230648.3	1120.9

	Minor element (mg/kg)						
Depth (cm)	Co	Cr	Cu	Mn	Ni	Pb	Zn
TFA	21	145.3	32.8	387	62.2	50.33	48.5
1 cm	21.9	144.4	34.5	415	61.9	55.43	263.5
10 cm	21.9	130.9	38.7	415	57.4	59.01	54.2
20 cm	21.1	134.8	35.2	391	59	59.52	48.9
30 cm	21.5	132.6	37.3	407	58.4	57.92	50.4
Mean	21.6	135.7	36.4	407	59.2	57.97	104.3

Table 6.8: Chemical composition of the Tutuka solid residues (fly ash-brine-antiscalant) from the up-flow percolation tests at different depth (TRA 1 cm, TRA 10 cm, TRA 20 cm and TRA 30 cm) n=3

	Major element (mg/kg)										
Depth (cm)	Al	Ba	Ca	Cl	Fe	K	Mg	Na	S	Si	Sr
TFA	129495	983.7	42096	730.3	37907	6890	8204	2151	7025.1	242352	1164.4
1 cm	126862	849.1	32772	1761.9	37517	7018	8481	5844	6527.4	233755	1162.42
10 cm	126856	819.26	34634	1522.7	36881	7001	10789	8444	15608	231937	1140.28
20 cm	125734	872.37	37110	1303.9	36655	6900	11667	4848	7353.6	229482	1138.24
30 cm	124857	880.42	38590	1591	36273	6741	11472	4705	7353.3	226262	1135.52
Mean	126077.3	855.28	35776.5	1544.9	36831.5	6915	10602.3	5960.3	9210.6	230359	1144.1

	Minor element (mg/kg)						
Depth (cm)	Co	Cr	Cu	Mn	Ni	Pb	Zn
TFA	21	145.33	32.8	387	62.2	50.33	48.5
1 cm	22.88	222.65	46.03	399	60.37	52.38	131.11
10 cm	19.78	139.75	37.54	407	58.66	60.3	52.16
20 cm	20.58	135.05	39.77	391	58.92	62.56	49.83
30 cm	20.41	132.63	45	375	57.41	63.59	62.28
Mean	20.9	157.52	42.1	393	58.84	59.7	73.8

6.3.2.2.1 Aluminum and Silicon

The concentrations of Al and Si in the solid residues recovered after the Secunda and Tutuka up-flow percolation tests are shown in Tables 6.5, 6.6, 6.7 and 6.8. The concentration of Al in the solid residues (Tables 6.8-6.11) was lower than what was observed in the fresh fly ashes across the entire depth of the columns. The reduction in Al concentration in the solid residues is an indication that Al was leached from the fly ashes after the dissolution of its oxides in the fly ash during the up-flow percolation tests. This is in agreement with what was observed in the leachates of the up-flow percolation tests (Figure 6.2; SC3 and TC3) where an increase in Al concentration was observed in the leachates indicating its leaching from the fly ashes into the systems. The mean concentration of Al that was leached out of Secunda fly ash was 8040 mg/kg (5.8 %) Al while 3570 mg/kg (2.8 %) Al was leached from Tutuka fly ash showing that Secunda fly ash released more Al into the systems than Tutuka fly ash. This variation could be attributed to the variation in Al concentration in the two fly ashes (Tables 6.3 and 6.4). The concentration of Si in the solid residues (Tables 6.8-6.11) also followed the same trend with the concentration of Al in the residues.

The concentration of Si in the solid residues of the up-flow percolation tests was lower than what was measured in the fresh fly ashes indicating that Si was leached out of the fly ashes during the percolation tests. Although the removal of Si was observed in the leachates at the beginning of the up-flow percolation tests [Figure 6.2 (SC4 and TC4)], which suggested the formation of new Si-rich mineral phases, the increase in the concentration of Si in the leachates thereafter was ascribed to the dissolution of more SiO_2 from the fly ashes thereby reducing its concentrations in the solid residues. The XRF data showed that the mean concentration of Si leached from Secunda fly ash was 19414 mg/kg (8 %) but approximately 11704 mg/kg (5 %) Si was leached from Tutuka fly ash. Amorphous aluminosilicate and silica in fly ash dissolve easily when in contact with aqueous solution (Seoane and Leirós, 2001) and can transform into insoluble Al hydroxide phases and amorphous Si-bearing mineral phases such as $Al(OH)_3$, kaolinite [$Al_2Si_2O_5(OH)_4$]. The transformation of the insoluble phases may be hindered due to the continuous inflow of brine thereby resulting in flushing out of Al and Si from the systems. The continuous leaching of Al and Si over time will result in the release of other elements entrained in the glassy phases. The concentrations of Al and Si in the solid residues from the systems containing antiscalant were not significantly different from their concentrations in the solid residues of the systems without antiscalant.

6.3.2.2.2 Calcium, Strontium and Sulphate (as S)

The concentrations of Ca, Sr and S in the residues of Secunda and Tutuka up-flow percolation tests are presented in Tables 6.5-6.8. The mean concentration of Ca leached from Secunda fly ash was 15068 mg/kg (≈23 %) while the Ca concentration leached from Tutuka fly ash was 6974.7 mg/kg (≈17 %) (Tables 6.3 and 6.4). The concentration of Ca leached from Secunda fly ash was higher than the concentration leached from Tutuka fly ash which could be attributed to the difference in the concentration of Ca in the two fly ashes.

The concentration of Ca in the solid residues was found to be lower than what was observed in the fresh fly ashes especially in the section of the column where brine was inflowing indicating the rapid dissolution of CaO. The solubilized Ca appeared to re-precipitate as new Ca-containing mineral phases down the column at 20 and 30 cm depth in Secunda and Tutuka systems (Tables 6.5-6.8). At 20 and 30 cm depth, the Ca content was close to that of the fresh fly ash. Secunda fly ash-brine-antiscalant residue (Table 6.6) showed the effect of antiscalant to retain Ca as the concentration of Ca was almost equal to that in the fresh fly ash (SFA). The initial reduction in the concentration of Ca was as a result of the dissolution of CaO in the fly ashes and the leaching of Ca out of the systems during the up-flow percolation tests. This is in agreement with what was observed in the leachates of the up-flow percolation tests [Figure 6.3 (SC5 and TC5)] where increase in the concentration of Ca in the systems indicates significant leaching from the fly ashes during the tests. After the initial significant reduction in the concentration of Ca in the solid residues from 66467 mg/kg in the case of Secunda to between 39276 and 42733 mg/kg (Tables 6.5 and 6.6) and from 42096 mg/kg to between 32772 and 33977 mg/kg in the case of Tutuka (Tables 6.7 and 6.8) at 1 cm depth, the gradual increase observed thereafter in Ca concentration at 20 and 30 cm in the columns could indicate the formation of Ca-rich secondary mineral phases or due to accumulation as a result of slow mobility of soluble Ca down the columns.

The concentration of S (presumably SO_4) in the solid residues showed a very significant increase irrespective of the depth of the columns compared with the concentration in the fresh fly ashes (Tables 6.5-6.8). The mean concentration of S captured from brine by the Secunda fly ash (in the solid residues) was 8224 mg/kg (597 %) while the mean concentration of S captured in Tutuka solid residue was 849 mg/kg (12 %) over time. This trend showed that S was significantly removed from the brine solutions by the fly ashes, and that Secunda fly ash was able to significantly capture more S than Tutuka fly ash. Corroborating the increase observed in the concentration of S in the solid residues, the leachates of the up-flow percolation tests showed a significant decrease in the concentration of SO_4 in the systems [Figure 6.3 (SC7 and TC7)] up to certain L/S ratio indicating its rapid removal from the brine solutions during the interactions with the fly ashes. The removal of SO_4 from the leachates and the increase in its concentration in the solid residues could be as a result of formation of S-rich phases in the solid residues. The trends observed in the concentrations of Ca and S (presumably as SO_4) in the solid residues suggest the formation of transient Ca, S-rich mineral phases such as gypsum and anhydrite (Hyks *et al.*, 2009) as predicted in section 6.3.1.3. However, the concentration of S at 1 cm depth seemed to be lower than the concentration in depths 10 cm to 30 cm. This could indicate the gradual dissolution of the transient S-containing mineral phases formed in the systems as was observed in the ANC tests with decreasing pH trends.

The concentration of Sr in the solid residues decreased by 479 mg/kg (15 %) in the case of Secunda and by 43 mg/kg (4 %) in the case of Tutuka (Tables 6.3 and 6.4) when compared with the concentration in the fresh fly ashes (3268 mg/kg SFA and 1164 mg/kg TFA) indicating that Sr was consistently leached from the fly ashes during the up-flow percolation tests. This observation supports what was observed in Figure 6.3 (SC6 and TC6) which showed that Sr was leached from the fly ashes during the percolation tests. Notwithstanding the leaching observed in the solid residues, its presence in the systems could result in the formation of secondary mineral phases. In alkaline solution containing high concentration of Ba and SO_4, Sr may co-precipitate with barite to form $Ba(Sr)SO_4$ (Fallman, 2000; Felmy *et al.*, 1993). The co-precipitation with barite could responsible for the slow decrease of Sr in the solid residues at some stages along the depth of the columns.

6.3.2.2.3 Magnesium and Barium

The solid residues recoverd from Secunda and Tutuka up-flow percolation tests showed an increase in the concentration of Mg irrespective of the depth of the column when compared with what was observed in the fresh fly ashes (SFA and TFA) (Tables 6.5-6.8). This observation indicates that Mg was removed from the brine solution by the fly ashes during the up-flow percolation tests. The mean concentration of Mg captured the Secunda solid residue over time was found to be 4247 mg/kg (31 %) while the concentration captured in Tutuka solid residue was 2938 mg/kg (36 %) (Tables 6.3 and 6.4). The increase in Mg concentration in the solid residues support what was observed in the leachates of the percolation tests, which showed a significant removal of Mg from the systems [Figure 6.4 (SC8 and TC8)]. The removal of Mg by the fly ashes was suggested to be controlled by the precipitation of Mg-rich mineral phases such as $Mg(OH)_2$.

The concentration of Ba in the solid residues (Tables 6.5-6.8) was lower than the concentration of Ba in the fresh fly ashes (SFA and TFA). The lower concentrations of Ba indicates its leaching from the fly ashes during the up-flow percolation tests. The mean concentration of Ba leached from Secunda fly ash over time was 621 mg/kg (27 %) and the concentration leached from Tutuka fly ash over time was 131 mg/kg (13 %) (Tables 6.3 and 6.4). There is an agreement between the trend of Ba in the solid residues and the trend of Ba in the leachates as the latter showed an increase in Ba concentrations indicating that Ba was leached from the fly ashes during the tests. Despite the lower concentration of Ba in the solid residues, the possible precipitation of Ba-rich phases in alkaline systems cannot be ruled out. The formation of Ba-rich phases could account for the slight increase in the concentration of Ba (not up to the concentration in the fresh fly ash) as observed at 30 cm depth. Due to high concentration of SO_4 in the systems, the formation of barite ($BaSO_4$) is possible during the up-flow percolation tests (Hyks *et al.,* 2009).

6.3.2.2.4 Sodium, Potassium and Chloride

As observed in Tables 6.5-6.8, the concentrations of Na and Cl in the solid residues were found to be significantly higher than the concentrations observed in the fresh fly ashes (SFA and TFA). The mean concentration of Na captured in Secunda solid residue over time was 2461 mg/kg (54 %) while the concentration captured in Tutuka solid residue over time was 3173 mg/kg (148 %). The mean concentration of Cl captured in Secunda solid residue was 1205 mg/kg (1630 %) and the mean concentration captured in Tutuka solid residue was 1210 mg/kg (166 %) (Tables 6.3 and 6.4). The trends observed showed that the capacity of Tutuka fly ash to remove Na from the brine solution was higher than the capacity of Secunda fly ash while the capacity of the two fly ashes to remove Cl was almost the same (see section 6.3.1.5, Figure 6.5). The increase observed in the concentrations of Na and Cl in the solid residues indicates that these species were removed from the brine solutions by the fly ashes during the up-flow percolation tests over time. As suggested in section 6.3.1.5, the removal of Na and Cl could be as a result of the formation of transient NaCl due to the super-saturation of these species in the systems. The increase observed in the concentrations of Na and Cl in the solid residues agrees with what was observed in the concentrations of these species in the leachates of the up-flow percolation tests where the concentrations of Na and Cl was reduced indicating their removal from the brine solutions by the fly ashes.

The trend of K in the solid residues was slightly different from what was observed in the solid residues for Na (Tables 6.5-6.8). The mean concentration of K leached from Secunda fly ash over time was 325 mg/kg (5 %) while the mean concentration of K leached from Tutuka fly ash was 2 mg/kg (0.03 %) (Tables 6.3 and 6.4). There was an increase in the concentration of K observed at the top section of the columns (1 cm depth) but gradually reduced thereafter (10-30 cm depth) to an amount lower than the concentration of K in the fresh fly ashes. The trend observed at 1 cm depth shows the removal of K from the brine solution by the fly ashes at the top of the column. Apart from the soluble salts of K in fly ash, K also exists in the carbonates, sulphates, silicate minerals, and silicate glasses of fly ash which could dissolve over time (Kirby *et al.,* 1994). The dissolution of K-rich phases and the slow dissolution of the less soluble glass matrix could account for the lower concentration of K at 10-30 cm depth. The decrease in K concentration in the residues agrees with what was observed in the leachates [Figure 6.5 (SC12 and TC12)] as there was an increase in the concentration of K in the leachates during the up-flow percolation tests indicating that K was leached from the fly ashes.

6.3.2.2.5 Iron and Manganese

The concentration of Fe in the solid residues showed that Fe was leached from the two fly ashes over time. The mean concentration of Mn in Secunda solid residue showed a decrease while its concentration in Tutuka solid residue showed that Mn was captured in the fly ash over time. About 188 mg/kg (1.1 %) Fe was leached from SR while about 735 mg/kg (2 %) was leached from TR (Tables 6.3 and 6.4). The mean concentration of Mn leached from Secunda fly ash over time was 37 mg/kg (9 %) while the mean concentration of Mn captured in Tutuka solid residue over time was 20 mg/kg (5 %). The concentration of Fe as shown in Tables 6.5, 6.6, 6.7 and 6.8, was found to be slightly higher at the top of the columns (1 cm depth) than what was observed in the fresh fly ashes especially in Secunda solid residues. The higher concentrations observed in the solid residues at the top of the column could be as a result of the formation of transient Fe - oxyhydroxides during the up-flow percolation tests. The lower concentration of Fe in the solid residues thereafter could be accounted for by the dissolution of the Fe-oxyhydroxides in the fly ash-brine systems during the percolation tests. The concentration of Mn in the solid residues showed little or no difference to what was observed in the fresh fly ashes. Similar trends were observed in the leachates from the up-flow percolation test where the leaching trends of these species fluctuated [Figure 6.6 (SC14, TC14, SC15 and TC15)].

6.3.2.2.6 Cobalt, Nickel and Lead

The mean concentration of Co and Pb in the solid residues showed that these species were captured by Secunda and Tutuka fly ashes during the period of the up-flow percolation tests. The mean concentration of Co in Secunda solid residue showed that Co was leached by 0.5 mg/kg (5 %) over time while the mean concentration of Co captured in Tutuka solid residue was 0.6 mg/kg (2.8 %). The mean concentration of Pb captured in Secunda and Tutuka solid residues are 5.4 mg/kg (13 %) and 7.6 mg/kg (15 %) respectively (Tables 6.3 and 6.4). The concentrations of

Co and Pb in the solid residues were observed to be higher that their concentrations in the fresh fly ashes (Tables 6.5-6.8) indicating that a proportion of these species were removed from the brine solutions by the fly ashes over the period of the up-flow percolation tests. At some stages (10 and 20 cm depth) in the solid residues from the fly ash-brine-antiscalant systems (Tables 6.6 and 6.8), the concentration of Co was lower that what was observed in the fresh fly ashes. The removal of these species as suggested in section 6.3.1.7 could be controlled by co-precipitation, surface complexation or adsorption on the surfaces of the fly ash particles (Meima and Comans, 1998). Desorption of the adsorbed species could account for the lower concentration of Co at 10 and 20 cm depth. The increase observed in the residues agrees with what was observed in the leachates of the up-flow percolation tests where the concentrations of these species were found to be very low in the systems at some stage (Figure 6.7).

The concentration of Ni in the solid residues was different as the concentration observed in the residues was lower than what was observed in the fresh fly ashes. The mean concentration of Ni leached from Secunda and Tutuka fly ashes was found to be 4 mg/kg (7 %) and 3 mg/kg (5 %) respectively (Tables 6.3 and 6.4). Although the leaching trend, as observed in section 6.3.1.7, showed that Ni was removed from the brine solutions at the beginning of the up-flow percolation tests, the increase observed in the leachates thereafter, which indicates the leaching of Ni from the fly ashes, supports the trend observed in the solid residues. At high pH, Ni precipitates as insoluble hydroxides but dissolves at lower pH thereby causing its leaching from the fly ashes (Shim *et al.,* 2005; Ram *et al.,* 2006).

6.3.2.2.7 Copper, Zinc and Chromium

The concentration of Cu in the solid residues fluctuated, especially in Secunda solid residues (Tables 6.5 and 6.6), but in the case of Tutuka solid residues (Tables 6.7 and 6.8) the concentration of Cu was observed to be higher than its concentration in the fresh fly ash. Notwithstanding the fluctuation observed in the trend of Cu in Secunda solid residues, the concentration of Cu in the solid residues showed that a proportion of Cu was removed from the brine solutions by the fly ashes during the up-flow percolation tests. This agrees with what was observed in the leachates of the up-flow percolation tests where a decrease in Cu concentration was observed in the systems (see section 6.3.1.8).

In the case of the concentration of Zn in the Secunda solid residues, an increase was observed at 1 and 10 cm depth after which the concentration of Zn in the solid residues was almost the same as the concentration in the fresh fly ashes (Tables 6.5 and 6.6). The concentration of Zn in Tutuka solid residues was higher that what was observed in the fresh fly ashes (Tables 6.7 and 6.8). The mean concentration of Zn captured in Secunda and Tutuka solid residues was found to be 56.8 mg/kg (177 %) and 55.7 mg/kg (115 %) respectively (Tables 6.3 and 6.4). The increase observed in the concentration of Zn in the solid residues supports what was observed in the leachates of the up-flow percolation tests showing the removal of Zn from the brine solutions during the up-flow percolation tests (section 6.3.1.8). Cu and Zn were observed to have minimum solubility at higher pH (Shim *et al.*, 2005) but leach at lower pH. The leaching of Cu and Zn due to the decrease in the pH of the systems towards the end of the up-flow percolation tests could be responsible for the lower concentration observed at some stage in the residues.

The mean concentration of Cr in Secunda and Tutuka solid residues was reduced by 1.8 mg/kg (1 %) and 9.6 mg/kg (7 %) respectively (Tables 6.3 and 6.4). This shows that Cr was leached from the fly ashes over time into the systems during the up-flow percolation tests. The trend observed in the solid residues agreed with what was observed in the leachates of the up-flow percolation tests (section 6.3.1.9, Figure 6.9). According to Jankowski *et al.* (2006) and Meima and Comans (1998), the leaching of Cr is dependent of the pH of the system as Cr was suggested to be soluble and mobile at high pH but precipitates out when the pH is low. The concentration of Cr in the fly ash-brine-antiscalant solid residues (Table 6.4) especially in TRA, showed a slight increase compared with Cr concentration in the fresh fly ash. The observation indicates that antiscalant could enhance the removal of Cr from the brine by the fly ashes.

In conclusion on this sub-section, the XRF data showed that some species such as Na, Mg, Cl, SO_4, Pb and Zn was removed significantly from the brine solution by the fly ashes during the up-flow percolation tests. The removal of these species from the brine solution could be as a result of formation of secondary mineral phases in the systems. On the other hand, significant concentrations of Ca, Ba, Al, Si, Sr and Cr were leached from the fly ashes into the systems over time. The mobility of the species captured in the solid residues will be determined by the sequential extraction tests presented in section 6.3.3. However, before the presentation of sequential extraction results, the possible crystalline mineral phases identified by the XRD in the solid residues are presented in sub-section 6.3.2.3 below.

6.3.2.3 Mineralogical composition of up-flow percolation solid residues: XRD analysis

This section presents and discusses the results of the results of the XRD carried out on the up-flow percolation solid residues. The XRD was employed to determine the mineralogical composition of the solid residues. The results are expected to show the effect of the fly ash and brine interactions on the mineralogical compositions of the solid residues. Since the effect of antiscalant was not significantly revealed in the leachates of the up-flow percolation tests (section 6.3.1) and on the XRF results solid residues, the XRD of the solid residues from the fly ash-brine-antiscalant systems was excluded. The preparation of the solid residue samples used for the XRD was described in section 3.3.6.

The results of the XRD analysis carried out to determine the mineralogical composition of the solid residues from the up-flow percolation tests are shown in Figures 6.11 and 6.12. The comparison of the X-ray diffractograms of the fresh fly ashes (SFA and TFA) and the solid residues at different depth along the column was done in order to determine the effect of the fly ash-brine interactions on the change in mineralogy.

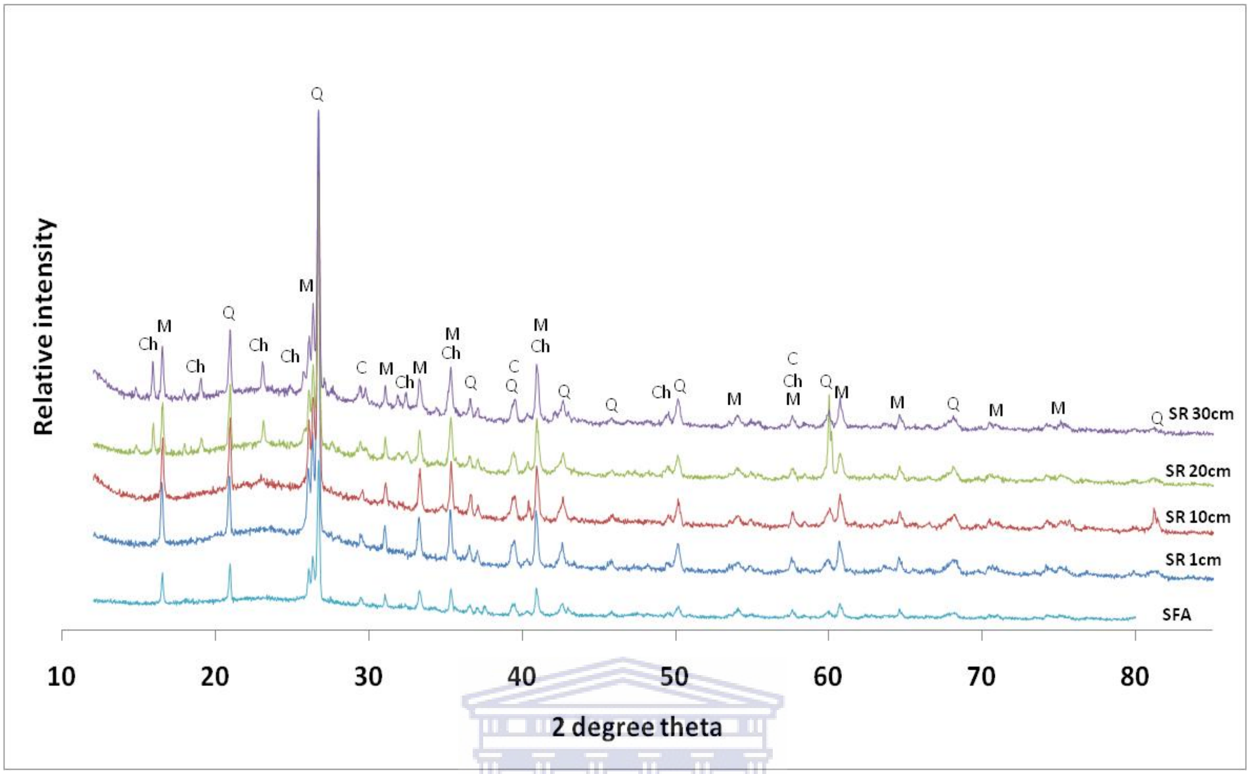

Figure 6.11: X-ray diffractograms of the residues from Secunda up-flow percolation systems as a function of depth. Peaks labelled are: M (mullite), Q (quartz), C (calcite), Ch (charlesite).

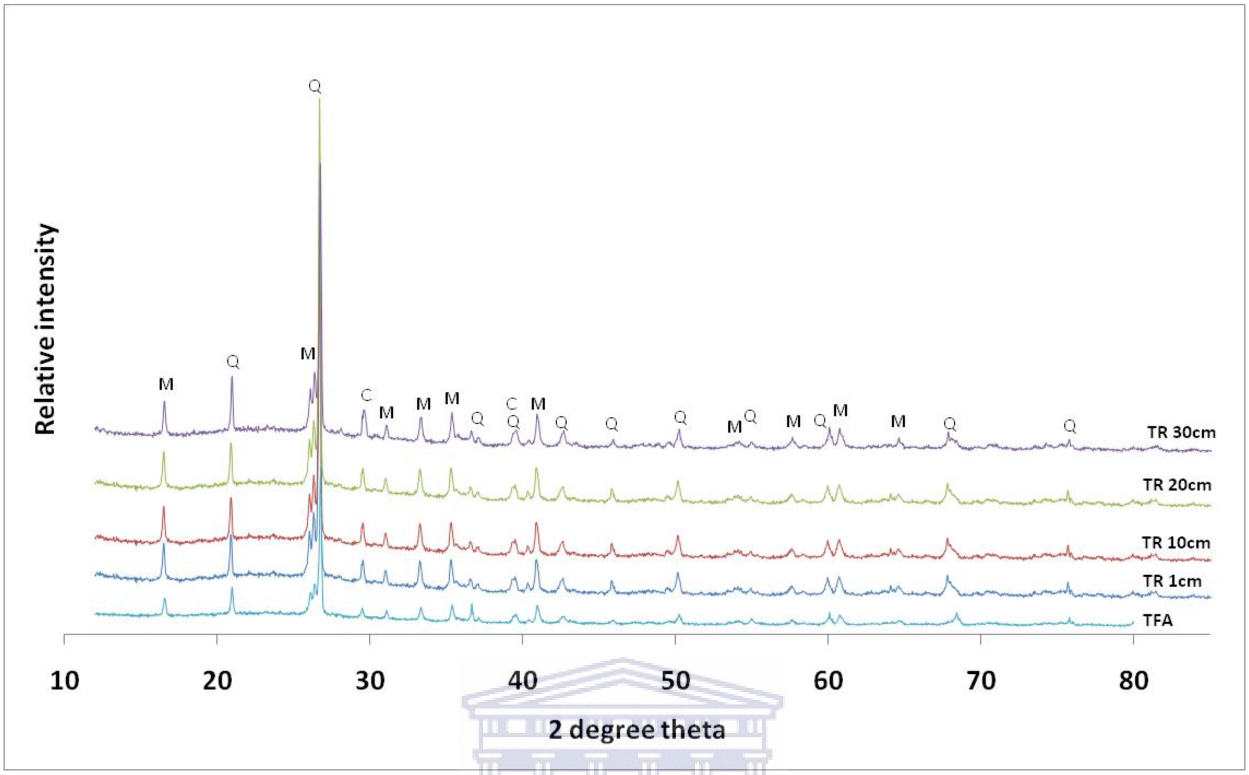

Figure 6.12: X-ray diffractograms of the residues from Tutuka up-flow percolation systems as a function of depth. Peaks labelled are: M (mullite), Q (quartz), C (calcite).

The prominent peaks identified in Secunda fresh fly ash (SFA) and the solid residues from Secunda up-flow percolation tests along the depth of the column (SR 1 cm, SR 10 cm, SR 20 cm and SR 30 cm) (Figure 6.11) were quartz (Q), mullite (M) and calcite (C). Apart from the identification of quartz, mullite and calcite, a new mineral phase known as charlesite (Ch) [$Ca_6(Al,Si)_2(SO_4)_2B(OH)_4(OH,O)_{12}.26(H_2O)$] was identified in the solid residues at SR 20 cm and SR 30 cm depth. The formation of this new mineral phase could partially be responsible for the removal of some species such as Ca, SO_4, Si and B as was observed by the lower concentrations of these species found in the leachates of the up-flow percolation tests (section 6.3.1).

In the case of Tutuka fresh fly ash (TFA) and the solid residues from the up-flow percolation tests (TR 1 cm, TR 10 cm, TR 20 cm and TR 30 cm), there was no secondary mineral phase identified in the solid residues (Figure 6.12) despite the removal of some species by the fly ash as was observed by the decreased concentrations in the leachates. The absence of secondary mineral phases in the residues does not necessarily indicate that secondary mineral phases were not formed in the residues during the up-flow percolation test, but that the phases may be in low concentration or in amorphous form, which may not be detectable by the XRD technique. Another reason for non-detection of new mineral phase(s) by XRD could be due to the masking effect by the fly ash alumino-silicate matrix and the highly crystalline mullite and quartz phases that are abundant in both the fresh fly ashes and the up-flow percolation solid residues (Figures 6.11 and 6.12).

The non-identification of more crystalline mineral phases apart from calcite and charlesite during the up-flow percolation tests supports the assumption that the removal of species from the brine solution by the fly ashes is transient. The continuous inflow of brine solution may not allow the interactions of the species to form significant quantities of secondary crystalline mineral phases despite the low flow rate (12 mL/h).

6.3.2.4 Scanning electron microscopy-energy dispersive X-ray spectroscopy (SEM-EDS) analysis of the up-flow percolation solid residues

Despite the observation in the previous section (section 6.3.1) that some species were significantly removed from the brine solution either by precipitation or adsorption on the surfaces of the fly ash particles during the up-flow percolation tests coupled with the XRF results that showed the capturing of some species by the fly ashes, the XRD analysis could only identify two new mineral phases (calcite and charlesite). This could be due to the poor crystallinity of other new phases or as a result of low concentration in the residues. The SEM-EDS analysis was therefore carried out on the solid residues from the up-flow percolation tests in order to semi-quantitatively identify most of the elements that may form mineral phases that could not be identified by XRD in the solid residues. Having considered the insignificant effect of the antiscalant on the release and removal of species from the up-flow percolation systems, the SEM-EDS analysis was only employed on the solid residues from Secunda and Tutuka fly ash-brine up-flow percolation systems. The solid residues (samples) were taken from the top and bottom sections of the columns. On the SEM photos of the solid residues (Figure 6.13), three different spots were identified for EDS analysis for each sample. Due to the limitation of SEM-EDS, the qualitative results obtained from the analysis can only provide a general trend of abundance of elements in the identified spots and hence only a general conclusion can be drawn.

Figure 6.13 presents the SEM micrographs of the residues from Secunda and Tutuka up-flow percolation systems while the weight % of the elements available at selected analyzed spots are presented in Tables 6.9 and 6.10.

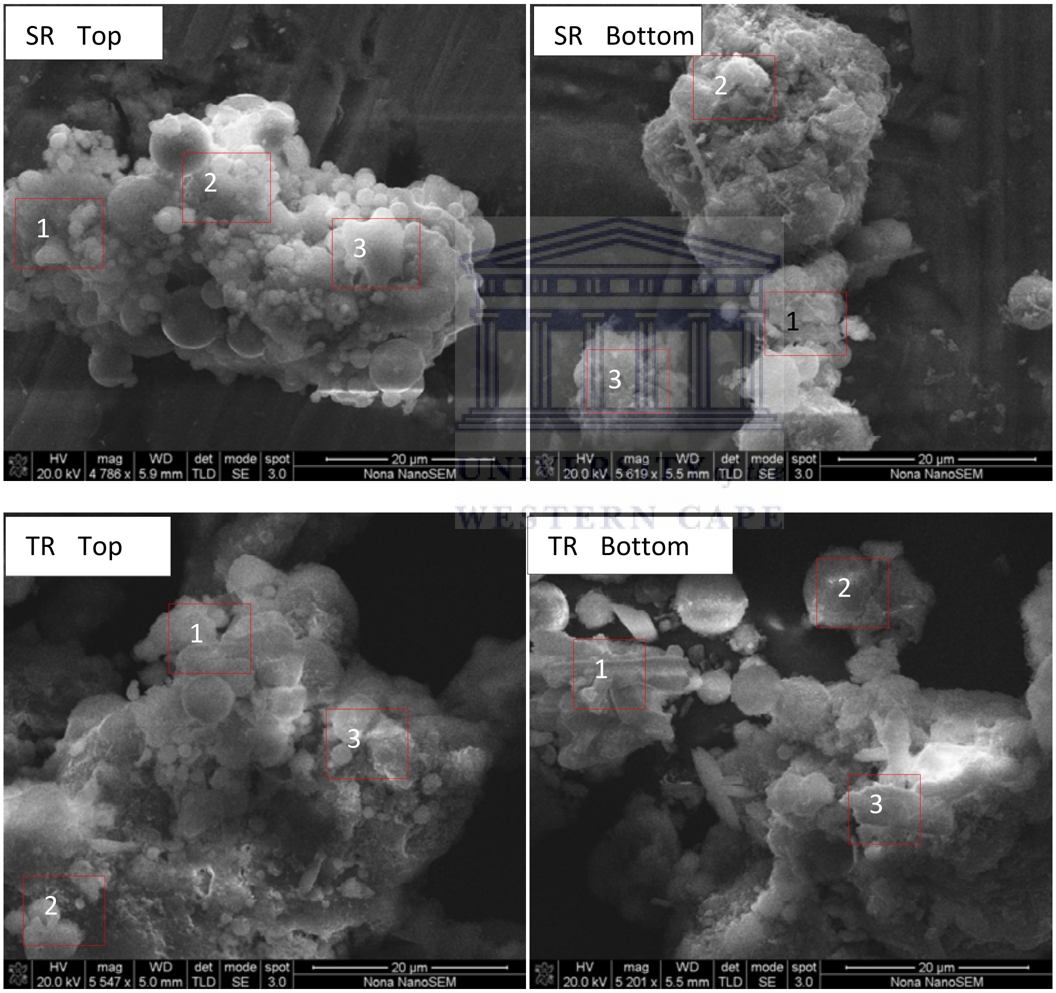

Figure 6.13: SEM-EDS micrograph of Secunda solid residue (SR top and bottom) and Tutuka solid residue (TR top and bottom) showing spots of EDS analysis

Table 6.9: EDS spot analysis (weight %) of solid residues (SR) recovered from Secunda up-flow percolation tests

	SR					
	Top			Bottom		
Element	1	2	3	1	2	3
O	58.54	42.52	42.09	43.7	43	54.49
Na	1.59	0.72	0.78	0.75	1.07	0.57
Mg	2.91	0.63	1.01	0.55	0.63	0.38
Al	11.6	35.92	30.5	30.03	28.31	14
Si	15.65	15.3	19.46	15.02	16.85	25.22
S	0.67	0	2.2	1.36	1.35	0.88
Cl	0.32	0	0.69	0	0	0
K	0.7	1.83	0.8	0.53	0.65	0.44
Ca	7.28	0.59	1.24	4.87	5.98	2.63
Ti	0.73	0	0	0.39	0	1.01
Fe	0	0.7	0	0.96	0.61	0.39
Cu	0	1.79	1.59	1.38	1.55	0

Table 6.10: EDS spot analysis (weight %) of solid residues (TR) recovered from Tutuka up-flow percolation tests

	TR					
	Top			Bottom		
Element	1	2	3	1	2	3
O	58.22	56.57	52.11	54.44	52.56	51.58
Na	4.06	0.62	1.34	0.72	1	0.88
Mg	2.58	0.67	0.93	1.39	1.68	3
Al	8.92	16.64	16.67	14.47	14.29	13.96
Si	12.59	21.15	24.25	18.64	26.16	24.04
S	1.65	0	0.38	0.48	0.4	0.65
Cl	1.22	0	0	0	0.41	0
K	0	0.31	1.12	0.71	0.78	0.7
Ca	4.88	1.32	2.32	6.66	1.59	1.89
Ti	0	0.83	0.89	1.09	0	0.65
Fe	4.64	1.89	0	1.4	1.14	2.65

The SEM micrographs showed structural alteration of the fly ash matrix with some agglomerated particles which morphology was similar to what was observed in section 5.3.1.4 (Figures 5.11 and 5.12). The agglomeration could be due to the formation of amorphous phases or as a result of inter-particle contact (Kutchko & Kim, 2006) during the up-flow percolation tests.

As determined by the EDS, the results of the analyzed spots 1, 2 and 3 on the SR top (Table 6.9) showed that, apart from the high concentrations of Al and Si, species such as Na, Mg, Ca, K, S and Cl were enriched in the solid residue from the top of the column. The presence of Ca and S in spots 1 and 3 could suggest the precipitation of Ca, S-rich mineral phases such as $CaSO_4$ and gypsum while the presence of Na, K and Cl could be as a result of the interactions of the fly ash with the brine solution. Spot 2 on the SR top showed the presence of Fe and Cu while S and Cl were missing. The presence of Fe and Cu could probably be due to adsorption of Cu on the Al or Fe-oxyhydroxides expected to form in the solid residues. The results of the up-flow percolation tests presented in section 6.3.1 [Figure 6.4 (SC8 and TC8)] revealed the removal of Mg by the

fly ash. Therefore, the presence of Mg in the solid residues could be as a result of the formation of Mg-rich mineral phases such as $Mg(OH)_2$ during the up-flow percolation tests.
On the SR (bottom), the elements identified in the analyzed spots 1, 2 and 3 were similar to those observed on top of the column except for Cl that was not identified in the analyzed spots. The missing of Cl in the analyzed spots at the bottom of the column did not indicate its non existence in the solid residue because the leachates of the up-flow percolation tests [Figure 6.5 (SC13 and TC13)] showed Cl removal from the systems.

The results of the EDS analysis (Table 6.10) carried out on some spots on the solid residues from Tutuka up-flow percolation systems showed the enrichment of Al, Si, O, Na, Mg, S, Cl, Ca, K and Fe in the residues. The elements identified in Tutuka solid residues (Table 6.10) were almost the same as those found in Secunda residues (Table 6.9) except for Cu. Apart from the aluminosilicates phases present in the residues, the presence of Ca and S in the residues from the top and bottom of the columns could be attributed to the formation of anhydrite or gypsum. As observed in Secunda residues, the presence of Na, K and Cl could indicate probable formation of Na, K or Cl-rich phases in the solid residues.

In conclusion, the presence of elements such as Al, Si and O are due to the aluminosilicate phases in the solid residues such as quartz and mullite while the presence of Ca and S could indicate the precipitation of hydrated or anhydrous Ca and SO_4-rich mineral phases such as charlesite and calcite identified by the XRD in the solid residues. The presence of Na, K and Cl could be attributed to the formation of Na, K or Cl-rich phases while the presence of Cu could be due to it adsorption on the surfaces of the fly ashes or on Al, Fe oxyhydroxides in the solid residues. As stated earlier, the results of the EDS analysis cannot be conclusively used to determine the particular mineral phases present in the solid residues due to its limitation but the significant presence of these elements suggests the precipitation of secondary mineral phases.

6.3.2.5 Summary

The characterization of the solid residues recovered from the up-flow percolation tests using different analytical techniques such as XRF, XRD and SEM-EDS was performed to understand the chemical and mineralogical compositions of the solid residues.

The XRF results showing the chemical composition of the solid residues correlated with the leaching trends observed of some species from the fly ashes or the removal of some species from the brine solutions. The concentrations of species such as Mg, Na, Cl, Co, Pb, Zn and S in the solid residues recovered from the up-flow percolation tests were observed to be higher than their concentrations in the fresh fly ashes indicating that these species were removed from the brine solutions by the fly ashes over the test period of 173 days. The XRF results also revealed that species such as Al, Si, Ca, Ba and Ni were leached from the fly ashes during the up-flow percolation tests. Species such as Fe, Mn, K and Cr in the solid residues increased and later decreased at certain depths of the columns. This suggests that the transient secondary mineral phases formed during the percolation tests containing these species could leach out when the conditions of the systems are not favourable. The results of the XRF correlate significantly with trends found by the ICP-MS and IC analyses of the leachates (section 6.3.1) of the up-flow percolation tests. The XRF results predict the probable precipitation of transient phases during the up-flow percolation tests as the results showed an increase in the concentrations of some species when compared with their concentrations in the fresh fly ashes.

Generally, the XRF results showed that the major species such as Na, Mg, S and Cl in the brine solution were significantly removed by the fly ashes over the test period of 173 days. The capacity of Secunda fly ash and Tutuka fly ash to remove Cl from the brine solution was almost equal despite the fact that Tutuka fly ash was conditioned with brine solution before being sampled. This indicates that if Tutuka fly ash had not contacted brine before sampling, its capacity to removed Cl could be more than Secunda fly ash. The capacity of Tutuka fly ash to remove Na from the brine solution is higher than that of Secunda fly ash as higher concentration of Na (3173 mg/kg) was found in Tutuka solid residue despite its contact with brine solution before sampling. On the other hand, the capacity of Secunda fly ash to remove Mg and S was

higher than the removal capacity of Tutuka fly ash. The development could be attributed to the slightly higher pH of Secunda up-flow percolation systems than the pH of Tutuka up-flow percolation systems. However, the higher pH of Secunda up-flow systems helped in the removal of species that are controlled by pH but did not affect other species such as Na and Cl that are independent of pH. The higher pH in Secunda systems favoured the precipitation of more Mg and S-containing mineral phases.
The effect of the antiscalant on the leaching or the removal of species from the up-flow percolation tests was not significant in the concentrations of species in the solid residues except for some species such as Ca, Sr and K where leaching was observed to be slightly reduced in the fly ash-brine-antiscalant residues.

Apart from quartz, mullite and calcite that were identified in both fresh fly ashes and the residues, the XRD analysis revealed the formation of a secondary mineral phase known as charlesite during the up-flow percolation tests. As stated earlier (section 6.3.2.3), non identification of other mineral phases does not imply their non-existence but could be as a result of the amorphous form in which they exist. The SEM-EDS results revealed the abundance of some species such as Al, Si, O, Na, Mg, S, Cl, Ca and K in the solid residues as a result of the interactions between the fly ash and the brine solutions during the up-flow percolation tests. The abundance of these species could signify the existence of some mineral phases in the solid residue which were not identified by the XRD analysis due to their presence in amorphous phases or as a result of their low concentrations in the residues.

Generally, the results of the characterization tell us that the interactions of fly ashes with the brine solution could remove major species such as Na, Ma, Cl and SO_4 from the brine solution. Therefore, having established the removal of some species from the brine solutions by the fly ashes, the mobility of the species in the solid residues under different physicochemical conditions has to be examined in order to understand the stability of the phases formed during the up-flow percolation tests. The next section (6.3.3) of this chapter deals with the mobility of species in the solid residues recovered from the up-flow percolation tests by presenting the results of the sequential chemical extraction tests.

6.3.3 Mobility and partitioning of major and minor species in solid residues from the up-flow percolation tests

The results and discussion of the sequential extraction tests carried out on the fresh fly ash and the solid residues from the up-flow percolation tests are presented in this section. The sequential extraction tests were carried out only on the fly ash-brine solid residues (see section 3.3.8 for sequential extraction procedure). The solid residues from the fly ash-brine-antiscalant were not included. The solid residues used was taken from the top, middle and bottom of the column and prepared as described in section 3.3.6. Representative samples were taken, after the samples from each section were crushed, milled and homogenized. In the previous sections (6.3.1 and 6.3.2) of this chapter, the results presented showed that some species such as Na, Mg, Cl, SO_4, Fe, Mn, Co, Ni, Cu, As, Pb and Zn were removed by the fly ashes during the fly ash-brine up-flow percolation tests while species such as Ca, Ba, Al, Si, Sr, Cr and Mo were leached from the fly ashes into the systems during the up-flow percolation tests. Having confirmed the removal of some species by the fly ashes during the up-flow percolation tests, determining the physicochemical forms in which these species may exist and their mobility under different conditions was considered necessary in order to determine the stability of the species trapped in the solid residues. Although the results of the sequential extraction tests are presented for both the leached and the removed species in the residues, the partitioning and the mobility of the species (Na, Mg, Fe, Mn, Co, Ni, Cu, As, Pb and Zn) removed from the brine solution during the up-flow percolation tests are discussed in this section. The release of B, Cl and SO_4 from the solid residues is not presented in the sequential extraction tests' results because most of the chemicals used to carry out the extraction tests contained these species and may not give the actual concentrations of these species in the systems. However, the results of the ANC tests presented in chapter 5 have conclusively shown the high mobility of these species thus their water soluble nature when the solid residues contact water.

The concentrations of major and minor species (mg/kg) in the fresh fly ash (SFA and TFA) and the solid residues (SR and TR) recovered from the up-flow percolation tests are shown in Tables 6.11 and 6.14 while the results showing the release of selected species (mg/kg) from the sequential extraction tests and the extraction yields (%) are presented in Tables 6.12, 6.13, 6.15 and 6.16, and Figures 6.16 and 6.17 respectively. The concentrations of species in the solid residues recovered from the up-flow percolation tests was compared with their concentrations in the fresh fly ashes in order to calculate the concentration of each of the species leached out of the fly ashes or captured from the brine solution by the fly ashes over time (Tables 6.11 and 6.14).

These results presented in Tables 6.11 and 6.14 showed that Na and Mg are the major elements that were significantly removed from the brine solution by the fly ashes while minor species such as Co, Pb, Cu, Mn and Zn were removed from the brine solution by the fly ashes at some stages. Detailed discussion of these results has been presented in section 6.3.2.2. The main reason for presenting these results is to compare the concentrations of species captured in the solid residues with the results of the water soluble fraction of the sequential extraction tests in order to determine the amount of the captured species in the solid residues that are easily soluble and the amounts that are not mobile.

Table 6.11: Mean concentration of major and minor species in Secunda fresh fly ash (SFA) and solid residues (SR) recovered from Secunda up-flow percolation systems, and the concentration of major and minor species leached or removed from the up-flow percolation systems

	Major element (mg/kg)							
Parameter	Al	Ba	Ca	K	Mg	Na	Si	Sr
SFA	137751	2292	66467	6724	13572	4525	231787	3268.1
SR	129710.8	1670.9	51399.5	6398.5	17819.3	6985.8	212373	2788.6
Mean conc. leached/retained	-8040.2	-621.1	-15067.5	-325.5	4247.3	2460.8	-19414	-479.5

	Minor element (mg/kg)									
Parameter	As*	Co	Cr	Cu	Fe	Mn	Mo*	Ni	Pb	Zn
SFA	33.86	10.5	129.8	37	16506	387	5.83	58.5	41	32.1
SR	ND	10	128	28.5	16317.8	350.3	ND	54.6	46.4	88.9
Mean conc. leached/retained	ND	-0.5	-1.8	-8.5	-188.2	-36.7	ND	-3.9	5.4	56.8

*Data from total acid digestion tests, negative (-) sign indicates leaching

Table 6.12: Mobility of major elements (mg/kg dry weight) from Secunda fresh fly ash and solid residues at different sequential extractions fraction; SFA = fresh fly ash, SR Top = Solid residue on top of the column, SR Middle = Solid residue at the middle of the column, SR Bottom = Solid residue at the bottom of the column. (*n=3*)

		Major element							
Extraction fraction	Sample description	Al	Ba	Ca	K	Mg	Na	Si	Sr
Water soluble	SFA	367.6±9	40.1±2.7	14903.5±150	14.8±3.6	20.2±1.4	86.3±5	759.3±193.8	266.3±1.8
	SR-Top	67.5±44.7	3.2±1.4	199.5±51.5	150.2±14.6	143.6±20	2444.8±174	214.6±32.7	7.4±0.8
	SR-Middle	158.7±18.4	5.7±0.3	3868.9±83	146±23.2	135.8±3	2772.1±40.8	123.7±18.3	66.6±0.4
	SR-Bottom	317.9±4.4	6.2±0.2	4565.8±71.4	139.5±15.4	76.2±0.6	2253.9±24.6	124.4±10	92.4±1.1
Exchageable	SFA	2.6±0.3	83.2±4.3	15714.3±43.5	39.2±2.5	1882.6±24.4	BDL	761.4±13	384.1±3.7
	SR-Top	6.5±9.3	92.8±3.5	6511.3±60	243.3±54.7	941.2±6.6	429±7.6	259±18.9	155.6±1.1
	SR-Middle	6.5±1.5	106.7±3	22423.4±167	211.2±16.2	780.7±11.5	517±3.2	290.5±8	290.4±6.6
	SR-Bottom	10.4±4	103.1±3.6	24020.7±235	179.9±6.5	1062±8.1	420.7±10	211±6.4	358.9±3.2
Carbonate	SFA	192.1±17.3	41.6±1.2	3018.4±29.1	28.7±1	2376.6±16.8	17.9±7.8	1010.1±44.4	103.4±2.6
	SR-Top	975.1±12.4	57.5±1.5	3197.2±23.2	56.6±13.6	4805±50	222.7±4.6	1080.8±101	66±0.2
	SR-Middle	1791.7±28.8	157.9±0.5	11188.8±97	60.3±22.2	4064.9±26	76.7±16.7	3155.2±284	160.6±1.3
	SR-Bottom	1618.2±16	151.4±6	9266.4±201	54.2±10.5	2869.7±31.8	77±10	3558.6±274	165±1.1
Iron and Manganese	SFA	330.7±5.4	30.7±0.4	1942.7±10.5	13.1±1	1009.8±7	85.4±14.7	198.5±7.5	68±1.3
	SR-Top	213.3±3.2	17.6±0.2	607.4±32.6	59.1±8.6	828.5±5.5	335.8±49	472.3±57.4	10.5±0.1
	SR-Middle	347.8±2.3	54.9±0.6	1348.2±22.2	82.1±3.6	2127.5±31.3	299.9±3.1	1149.9±6.4	24.5±0.5
	SR-Bottom	303.2±7.4	36.8±0.3	1031.1±1.3	81±6.1	1078±19.3	363.7±8.4	1214.5±131	20.8±0.3
Residual	SFA	20560.2±71.7	993.4±89	7160.8±27.6	1039±87.9	290±8.5	2493.4±28.3	141703±1326	390.2±4.8
	SR-Top	10721.3±229	743.9±15.4	1631.7±31	1368.4±96.2	182±9.5	2945±96.5	209519±3880	392.9±12.1
	SR-Middle	12315.3±70.3	260.2±2	1364.4±50.6	1036.6±50.3	186.3±5.4	2270.6±70	198489±3780	221.2±1.7
	SR-Bottom	12050.7±115	302.7±2.2	1719.3±40.1	1470.3±112	264.6±4.9	4550±32.7	191840±2533	139.8±2.1

Table 6.13: Mobility of minor elements (mg/kg dry weight) from Secunda fresh fly ash and solid residues at different sequential extractions fraction; SFA = fresh fly ash, SR Top = Solid residue on top of the column, SR Middle = Solid residue at the middle of the column, SR Bottom = Solid residue at the bottom of the column. (*n=3*)

		Minor element									
Extraction fraction	Sample description	As	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
Water soluble	SFA	0.05±0.01	0.01±0	5.04±0.6	0.2±0.1	16.8±2	0.5±0.1	1±0.1	0.9±0.1	0.2±0.1	0.7±0.3
	SR-Top	0.2±0	0.04±0	1.4±0.7	0.4±0.2	13.5±8.5	0.9±0.33	0.09±0.1	0.6±0.3	0.07±0	2.6±1.2
	SR-Middle	0.1±0	0.03±0	2.5±0.6	1±0.8	16.1±4.2	0.6±0.1	0.2±0	1±0.2	0.1±0	1.5±1.1
	SR-Bottom	0.2±0	0.03±0	2.4±0.2	0.5±0.04	14±1.3	0.6±0.1	0.2±0.04	0.7±0.2	0.06±0.01	0.3±0.1
Exchageable	SFA	5.5±0.2	0.1±0	30.3±2.3	1.7±0.1	0.3±0.02	18.6±1.3	2.1±0.1	1.01±0.1	0.02±0	1.6±0.1
	SR-Top	1.7±0.2	0.1±0	6.6±0.6	0.9±0.1	1.8±0.2	18.8±1.2	0.4±0.01	0.5±0.1	0.03±0	18.3±1.2
	SR-Middle	1.3±0.1	0.05±0	7.8±0.1	0.6±0.1	0.8±0.3	5±0.3	0.6±0	0.2±0	0.02±0	BDL
	SR-Bottom	1.4±0.1	0.07±0	9.6±0.2	0.9±0.05	1.3±0.1	7.7±0.1	0.7±0.1	0.4±0.02	0.02±0	BDL
Carbonate	SFA	1.8±0.1	0.3±0	15.2±0.3	1.5±0.1	8.2±0.3	44.2±1	0.5±0.02	1.8±0.04	0.2±0	4.1±0.5
	SR-Top	1.6±0.1	0.4±0	6.9±0.5	10.2±0.2	56.7±3.6	56.4±2.2	0.2±0.03	1.9±0.1	0.5±0	127.8±5.5
	SR-Middle	1.6±0.1	0.6±0.03	15.6±0.3	2.2±0.1	98.5±2.1	47.5±2.5	0.1±0	3.1±0.2	0.7±0	2±0.2
	SR-Bottom	1.7±0.1	0.5±0.02	15.7±0.2	3±0.1	135.3±5.2	47.5±2.6	0.2±0	2.6±0.2	1.2±0.1	2.5±0.2
Iron and Manganese	SFA	0.1±0.01	0.2±0	2.4±0.1	0.2±0.02	73.5±63.7	67.6±1.4	0.1±0	0.8±0.03	0.1±0.03	2±0.2
	SR-Top	0.2±0	0.2±0	1±0.1	1.3±0.1	150.1±2.5	39.4±1.2	0.03±0	0.4±0.02	0.07±0	26.1±1
	SR-Middle	0.1±0	0.3±0.01	2.9±0.03	0.7±0.1	174.1±2.4	47.9±0.6	0.02±0	1±0.1	0.05±0	1.1±0.1
	SR-Bottom	0.2±0	0.2±0.03	2.6±0.1	0.6±0.03	194.7±4.1	42.4±1.3	0.02±0	0.9±0.04	0.1±0	1.5±0.6
Residual	SFA	17.2±1.8	8.1±0.7	96.1±8.5	35.5±15.3	10255.6±132	139.8±12.2	1.6±0.2	46.5±3.8	23.1±2.1	75±14.5
	SR-Top	17.4±0.2	10.1±0.1	125.1±0.8	64.2±0.2	15003.8±167	215.6±9.4	1±0.02	47.4±0.5	32.7±0.5	77±2.5
	SR-Middle	21.8±0.5	10±0.3	134.1±0.8	62.3±0.9	14367.2±100	187±8	1.4±0.1	46.5±1	28.9±0.2	65.5±2.1
	SR-Bottom	22.8±1.1	8.8±0.3	118.8±2.4	56.8±1	12862.4±188	138.6±9.1	2±0.1	48.2±1	26.9±0.2	199.5±0.8

Table 6.14: Mean concentration of major and minor species in Tutuka fresh fly ash (TFA) and solid residues (TR) recovered from Tutuka up-flow percolation systems, and the concentration of major and minor species leached or removed from the up-flow percolation systems

	Major element (mg/kg)							
Parameter	Al	Ba	Ca	K	Mg	Na	Si	Sr
TFA	129495	983.7	42096	6890	8204	2151	242352	1164.4
TR	125925	852.9	35121.3	6888	11141.5	5323.8	230648.3	1120.9
Mean conc. leached/retained	-3570	-130.8	-6974.7	-2	2937.5	3172.8	-11703.7	-43.5

	Minor element (mg/kg)									
Parameter	As*	Co	Cr	Cu	Fe	Mn	Mo*	Ni	Pb	Zn
TFA	44.79	21	145.3	32.8	37907	387	8.3	62.2	50.3	48.5
TR	ND	21.6	135.7	36.4	37172	407	ND	59.2	58	104.3
Mean conc. leached/retained	ND	0.6	-9.6	3.6	-735	20	ND	-3	7.6	55.8

*Data from total acid digestion tests, negative (-) sign indicates leaching

Table 6.15: Mobility of major elements (mg/kg dry weight) from Tutuka fresh fly ash and solid residues at different sequential extractions fraction; TFA = fresh fly ash, TR Top = Solid residue on top of the column, TR Middle = Solid residue at the middle of the column, TR Bottom = Solid residue at the bottom of the column. (*n=3*)

		Major element							
Extraction fraction	Sample description	Al	Ba	Ca	K	Mg	Na	Si	Sr
Water soluble	TFA	371.8±12.8	4.4±0.3	2200.5±13.6	81.7±3.5	28±1.5	495.6±17.8	544.6±164.2	36.1±0.5
	TR-Top	85.2±2	4.3±0.5	456.4±43	158.5±5.6	122.4±2.7	3768.2±285	313.8±38.7	7.5±0.4
	TR-Middle	25.7±2.8	2.2±0.3	339.9±19.3	149±23.4	138±5.4	3790.2±39	119.6±2.3	7.8±0.2
	TR-Bottom	72.2±5	3.9±0.4	534.4±8.5	102.7±7.6	166±1.8	3674.5±29.2	329.8±124.7	10.5±0.1
Exchangeable	TFA	2.1±0.3	97.9±3.5	11587±82.7	142.9±16.2	872±4.2	161±8.2	457.3±63.1	182.5±2.4
	TR-Top	2.7±0.1	60.3±4.7	5434±77	292.7±16.4	582.1±11	853.7±10.5	176.4±11.2	102.9±0.4
	TR-Middle	3.6±3.2	113.2±1.1	10617±1506	151.6±32.8	984.2±28.5	477.2±64.3	259.2±18.6	123.8±11.5
	TR-Bottom	3.5±2.8	114.4±3.1	8851.8±88.6	148.6±22.3	957.3±7.7	607.1±5.7	251±30	142.4±1.6
Carbonate	TFA	995.4±15.1	51.5±1.9	3741.5±18.7	16.6±3.3	958.5±3.7	BDL	1881.8±39	58.1±0.6
	TR-Top	471.2±12.4	28.7±0.4	2391.5±24.7	36.3±6.4	895.1±6	160.4±99	632±9.7	33.3±0.4
	TR-Middle	955.8±6.1	32.6±0.6	2420.2±9.8	32.5±18.3	2860.9±45.8	285.8±3.7	1119.3±32	33.2±0.2
	TR-Bottom	1117.4±16.3	40.5±0.4	2991.8±102	23.9±4.7	2757.5±21.7	281.5±7.2	1373.3±12.4	39.7±0.4
Iron and Manganese	TFA	314.4±12.2	19.5±0.8	2032.4±24.3	14.9±5.5	672.6±7.2	81.3±4.3	223.7±15	27.5±0.2
	TR-Top	165.4±9.3	7.1±0.6	775.4±104	65.9±11.1	366.4±11	360.3±30	475.7±19.2	6.2±1
	TR-Middle	222.6±1.4	6.6±0.9	543.5±13.4	28.8±10.4	771.7±12.3	280.7±10	405.8±10	3.4±0.3
	TR-Bottom	248.8±14	7.4±0.3	533.5±22.5	18.2±12	781.9±34.6	367.1±15.2	488.4±12.4	5.3±0.2
Residual	TFA	17389±187.2	323.9±24.5	2014.5±64	2107±185	153.8±5.5	1456±25.3	172048±2385	112±1.2
	TR-Top	13559.2±131	134.2±2.3	897.1±23.3	1509.5±9.8	117.9±6	2617.1±50.8	196935±2340	66.3±0.7
	TR-Middle	10272.2±190	124.9±0.9	1189.2±15	1030±67.5	133.4±3.7	1773.2±31.1	207034±1826	53±2
	TR-Bottom	12627.4±326	143.7±2.2	960.2±56	1101.6±119.8	154.3±5.9	2165.7±55.2	193839±4419	68.8±2

Table 6.16: Mobility of minor elements (mg/kg dry weight) from Tutuka fresh fly ash and solid residues at different sequential extractions fraction; TFA = fresh fly ash, TR Top = Solid residue on top of the column, TR Middle = Solid residue at the middle of the column, TR Bottom = Solid residue at the bottom of the column. (*n=3*)

		Minor element									
Extraction fraction	Sample description	As	Co	Cr	Cu	Fe	Mn	Mo	Ni	Pb	Zn
Water soluble	TFA	0.5±0.03	0.03±0	6±0.4	0.2±0.4	24.5±1.8	0.8±0.04	1.5±0.05	0.9±0.2	0.1±0	0.6±0.1
	TR-Top	0.2±0.01	0.07±0.01	2±0.4	1.5±0.1	35.4±3.1	2.2±0.04	0.1±0.03	1±0.2	0.1±0.01	5.2±0.2
	TR-Middle	0.3±0.03	0.05±0	1.8±0.3	0.4±0.1	15.8±1.8	0.7±0.1	0.1±0.04	0.9±0.2	0.04±0	0.4±0.1
	TR-Bottom	0.4±0.02	0.1±0.01	1.4±0.1	0.3±0.04	27.9±3.6	1.1±0.1	0.1±0.03	0.8±0.1	0.1±0.02	0.5±0.05
Exchangeable	TFA	4.1±0.2	0.2±0.01	9±0.5	0.3±0.1	0.3±0.02	8.8±0.5	1.5±0.05	0.7±0.03	0.1±0.04	2.1±0.3
	TR-Top	1.3±0.1	0.1±0.01	1.1±0.1	1.2±0.1	3.9±0.6	21.9±0.4	0.1±0.03	0.4±0.02	0.03±0.01	35.6±1.8
	TR-Middle	2.9±0.1	0.06±0.01	1.4±0.02	0.3±0.04	1.8±0.6	3.6±0.03	0.3±0.03	0.3±0.04	0.02±0	BDL
	TR-Bottom	3.04±0.2	0.05±0	1.3±0.1	0.1±0.05	1.2±0.2	5.3±0.4	0.3±0.03	0.2±0.07	0.01±0	BDL
Carbonate	TFA	1.4±0.1	0.4±0.01	4.2±0.2	0.8±0.03	135.7±7.7	31.2±0.5	0.2±0.01	1.5±0.05	1.3±0.05	4.9±0.3
	TR-Top	1±0.1	0.2±0.02	1.7±0.1	3.4±0.2	101.2±2.6	25.7±0.3	0.1±0.01	0.8±0.1	1.2±0.1	86.2±0.8
	TR-Middle	2±0.1	0.4±0.01	2.9±0.2	1.6±0.1	91.3±0.8	25.7±1.1	0.1±0	1.2±0.04	0.7±0.04	3.1±0.4
	TR-Bottom	2.4±0.2	0.4±0	3.2±0.01	1.2±0.1	130.5±4.2	28.7±1.1	0.1±0.01	1.3±0.04	0.8±0.03	4.3±0.2
Iron and Manganese	TFA	0.2±0.02	0.3±0.01	2.2±0.1	0.07±0.03	281.9±244.6	61.4±4.4	0.04±0.02	0.9±0.02	0.2±0.05	2.5±0.3
	TR-Top	0.2±0.05	0.2±0.02	0.9±0.02	0.6±0.03	187.4±4.1	16.5±0.5	0.01±0	0.5±0.1	0.1±0.01	20.5±0.8
	TR-Middle	0.3±0.03	0.3±0.02	0.9±0.04	0.3±0.03	174.7±1	31.9±0.1	0.01±0	0.5±0.04	0.09±0.01	1.8±0.4
	TR-Bottom	0.3±0.05	0.3±0.02	0.9±0.1	0.1±0.03	187.6±11.3	31.4±1.8	0.01±0	0.6±0.06	0.1±0	1.9±0.3
Residual	TFA	25.4±2	17.1±1.3	186.7±9.4	33.7±3.1	26650±135.7	200.6±14	10±0.5	110.3±4.7	35±2.5	134.2±6.7
	TR-Top	17.7±0.6	15.9±0.5	139.6±2.1	51.7±0.1	29424.7±323	200±3	2.2±0.2	54.1±0.6	34.8±0.1	123.2±2.8
	TR-Middle	19.5±1.1	16.6±0.2	140.6±2	45±1.4	34473.1±171	200.8±2.3	2.2±0.3	54.5±3.4	39±0.2	84.8±0.8
	TR-Bottom	19.2±0.3	15.6±0.3	132.4±3.6	43.3±1.1	29852.9±457	198.1±1.3	3.7±0.4	66.9±2.1	36.4±1.1	72.4±3.3

As stated above, the results of the species removed from the brine solution by the fly ashes during the up-flow percolation tests will only be discussed. These species include Na, Mg, Fe, Mn, Co, Ni, Cu, As, Pb and Zn. The reason for discussing these species was to determine the physiochemical forms in which the captured species in the solid residues exist, and then compare the concentrations of these species in the water soluble and exchangeable fraction of the sequential extraction tests with the concentrations captured in the solid residues in order to determine the concentrations of the captured species that are mobile. Other species such as Al, Ba, Ca, K, Si and Sr was presented to show their continuous mobility when in contact with water despite their leaching during the up-flow percolation tests.

6.3.3.1 Magnesium and Sodium

The concentrations of Mg and Na in the sequential extraction tests were shown in Tables 6.12 to 6.16. The comparison of the concentration of Mg in the solid residues (SR-Top, SR-Middle, SR-Bottom, TR-Top, TR-Middle and TR-Bottom) with what was observed in the fresh fly ashes (SFA and TFA) showed that the concentration of Mg, in most cases, was higher in the solid residues than in the fresh fly ashes. This is an indication that Mg was removed (Pueyo *et al*., 2003) from the brine solution by the fly ashes during the up-flow percolation tests. This observation corroborates what was presented in the previous sections where the concentration of Mg was found to be lower in the leachates after the up-flow percolation tests. Mg was predominantly found in the exchangeable, carbonate and iron and manganese fractions of the sequential extraction tests with the carbonate fraction having the highest Mg concentration. The concentration of Mg in the carbonate fraction was found to be 2376.6 mg/kg, 4805 mg/kg, 4064.9 mg/kg and 2869.7 mg/kg for Secunda fresh fly ash (SFA) and the solid residues (SR-Top, SR-Middle and SR-Bottom) respectively while in Tutuka fresh fly ash (TFA) and the solid residues (TR-Top, TR-Middle and TR-Bottom) were found to be 958.3 mg/kg, 895.1 mg/kg, 2860 mg/kg and 2757.5 mg/kg respectively. The predominance of Mg in the carbonate fraction coupled with the low concentration of Mg in the water soluble fraction is an indication that the Mg-rich mineral phase(s) that formed during the up-flow percolation tests are not easily soluble under normal environmental condition. The Mg removed from the brine solution by the fly ashes could exist as an insoluble phase such as $Mg(OH)_2$ which can only be released at low pH (Gitari *et al.,* 2009). The summation of the concentration Mg released in the water soluble and the exchangeable fractions compared with the concentration of Mg captured in the solid residues recovered from the up-flow percolation tests (Tables 6.17 and 6.18) showed that 1046.5 mg/kg of the 4247.3 mg/kg captured in the Secunda solid residue was easily soluble while 983 mg/kg of the 2937.9 mg/kg captured in Tutuka residue was easily soluble. This shows that 24.6 % of the Mg removed from the brine solution by Secunda fly ash during the up-flow percolation tests was easily soluble while 33.5 % of the Mg removed from the brine solution by Tutuka fly ash during the up-flow percolation test was easily soluble.

The concentration of Na (Tables 6.12-6.13 and 6.15-6.16) in the solid residues showed its predominance in the water soluble and residual fractions whereas in the fresh fly ashes, it is mainly associated with the residual fraction. 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). Therefore, the concentration of Na in the water soluble fraction is of importance in this study in order to study its mobility in the solid residues over time. The concentrations of Na in Secunda fresh fly ash (SFA) in the water soluble fraction was found to be 86.3 mg/kg while its concentrations in the case of Tutuka fly ash (TFA) was 495.6 mg/kg. The concentrations of Na released from the solid residues into the water soluble fraction irrespective of the section of the column were observed to be higher than the concentrations of Na released from the fresh fly ashes. This higher concentration of Na in the solid residues compared with its concentration in the fresh fly ashes is an evidence of the removal of Na from the brine solution by the fly ashes during the up-flow percolation tests. The concentrations of Na released from Secunda solid residues (SR-Top, SR-Middle and SR-Bottom) in the water soluble fraction ranged from 2253.9 to 2772.1 mg/kg while the Na concentration released from Tutuka solid residues (TR-Top, TR-Middle and TR-Bottom) ranged from 3674.5 to 3790.2 mg/kg. The summation of the concentration of Na released in the water soluble and exchangeable fractions was found to be higher than the concentration of Na removed from the brine solution by the fly ashes during the up-flow percolation tests. The total amount of Na removed from the brine solution by Secunda and Tutuka fly ashes was 2460.8 mg/kg and 3172.8 mg/kg respectively while the concentration of Na released from the Secunda and Tutuka solid residues into the water soluble and exchangeable fractions was 2945.8 mg/kg and 4390.3 mg/kg respectively (Tables

6.17 and 6.18). This shows that, apart from the release of all the Na removed from the brine solution, significant amounts of Na originally contained in the fly ash was easily released during the sequential extraction tests. The predominance of Na in the water soluble fraction of the solid residues indicates its existence as highly soluble salts such as NaCl (Kirby and Rimstidt, 1994; Mattigod *et al*., 1990; van Herck and Vandecasteele 2001) which is mobile under natural environmental conditions. In the study carried out by Eighmy *et al*., (1995) on speciation and leaching behaviour of elements in municipal solid waste incineration MSWI (which has similar characteristics with fly ash), the XRD analysis revealed the occurrence of Na and K as NaCl or $NaSO_4$ and KCl and K_2SO_4 respectively. The species that exist in the water soluble and exchangeable fractions are the most labile form that can be easily leached and readily reach the environment when fly ash is rinsed by rain water (Yuan, 2009). The release of Na in the water soluble fraction showed that Na removed from the brine during the interactions with fly ash could be rapidly leached 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.

6.3.3.2 Iron and Manganese

The concentrations of Fe and Mn are presented in Tables 6.12-6.13 and 6.15-6.16. The bulk of Fe and Mn released during the sequential extraction tests were in the iron and manganese and residual fractions. Significant concentrations of these species were also contained in the carbonate fraction. The fluctuation observed in the release of Fe and Mn in the previous sections was also revealed in the sequential extraction tests. Comparison of the Fe and Mn released from the fresh fly ashes with what was released from the solid residues showed that the concentrations of Fe and Mn in the latter were higher than in the former in some cases in iron and manganese and residual fractions. The concentration of Fe in Secunda solid residues in iron and manganese fraction ranged between 150 mg/kg and 194.5 mg/kg (Tables 6.12 and 6.13) while in Tutuka solid residues, the concentration of Fe in iron and manganese fraction ranged between 174 and 187.6 mg/kg (Tables 6.15 and 6.16). The concentration of Mn released in iron and manganese fraction in the case of Secunda solid residues ranged between 39 and 47.9 mg/kg while its concentration in Tutuka solid residues were between 16 and 31.9 mg/kg (Tables 6.12-6.13 and 6.15-6.16). The increase observed in the concentrations of Fe and Mn in iron and manganese and residual fractions, when their concentrations in the solid residues were compared with those in the fresh fly ashes, showed that these species were removed at some stage from the systems during the up-flow percolation tests. The predominance of Fe and Mn in iron and manganese and residual fractions indicates that the phases containing these species in the solid residues cannot be easily leached to the environment under normal environmental conditions. Smeda and Zyrnicki, (2002) observed that Fe and Mn in fly ash exists in their oxides which may not be easily dissolved except under extreme condition.

6.3.3.3 Cobalt and copper

The results of the sequential extraction tests showing the release of Co and Cu from fresh fly ashes and the solid residues at different extraction steps are shown in Tables 6.12-6.13 and 6.15-6.16. Apart from the predominance of Co and Cu in the residual fraction of Secunda and Tutuka solid residues, the concentrations of Co and Cu were observed to be slightly high in the carbonate fraction. The concentration of Co in the carbonate fraction ranged between 0.4 and 0.6 mg/kg for Secunda solid residues while Co concentration in the carbonate fraction for Tutuka solid residues was found to be in the range of 0.2 and 0.4 mg/kg. The concentration of Cu in the carbonate fraction of Secunda solid residues ranged between 2.2 and 10.2 mg/kg while in Tutuka solid residues, the concentration of Cu in the carbonate fraction was found to be in the range of 1.2 and 3.4 mg/kg. Comparison of the concentrations of Co and Cu released from the fresh fly ashes with the concentrations of Co and Cu released from the solid residues showed an increase in the concentrations of Co and Cu in the solid residues in most cases which indicates that a fraction of these species were removed from the brine during the up-flow percolation tests. But the mean concentration showed that Co and Cu were slightly leached from Secunda fly ash during the up-flow percolation tests while in Tutuka fly ash, the concentration of Co and Cu captured by the fly ash from the brine solution were 0.6 mg/kg and 3.6 mg/kg respectively (Tables 6.17 and 6.18). Only a small amount of the Co (0.12 mg/kg) (20 %) and Cu (1.3 mg/kg) (36 %) that was removed from the brine solution by Tutuka fly ash during the up-flow percolation tests was released into the water soluble and exchangeable fractions (Tables 6.17 and 6.18). The predominance of Co and Cu in the carbonate and residual fractions (Tables 6.12-6.13 and 6.15-6.16) showed that the forms in which these species exist in the solid residues are not easily soluble under normal environmental conditions except at very low pH. Species that occurred in the carbonate fraction may be thought to be present as co-precipitates with carbonate minerals and strong-sorbed metal forms on the surface of the fly ash particles (Goldberg, 1986; Raven *et al*., 1998). These species in the carbonate fraction are sensitive to pH changes, and can only be released to the environment as a result of the dissolution of the carbonate phases at low pH.

6.3.3.4 Nickel, Lead and Zinc

The bulk of Ni, Pb and Zn were contained in the residual fraction indicating that the significant concentrations of Ni, Pb and Zn cannot be leached out of the solid residues under normal environmental conditions (Tables 6.12-6.13 and 6.15-6.16). Metals in the residual fraction are suggested to be safer for the environment due to their lowest mobility and bioavailability (Yuan, 2009). Next to the residual fraction which had the highest concentrations of Ni, Pb and Zn is the carbonate fraction with concentrations ranging between 1.9 and 3.1 mg/kg, 0.5 and 1.2 mg/kg and 2 and 127.8 mg/kg for Ni, Pb and Zn respectively in Secunda solid residues. The concentrations of Ni, Pb and Zn in Tutuka solid residues as contained in the carbonate fraction were found to be in the range of 0.8-1.3 mg/kg, 0.7-1.2 mg/kg and 3.1-86.2 mg/kg respectively. Tables 6.17 and 6.18 showed that the concentration (mean) of Pb and Zn removed from the brine solution by the fly ashes were higher than the summation of their concentrations release from the solid residues to the water soluble and exchangeable fractions. Out of 5.4 mg/kg Pb removed from the brine solution by Secunda fly ash, 0.1 mg/kg (≈2 %) was released into the water soluble and exchangeable fractions during the sequential extraction tests. In the case Tutuka solid residues, 7.6 mg/kg Pb was removed from the brine solution by the fly ash out of which 0.1 mg/kg (1 %) was released into the water soluble and exchangeable fractions of the sequential extraction tests (Tables 6.17 and 6.18). 56.8 mg/kg and 55.8 mg/kg Zn was removed from the brine solution by Secunda and Tutuka fly ashes respectively. 7.6 mg/kg (≈13 %) of the 56.8 mg/kg Zn captured in Secunda solid residue was released into water soluble and exchangeable fractions while 13.9 mg/kg (≈25 %) of the 55.8 mg/kg Zn removed from the brine solution by Tutuka fly ash was released to the water soluble and exchangeable fractions. This shows that Pb and Zn are not easily soluble, once removed from the brine solution by the fly ashes. The concentrations of Ni, Pb and Zn in the carbonate fraction coupled with very low concentrations of these species in the water soluble fraction suggest that Ni, Pb and Zn in the fresh fly ashes and the solid residues recovered from the up-flow percolation tests cannot be released under normal environmental conditions to the environment except at low pH. Therefore, the mobility of Ni, Pb and Zn in both the fresh fly ashes and the solid residues is low. Lee and Saunders, (2003), Cho, *et al*. (2005) and Steenari, *et al*. (1999) suggested that the presence of Fe and Mn in solution as Fe and Mn oxy-hydroxides could control the release of heavy metal such as Ni, Pb and Zn as these species adsorbed to the surface of the oxy-hydroxides. This suggestion supports the low mobility of these heavy metals in the solid residues.

Table 6.17: The easily soluble fraction of the species captured in Secunda solid residue; concentration in mg/kg

Element (mg/kg)	Fresh fly ash (SFA)	Solid residue (SR)	Leached/ captured in the solid residue (SR)	Water soluble fraction (A)	Exchageable fraction (B)	Easily soluble fraction (A + B)
Al	137751	129710.8	-8040.2	181.4	7.8	189.2
Ba	2292	1670.9	-621.1	5.0	100.9	105.9
Ca	66467	51399.5	-15067.5	2878.1	17651.8	20529.9
K	6724	6398.5	-325.5	145.2	211.4	356.7
Mg	13572	17819.3	4247.3	118.5	928.0	1046.5
Na	4525	6985.8	2460.8	2490.3	455.6	2945.8
Si	231787	212373	-19414	154.2	253.5	407.7
Sr	3268.1	2788.6	-479.5	55.5	268.3	323.8
Fe	16506	16317.8	-188.2	14.5	1.3	15.8
As*	33.86	ND	ND	0.2	1.5	1.6
Co	10.5	10	-0.5	0.03	0.1	0.13
Cr	129.8	128	-1.8	2.1	8.0	10.0
Cu	37	28.5	-8.5	0.6	0.8	1.5
Mn	387	350.3	-36.7	0.8	10.5	11.2
Mo*	5.83	ND	ND	0.2	0.6	0.7
Ni	58.5	54.6	-3.9	0.8	0.4	1.1
Pb	41	46.4	5.4	0.1	0.02	0.1
Zn	32.1	88.9	56.8	1.5	6.1	7.6

Table 6.18: The easily soluble fraction of the species captured in Tutuka solid residue; concentration in mg/kg

Element (mg/kg)	Fresh fly ash (TFA)	Solid residue (TR)	Leached/ captured in the solid residue (TR)	Water soluble fraction (A)	Exchageable fraction (B)	Easily soluble fraction (A + B)
Al	129495	125925	-3570	61.0	3.2	64.3
Ba	983.7	852.9	-130.8	3.5	96.0	99.4
Ca	42096	35121.3	-6974.7	443.6	8300.9	8744.4
K	6890	6888	-2	136.7	197.6	334.3
Mg	8204	11141.5	2937.5	142.1	841.2	983.3
Na	2151	5323.8	3172.8	3744.3	646.0	4390.3
Si	242352	230648.3	-11703.7	254.4	228.9	483.3
Sr	1164.4	1120.9	-43.5	8.6	123.0	131.6
Fe	37907	37172	-735	26.4	2.3	28.7
As*	44.79	ND	ND	0.3	2.4	2.7
Co	21	21.6	0.6	0.04	0.08	0.12
Cr	145.3	135.7	-9.6	1.8	1.3	3.0
Cu	32.8	36.4	3.6	0.7	0.5	1.3
Mn	387	407	20	1.3	10.3	11.6
Mo*	8.3	ND	ND	0.1	0.2	0.3
Ni	62.2	59.2	-3	0.9	0.3	1.2
Pb	50.3	58	7.6	0.1	0.02	0.1
Zn	48.5	104.3	55.8	2.0	11.9	13.9

The leaching of Al, Ba, Ca, K, Si and Sr from the fly ashes that was observed during the up-flow percolation tests corresponded to the leaching of these species that was observed during the sequential extraction tests (Tables 6.17 and 6.18). Although significant concentrations of these species are in the residual fraction, the concentrations Al, Ba, Ca, K, Si and Sr released into the water soluble and exchangeable fractions were high. This implies that the leaching of these major species in real ash-brine co-disposal scenario is a continuous process. The continous release of these major species has implication on the release of toxic trace elements over time from the matrix of the ash.

6.3.3.5 Summary

The sequential extraction tests gave an insight into the physicochemical forms in which the species removed from the brine solution by the fly ashes exist. The sequential extraction tests revealed that the bulk of the major and minor species such as Al, Si, Ba, K, As, Co, Cr, Cu, Mo, Ni, Pb and Zn in the solid residues were predominantly in the residual fraction while the bulk of Fe and Mn were present in the iron and manganese and the residual fractions of the sequential extraction. This implies that bulk of these species is not mobile under normal environmental conditions. Ca concentration in the water soluble and exchangeable fractions was high indicating that Ca-containing phases in the solid residues are highly soluble. Despite the leaching of Al, Ba, Ca, Si, Sr, Cr and Mo from the fly ashes observed during the up-flow percolation tests (see section 6.3.1), these species were significantly leached from the solid residues into the water soluble and exchangeable fraction of the sequential extraction tests. This indicates that the release of Al, Ba, Ca, Si, Sr, Cr and Mo from fly ash is a continuous process even when the pH of the ash system is high. The continous leaching of species such as Al, Ca and Si could cause the release of toxic elements from the matrix of the fly ash over time. The concentration of Na was very high in the water soluble and exchangeable fractions, which is an indication that the mobility of this species in the solid residues is high. The high concentration of Na in the water soluble and exchangeable fractions shows that the Na captured from the brine by the fly ashes are not in stable form and can be released even at high pH. The predominance of Fe and Mn in the iron and manganese and residual fractions showed the existence of these species as insoluble Fe and Mn oxyhydroxides and in the matrix of the fly ash residues. The species in these fractions may not be released to the environment. Apart from the bulk of the Co, Cu, Ni, Pb and Zn that are contained in the residual fraction, the increase in the concentrations of these species in the carbonate fraction showed their existence as co-precipitates with carbonate minerals which are not easily mobile under natural environmental conditions except when the pH is very low. The results of the sequential extraction tests shows that major species such as Na that was removed from the brine solution by the fly ash during the up-flow percolation tests are available in water soluble form and are highly mobile when in contact with water. Therefore, fly ash may not be a sustainable salt sink.

Chapter 7

Conclusions and Recommendations

7 Introduction

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

7.1 Overview

The aims and objectives of this study were to provide a detailed insight into the leaching and removal of major and trace elements from fly ash-brine systems as a result of the chemical interactions in the systems, to assess the possibility of using South African fly ash as sustainable salt sink for brine, and to understand the mobility of major and minor species when fly ash and brine are co-disposed. In order to achieve the aims and objectives of this study, several leaching procedures such as batch reaction tests, long-term fly ash-brine interaction tests, acid neutralization capacity (ANC) tests, up-flow percolation tests and sequential extraction tests were carried out. The geochemical modeling software, PHREEQC, was applied to calculate the saturation indices (SI) by using the data generated from the batch reaction tests in order to predict the formation of secondary mineral phases controlling the release of species in the fly ash-brine systems. Several analytical techniques such as x-ray diffraction (XRD), x-ray fluorescence (XRF), scanning electron microscopy-energy dispersion spectroscopy (SEM-EDS), inductively coupled plasma-mass spectroscopy (ICP-MS) and ion chromatograph (IC) were applied to characterize the fresh fly ashes, solid residues recovered from the fly ash-brine interaction tests and the brine sample used in this study in order to determine the chemical and mineralogical compositions and speciation of the waste materials. The results of the leaching tests and the analyses were integrated in order to give a conclusive statement on this study.

7.2 Correlation between the co-disposal techniques practice by Secunda and Tutuka power utilities and the leaching procedures used in this study

The disposal techniques practice by Secunda and Tutuka power utilities where the samples used in the study were collected are different as stated in section 1.2. SASOL-Secunda power utility uses a wet disposal technique while ESKOM-Tutuka uses a dry disposal technique. In Secunda, fly ash directly from the precipitator is mixed with brine (at 70-80 % liquid/solid (L/S) ratio) to form slurry before being hydraulically transported and disposed of at the ash dumps, while at ESKOM (Tutuka) power station, a small amount (about 16 %) of brine is added to moisten the fly ash before disposal to the dumps in order to suppress dust. At the ash dump in Tutuka, the disposed moistened ash is irrigated with brine. These different co-disposal techniques were the basis for the choice of the different leaching procedures used in this study. For instance, the batch reaction tests (reported in chapter 4) was employed to simulate the first stage of Secunda fly ash and brine interactions where the fly ash directly from the precipitator was aggressively mixed with the brine solution before being transported to the ash dump. The reason for applying the batch reaction tests was to determine the leachability of species from the fly ashes and the removal of species from the brine solution at this aggressive interaction stage. The long-term fly ash-brine interactions experiments reported in chapter 5 is a static system which was used to simulate the co-disposal scenario in Tutuka where a small amount of brine was mixed with the fly ash before further irrigation with brine at the dump. This test (long-term fly ash-brine interaction experiment) was carried out to understand the leaching of species from the fly ashes and the removal of species from the brine solution by the fly ashes in static conditions. The up-flow percolation tests reported in chapter 6 was done to simulate the Secunda co-disposal technique where, after the initial aggressive mixture of the fly ash and brine, the slurry is pumped to the ash dump and the brine percolates through the ash systems. This was done to understand the leachability of species from the fly ash and the removal of species from the brine solution when brine percolates through the fly ash-brine systems over time. Finally, the ANC and sequential extraction tests were applied on the solid residues from the long-term fly ash-brine interaction experiments and the up-flow percolation tests respectively. The application of these leaching tests was to understand the stability and the mobility of the species captured in the fly ashes during the fly ash-brine interactions tests.

7.3 Characterization of the fresh fly ash and brine samples

The characterization of the fly ash and brine samples used in this study is very important in order to understand the physical, mineralogical and chemical composition of the samples as the case may be. The characterization was done to reveal what was originally contained in the samples so as to compare with the residues after the fly ash-brine interactions. The differences were used to show the effect of the fly ash-brine interactions on the fly ash and the brine compositions.

The XRF analysis was carried out to evaluate the chemical compositions of the fly ashes from the two power stations. This analysis revealed that all the elements analyzed for were present within the detectable limit (i.e the concentrations of the elements in the fly ashes are high enough to be detected during analysis). The concentrations of the major oxides in the fly ashes were very high. The weight % of Al_2O_3, SiO_2, CaO and Fe_2O_3 in Secunda fly ash were 26.03 %, 49.58 %, 9.3 % and 2.36 % respectively while the weight % of these oxides in Tutuka fly ash were 24.5 %, 51.8 %, 5.9 % and 5.4 % respectively. According to the American Society for Testing and Materials (ASTM, 1988), which classified fly ashes based on the percentage composition of Al_2O_3, SiO_2 and Fe_2O_3 in the ash, the fly ashes from Secunda and Tutuka respectively can be classified as class F fly ashes ($SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70$ %). The concentrations of these major oxides in the two fly ashes vary. For example, the CaO, Al_2O_3, MgO, concentrations in Secunda fly ash was higher than the concentrations of these oxides observed in Tutuka fly ash. On the other hand, the concentrations of SiO_2 and Fe_2O_3 in Tutuka fly ash were higher than what was observed in fly ash from Secunda. The variation in the concentrations of these oxides in the fly ashes was attributed to the different types of coal burnt or as a result of the preconditioning treatment of the Tutuka fly ash before the sample was taken (see chapter 3). The variation in the concentrations of these oxides accounted for the slight variation in the natural pH of the fly ash systems. Apart from these oxides, the concentrations of some elements such as Ba, Sr, Cl and S were high in the fly ashes. The higher concentrations of Cl and S in Tutuka fly ash than what was observed in Secunda fly ash was attributed to its contact with brine before being sampled.

The XRD analysis of the two fly ashes showed the complex nature of the fly ashes in terms of their mineralogical compositions. The major crystalline mineral phases of the fly ashes are quartz

(SiO_2) and mullite ($3Al_2O_3.2SiO_2$) with non-prominent peaks of lime in Secunda and calcium magnesium aluminum silicate chloride in Tutuka fly ash. The calcium magnesium aluminum silicate chloride phase identified in Tutuka fly ash was attributed to its interaction with brine before the sampling. Apart from these mineral phases, there could be other mineral phases that are not detected by XRD. This could be as a result of the masking effect of the alumino-silicate matrix of the fly ash, the crystalline mullite and quartz phases that are abundant in fly ash, the presence of minor phases in non-detectable concentrations or their amorphous nature.

The SEM micrographs of the two fly ashes suggested that most of the fly ash particles are spherical in shape and also revealed some agglomerated particles. The semi-quantitative elemental composition of the fly ashes measured by EDS revealed that the elements in the fly ashes are predominantly silicon, aluminum, calcium and oxygen. However, these elements identified by EDS cannot be conclusively used to identify the mineral compositions of the fly ashes due to the analysis volume limitations of EDS technique and the contribution of signal from the underlying residual fly ash matrix.

The ICP-MS and IC analysis carried out on the brine showed the hyper-salinity of the brine solution. Significantly high concentrations of Ca, Mg, K, Na, Cl and SO_4 were revealed in the brine. Trace elements such as As, Se, Cd, Cu, Cr, Fe, Mn, Co, etc were present in the brine solution. The pH of the brine solution was near-neutral while the TDS was very high with a value of 15400 mg/L. This characteristics and elemental composition were used as input parameters to establish the leachability of each element in a controlled leaching scenario as applied in the batch reaction, long-term fly ash-brine interactions and up-flow percolation tests.

7.4 Batch reaction tests

The batch reaction tests were carried out on both Secunda and Tutuka fly ashes to determine the leaching of species from the fly ashes or the removal of species from the brine solution by the fly ash interaction. The batch reaction tests showed that the release or removal of species from the fly ash-brine batch systems was not only a function of the total concentration of the species in the fly ashes and the brine solution but also depended on the L/S ratio and the contact time, under aggressive stirred conditions.

The pH of the brine solution when in contact with the fly ashes increased. The pH of the Secunda fly ash-brine batch systems ranged between 11 and 13 while the pH of Tutuka systems was in the range of 9 and 12. The increase in the pH of the systems was attributed to the dissolution of alkalinity-contributing oxides such as CaO and MgO in the fly ashes. The difference in the pH range of Secunda and Tutuka fly ash-brine batch systems was attributed to the difference in the CaO and MgO contents of the fly ashes. The high pH values of the systems contributed to the reactivity of the species in the fly ash-brine systems thereby leading to the leaching of species from the fly ashes and the removal of species from the brine solution. There was significant decrease in the TDS of the brine solution after contact with both Secunda and Tutuka fly ashes. The reduction in the TDS of the brine solution after contacting Secunda fly ash ranged between 42 and 55 % while the reduction after the contact with Tutuka fly ash was in the range of 63 and 79 %. This shows that the fly ash-brine interactions can lead to a cleaner brine solution with significantly reduced TDS within 1440 minutes (24 hours) of aggressive agitation.

The batch reaction tests showed that significant concentrations of Na, Mg, B, Cl, SO_4, As, Co, Cu, Ni and Zn were removed from the brine solution by the fly ashes during the 1440 minutes tests period under stirred conditions. The percentage removal of Na, Mg, B, Cl, SO_4, As, Co, Cu, Ni and Zn from the brine by Secunda fly ash ranged between 6-19 %, 99.9-100 %, 36-100 %, 5-29 %, 28-57 %, 70-100 %, 93-100 %, 92-100 %, 43-56 % and 11-85 % respectively while the percentage removal of species such as Na, Mg, B, Cl, SO_4, Co, Cu, Ni and Zn from the brine solution by Tutuka fly ash was in the range of 19-32 %, 90-100 %, 38-94 %, 21-45 %, 29-36 %, 29-74 %, 79-93 %, 11-32 % and 26-92 % respectively. Despite the removal of the above mentioned species from the brine solution by the fly ashes, some species such as Ba, Ca, Cr, Mo and Sr were leached from the fly ashes in significant quantities into the brine solution. Species such as Al, Fe, K, Mn and Pb were inconsistent in their availability in the fly ash-brine solution. The batch reaction tests considered the effect of the contact time and the L/S ratio on the removal of species from the brine solution. At 5 to 30 minutes, the removal of most of the species was at the maximum after which the removal of species from the brine solution by the fly ashes reduced. This is an indication that after 30 minutes of aggressive interaction with the fly ashes; the species initially removed from the brine solution could be gradually dissolved into the systems. Three L/S ratios (L/S 1:1, 1.5:1 and 5:1) were considered in this test. The L/S ratio at which the highest removal of species from the brine solution by the fly ashes was recorded was at L/S 1:1. The L/S 1:1 is much higher than what is used operationally in the real co-disposal scenario where pumpable slurry of 70-80 % brine is used. The L/S 1:1 may not be practicable because of the difficulty in pumping the fly ash-brine mixture to the ash dump. However, the possibility of using a lower liquid pasting process should not be ruled out. Therefore, the removal of species from the brine by the fly ashes at this L/S ratio (1:1) cannot be quantitatively used to determine the amount of species that would be removed from the brine solution in the real co-disposal scenario. The L/S ratio (5:1) which is closer to what is being practiced in Secunda power station showed a significantly lower removal percentage of the species from the brine; hence the current co-disposal techniques practice by Secunda power utility may not result in significant lowering of TDS.

The characterization of the solid residues recovered from the batch reaction tests corroborated the removal of species from the brine solution by the fly ashes as the concentrations of most of the species in the solid residues (as measured by XRF) were higher than their original concentrations in the fresh fly ashes. This gives a clear indication that the species removed from the brine solution were captured in the solid residues. The PHREEQC geochemical modeling predicted the formation of some new mineral phases responsible for the removal of species from the fly ash-brine systems. PHREEQC modeling predicted that mineral phases such as diaspore, gibbsite, barite, celestite, gypsum, anhydrite and brucite control the release of major species such as Al, Ba, Sr, Ca, SO_4 and Mg in the fly ash-brine batch reaction systems within the test period of 1440 minutes. The minor species such as Fe, Mn, Cu, Ni and Zn among others were predicted to be controlled by the precipitation of mineral phases such as goethite, hematite, cupricferrite, $Ni(OH)_2$ and $Zn(OH)_2$. Although, the formation of secondary mineral phases was predicted to control the release of major and minor species in the fly ash-brine batch reaction systems, the reduction in the percentage removal of species from the brine after 20 minutes contact time (in most cases) and the reduction in the concentrations of most of the species in the solid residues with increase in contact time showed the instability and transient nature of the mineral phases formed during the batch reaction tests. Therefore, most of the mineral phases initially formed during the batch reaction tests could be transient and re-dissolve over time. As this test was limited to 1440 minutes and the trends of redissolution were observed within this time frame, it should be expected that at longer periods more elements will be leached.

The batch reaction tests give an understanding that during the aggressive interactions of the fly ash and brine, as practice by Secunda power utility before pumping the slurry to the ash dump, a significant concentration of the species in the brine solution could be removed within 30 minutes of the aggressive interactions if the brine: fly ash ratio is 1:1. At higher L/S ratio and under longer periods of aggressive interaction, which could be likened to the time of the pumping of the slurry to the ash dump, the removal capacity of the fly ashes is predicted to be reduced.

7.5 Long-term fly ash-brine interaction tests

The long-term fly ash-brine interaction tests were carried out on both Secunda and Tutuka fly ashes to determine the leaching of species from the fly ashes and the removal of species from the brine solution when the fly ash-brine systems are left undisturbed at L/S 1:1. This test was done to simulate the dry disposal technique practiced in Tutuka power station where moistened ash is conveyed to the ash dump and then irrigated with brine.

The elemental analysis of the excess brine decanted from the solid residues after the long-term fly ash-brine interactions experiments showed that some species in the brine solution had been reduced and were captured by the fly ashes at different interaction periods (1 week to 12 months) under the static and closed conditions of the systems. Significant concentrations of species such as B, Co, Cu, Mg, Mn, Zn, Cl and SO_4 were removed from the brine solutions by Secunda and Tutuka fly ashes during the long-term fly ash-brine interactions experiments irrespective of the period of the interactions experiments. The % of Mg removed from the brine solutions by Secunda and Tutuka fly ashes ranged between 98 and 100 %. The removal of B from the brine solutions was in the range of 39 and 100 %. The percentage removal of Cu, Co and Zn from the brine solutions was found to range between 82 and 100 %, 61 and 100 %, and 5 and 80 % respectively. The percentage removal of Na, Cl and SO_4 from the brine solution was found to be in the range of 1 and 34 %, 13 and 34 % and 30 and 93 % respectively. The removal of major species such as Na, Cl and SO_4 from the brine solution by the fly ashes increased with increased interaction periods. This shows that the longer the fly ash-brine interaction period, under a static condition with no ingress of water or brine, the more of these species can be removed from the brine and captured in the solid residue. This was in contrast to what was observed in the batch reaction tests where most of the major species captured in the solid residues were gradually released into solution again after 30 minutes contact time. These results indicate that the dry disposal technique (simulated by the long-term fly ash-brine interaction tests) may offer an advantage over the wet disposal technique (simulated by the batch reaction tests) if all flows of brine or water can be prevented.

When compared, the removal capacity of the two fly ashes under static conditions showed that Secunda fly ash could remove more SO_4 than Tutuka fly ash. On the other hand, Tutuka fly ash showed higher removal capacity for Na and Cl than Secunda fly ash under static conditions. The capacity of Secunda fly ash to remove more SO_4 from the brine solution than Tutuka fly ash was attributed to the slight difference in the pH of the fly ash and the higher concentration of species such as Ca in Secunda fly ash that could interact with SO_4 to form new mineral phases.

Despite the significant removal of the species mentioned above from the brine solution under static conditions at L/S 1:1, the concentrations of species such as Al, Si, Ba, Ca, Sr, As, Mo, Cr, and Fe in the excess brine decanted after the long-term fly ash-brine interactions experiments were higher than their concentrations in unreacted brine solution within 1 month of the interactions. Thereafter, as the interaction period increased, the concentrations of these species decreased in the decanted brine solution which showed their removal from the systems with an increase in the interaction periods.

The analysis of the solid residues recovered from the long-term fly ash-brine interaction systems supports the removal and the leaching of species observed in the excess brine decanted from the systems. The characterization of the solid residues gave an insight into the interactions of fly ash and brine which resulted in the capturing of the brine components by the fly ashes. The XRF results of the solid residues showed that the concentrations of some species such as Na, Cl, SO_4, Co, Cu, Pb and Zn in the solid residues increased after the interactions experiments. The effect of the interaction periods was also shown on the removal of Na, Cl and SO_4 (the major constituents of brine) as an increase was observed in the concentrations of these species in the solid residues with an increase in the interaction periods. This shows that if fly ash and brine are mixed together and left undisturbed for a longer period of time, the amounts of Na, Cl and SO_4 that will be captured may continuously increase if no ingress of water or brine is allowed. The removal of species from the brine solution as a result of its interactions with the fly ashes at L/S 1:1 under static conditions was corroborated by the XRD data which showed the formation of new mineral phases such as wairakite [$CaAl_2Si_4O_{12}.2(H_2O)$], charlesite [$Ca_6(Al,Si)_2(SO_4)_2B(OH)_4(OH,O)_{12}.26(H_2O)$], spinel ($MgAl_2O_4$) and celestine ($SrSO_4$ in the solid residues recovered from the long-term fly ash-brine interactions experiments.

The mobility of the species captured in the solid residues when in contact with water and solutions of different pH was determined by the ANC tests. The concentrations of major species such as Al, Si, Ca, Ba, Sr, Mg and B released into the ANC leachates were very low at alkaline pH. The concentrations of minor species such as Fe, Mn, Co, Ni, Pb, Cu and Zn were observed to be very low at alkaline pH. The release of most of the species in the ANC systems increased with decrease in the pH of the leaching solution except species such as Na, Cl, As, Cr and Mo. The concentration of Na and Cl released into the ANC systems was very high when in contact with water (natural alkaline pH of the systems) and their release trends were independent of pH. The very high concentrations of Na and Cl at initial high pH of the ANC systems shows that the Na and Cl-rich solid phase(s) that formed during the long-term fly ash-brine interactions experiments are highly soluble and could easily dissolve when in contact with solution irrespective of the pH of the solution. The ANC results also showed that significant amounts of SO_4 that had been removed from the brine solution by the fly ashes during the long-term fly ash-brine interaction experiments are mobile when in contact with water even at high pH. The release of As, Cr and Mo is controlled by the pH. These species were released at pH 7-11, while low pH favoured their retention in the fly ash-brine interactions solid residues. The high concentrations of Cr and Mo at pH 7-8 could be a major concern as it is possible to attain this pH range in the real co-disposal scenario. The ANC results demonstrated the instability and the mobility of the species captured in the solid residues during the long-term fly ash-brine interaction tests.

Although the long-term fly ash-brine interaction tests carried out under static conditions showed that the dry disposal techniques operated by Tutuka power utility may remove some of the major components in the brine solution, the ANC tests has clearly shown that the captured salts in the ash dump cannot be retained when exposed to rainfall.

7.6 Up-flow percolation tests

The up-flow percolation leaching test simulates the disposal technique of Secunda fly ash where the brine in the slurry percolates through the ash systems. This test was done to understand the leachability of species from the fly ash and the removal of species from the brine solution when brine percolates through the fly ash-brine systems over time.

The up-flow percolation data showed that some species were leached from the fly ashes throughout the percolation period while some species were removed from the brine solution by the fly ashes at the beginning of the tests but were released over time. Significant concentrations of Mg, Cl, SO_4, Si, As and Co were removed from the brine solution by Secunda fly ash throughout the period of the up-flow percolation tests while species such as Al, Ba, Ca, Sr, Na (except at L/S 20-55), Cr, Mn and Mo showed a continuous leaching from Secunda fly ash throughout the percolation tests. Cu, Fe, K, Pb and Zn were initially leached from Secunda fly ash at the beginning of the up-flow percolation tests but were later removed significantly from the brine solution by the fly ash after L/S 5 (after 11 days). In the case of Tutuka systems, Mg, Cl, SO_4, Si, Co, Cu and Pb were removed from the brine solution by Tutuka fly ash throughout the percolation tests. Al, Ba, Ca, Na (except at L/S 0.1), K, Sr, As, Cr, Mn and Mo were continously leached from Tutuka fly ash into the systems during the up-flow percolation tests. Fe was leached at from Tutuka fly ash at the beginning of the percolation tests up to L/S 5 but was removed from the brine solution between L/S 20-80. The removal and subsequent release of some species in the systems was attributed to the precipitation and dissolution of the transient mineral phases formed during the interactions. The removal and subsequent release of some species from the up-flow percolation systems shows that the removal capacity of the fly ashes could be exhausted at a stage due to continuous inflow of brine thereby overwhelming the removal capacity of the fly ashes. Apart from the reduction in the capacity of the fly ash to remove species from brine, metals held in the fly ash matrix could be released over time by brine flowing continuously through the ash system.

The concentration of Na in the brine solution was not significantly reduced during the up-flow percolation tests except at L/S 0.1 in Tutuka up-flow percolation systems. This was attributed to the reduction in the capacity of the fly ashes to remove this species after the initial removal during the 3 days equilibration periods. The decrease in the concentrations of Na, Cl and SO_4 with an increase in the L/S ratio under continous flow is in contrast to what was happened in the long-term interactions tests carried out under static conditions where Na, Cl and SO_4 were removed significantly from the brine solution with an increase in the interactions period. This could give the dry disposal techniques (simulated by the long-term fly ash-brine interaction tests) an advantage over the wet disposal technique (simulated by the up-flow percolation tests).

The removal of species from the brine solution by the fly ashes during the up-flow percolation tests was verified by characterizing the solid residues recovered from the up-flow percolation tests. The XRF showed that the concentrations of species such as Mg, Na, Cl, Co, Pb, Zn and S in the solid residues recovered from the up-flow percolation tests were higher than their concentrations in the fresh fly ashes indicating that these species were removed from the brine solutions by the fly ashes. The XRF results also revealed that species such as Al, Si, Ca, Ba and Ni were leached from the fly ashes during the up-flow percolation tests. Further characterization of the solid residues recovered from the up-flow percolation tests by XRD showed that, apart from quartz, mullite and calcite that were identified in the fresh fly ashes, the formation of charlesite was observed during the up-flow percolation tests. The non identification of any other new mineral phases was attributed to the probable low concentration of the new phases or their existence in amorphous form.

The mobility of the species captured in the solid residues during the up-flow percolation tests was determined by the use of sequential extraction tests. The concentration of Na was very high in the water soluble and exchangeable fractions, which is an indication that the mobility of Na in the solid residues is very high. The concentration of Na in the water soluble and exchangeable fractions was higher than the total concentration of Na removed from the brine by the fly ash over the period of the up-flow percolation tests. This shows that the Na captured in the solid residues was completely removed when in contact with water. The predominance of Fe and Mn in the iron and manganese and residual fractions showed the existence of these species as insoluble Fe and Mn oxyhydroxides in the matrix of the fly ash residues. The species in these fractions may not be released to the environment. Apart from the bulk of the Co, Cu, Ni, Pb and Zn that were contained in the insoluble residual fraction, the increase in the concentrations of these species in the carbonate fraction showed their existence as co-precipitates with carbonate minerals which are not easily mobile under natural environmental conditions except when the pH is very low. Although significant concentrations of Al, Ba, Ca, K, Si and Sr are in the residual fraction, the concentrations of these species released into the water soluble and exchangeable fractions were high. This implies that the leaching of these species in real ash-brine co-disposal scenario is a continuous process.

7.7 Major findings of the study

The results of the different fly ash-brine interaction experiments on Secunda and Tutuka fly ashes and brine have shown that some of the major species such as Na, Cl and SO_4 in the brine can be significantly removed within 30 minutes of its interaction with fly ash thereby resulting in a cleaner process water of low TDS if the L/S ratio of the fly ash-brine systems can be maintained at 1:1 without any flows of water or brine. This study has shown that the interaction of fly ash and brine can remove the salts in brine.

Apart from the transient removal of some major species from the brine, the study found that some species such as Ca, Ba and Sr were soluble and leached from the fly ashes during the fly ash-brine interaction experiments. The leaching of these major species from the fly ashes is considered beneficial as the abundance of these species in the fly ash-brine systems enhances supersaturation in solution thereby favouring the chemical interactions of the species in the systems to precipitate as mineral phases.

The study showed that toxic elements such as Cr and Mo would be continuously leached from the fly ashes when co-disposed with brine. This is a major concern as the increase in the concentrations of these species in the environment has negative implications.

The study has found that the transient removal of species from the brine solution was due to the formation of new mineral phases. This implies that when fly ash and brine are co-disposed in the dump, most of the salt in the brine could be captured in form of soluble mineral phases if low L/S ratios are applied and further ingress of water or brine is prevented. The study also proved that most of the transient mineral phases that were responsible for the removal of the species from the brine solution are not stable. The mobility of Na and Cl was very high when the solid residues had contact with water. It is clearly evident that, though the fly ash can remove 'salts' from the brine, the fly ash cannot sustainably capture the salts removed from the brine solution. Therefore, the fly ashes generated in Secunda and Tutuka power utilities cannot act as a sustainable salt sink.

In conclusion, the combination of the leaching tests employed in this study provided evidence on the chemical interactions of the Secunda and Tutuka fly ashes with brine and the impact of the interactions on the brine quality. This study has been able to show that some elements such as Na and Cl are leached out of the fly ashes at both alkaline and acidic pH. The study proved that the disposal techniques employed by the coal-fired stations could be simulated by the batch reaction tests, long-term fly ash-brine interaction tests and up-flow percolation tests, which were shown to be adequate methods for modeling the ash disposal scenario. These methods showed that the dry disposal system at Tutuka (simulated by long-term fly ash-brine interaction tests) could encourage equilibration of the ash-brine systems if only L/S 1:1 is employed with no ingress of water or brine thereby facilitating the precipitation of mineral phases that could control the removal of species from the brine. The release of both major and minor species from the fly ash occurs if lower pH or higher L/S ratios are applied. The wet disposal system at Secunda (simulated by the up-flow percolation tests) would promote the rapid leaching of species into the environment due to the continuous flow of brine.

7.8 Recommendations

This study recommends that alternative ways of disposing brine generated by the power station must be sought instead of co-disposing fly ash and brine as it is unsustainable to use the fly ash to capture the salts and many other elements in the brine. If there is a need to co-dispose fly ash and brine, the dry co-disposal practice by Tutuka power station is recommended and excessive flow of brine and rainwater through the ash dump must be avoided. The power utilities could also aggressively mix the fly ash and brine within a space of 30 minutes, and then decant the cleaner brine for reuse. Any rainwater infiltration or excessive flow of brine on the solid residues generated after the aggressive mixing of the fly ash and the brine must be avoided.

7.9 Recommendations for future study

The following recommendations are made for future research in order to better understand the removal of species from brine solution by fly ash.

- Due to the complexity of the mineralogy of the fly ashes and the fly ash solid residues, and the limitation of the XRD analytical technique used in this study, it is recommended that more analysis be done on the mineral compositions of both fresh and the solid residues generated from the fly ash-brine interaction tests by using different analytical techniques such as QEMSCAN in order to fully understand the mineral transformation in the fly ash.
- Apart from laboratory scale tests carried out on the fly ashes and the brine, it is recommended that field pilot scale study (lysimeter) be done at the disposal site to simulate the real natural exposure condition of the fly ashes and brine.

Academic output

O.O. Fatoba, W.M. Gitari, L.F. Petrik and E.I. Iwuoha, 2009: Fly ash-brine interactions: The interaction chemistry and its effect on brine quality. A paper presented at International Conference on Coal Science & Technology (ICCS&T), 26th-29th October 2009. Cape Town, South Africa.

O.O. Fatoba, W.M. Gitari, L.F. Petrik and E.I. Iwuoha, 2011: Fly ash-brine interactions: Removal of major and trace elements from brine. Manuscript submitted to Journal of Environmental Science and Health Part A

O.O. Fatoba, W.M. Gitari, L.F. Petrik and E.I. Iwuoha, 2011: Mobility of major and minor species in fly ash-brine co-disposal systems: up-flow percolation test. Abstract submitted to International Conference on Coal Science & Technology (ICCS&T), Oviedo, Spain. 9-13 October, 2011

Intended publications

O.O. Fatoba, W.M. Gitari, L.F. Petrik and E.I. Iwuoha: Chemical interactions of fly ash and brine: Mobility of major and minor species in fly ash-brine systems. Manuscript in preparation

O.O. Fatoba, W.M. Gitari, L.F. Petrik and E.I. Iwuoha: Effect of pH on the mobility of major and minor species in fly ash-brine solid residues. Manuscript in preparation

O.O. Fatoba, W.M. Gitari, L.F. Petrik and E.I. Iwuoha: Secondary mineral formation in fly ash-brine co-disposal systems: batch reaction tests. Manuscript in preparation

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Appendices

Appendix A: Batch reaction tests and PHREEQC modelling data

Table A1: pH, EC and TDS of Secunda fly ash-brine batch reaction tests (main) as a function of L/S ration and contact time.

	Secunda fly ash-brine batch reaction at L/S 1:1									
Reaction time (mins)	5	10	20	30	60	240	480	840	1080	1440
pH	11.26	11.19	11.16	12.72	12.65	12.87	12.67	12.64	12.71	12.81
EC mS/cm	14.74	15.5	14.8	16.33	14.18	13.9	13.01	14.02	13.08	15.21
TDS mg/L	7940	8360	7980	8810	7650	7500	7020	7580	7040	8200
	Secunda fly ash-brine batch reaction at L/S 1.5:1									
pH	11.36	11.27	11.47	12.75	12.57	12.88	12.55	12.69	12.66	12.81
EC mS/cm	14.71	16.52	15.74	16.79	15.79	16.04	16.09	14.29	13.95	17
TDS mg/L	7930	8900	8490	9020	8520	8640	8680	7720	7530	9190
	Secunda fly ash-brine batch reaction at L/S 5:1									
pH	11.4	11.33	11.32	12.64	12.55	12.74	12.6	12.56	12.53	12.66
EC mS/cm	27.12	28.84	29.24	28.4	30.52	29.2	31.44	29.32	29.8	31.84
TDS mg/L	14640	15560	15800	15360	16480	15840	16960	15960	16120	17160

Table A2: pH, EC and TDS of Tutuka fly ash-brine batch reaction tests (main) as a function of L/S ration and contact time.

	Tutuka fly ash-brine batch reaction at L/S 1:1									
Reaction time (mins)	5	10	20	30	60	240	480	840	1080	1440
pH	9.49	9.54	9.57	10.91	11.21	11.16	11.6	11.5	11.43	11.52
EC mS/cm	10.55	10.29	8.5	7.5	7.5	7.55	5.93	6.2	6.11	6.8
TDS mg/L	5400	5570	4540	4000	4060	4110	3200	3350	3310	3680
	Tutuka fly ash-brine batch reaction at L/S 1:1									
pH	9.42	9.46	9.57	10.6	10.77	11.06	11.49	11.41	11.48	11.3
EC mS/cm	15.68	15.83	15.41	7.76	9.32	10.17	6.58	7.98	7.3	7.72
TDS mg/L	8470	8560	8390	4170	4940	5490	3540	4270	3890	4160
	Tutuka fly ash-brine batch reaction at L/S 1:1									
pH	8.99	8.85	9.08	9.72	9.98	9.92	10.01	9.95	9.98	10.26
EC mS/cm	16.8	16.68	17.03	16.64	16.7	17.68	16.54	17.04	16.83	17.2
TDS mg/L	9080	9060	9210	9040	9030	9560	8950	9210	9130	9300

Table A3: Concentration of species released in Secunda fly ash-brine batch reaction tests (main) at L/S 1:1 as a function of contact time (concentration in mg/L)

Parameter/ Reaction time (min)	Secunda fly ash-brine batch reaction at L/S 1:1										
	UB	5	10	20	30	60	240	480	840	1080	1440
Al	0.04941	0.0438	0.10186	0.02549	0.25894	0.23718	0.4306	0.30774	0.8266	0.24654	0.4482
As	0.0068105	0.0017866	0.00182	0.0019656	0.00026608	BDL	BDL	0.0002878	0.001184	0.00061656	0.001362
B	2.239	BDL	BDL	BDL	2.6918	1.4294	1.036	0.44122	0.31746	0.40496	0.31922
Ba	0.057065	0.5016	0.483	0.4962	0.28324	0.33266	0.4466	0.37854	0.3295	0.24296	0.23084
Ca	106.9965	1812.086	1802.002	1773.3	2236.452	1423.374	1066.236	1016.908	940.704	968.496	939.02
Cd	0.00016935	BDL	BDL	BDL	0.00015452	0.000036336	0.0001595	0.0005764	0.00021102	0.00036618	0.00023712
Co	0.014205	0.00014644	0.00003108	1.5224E-06	0.0009536	0.000498	0.0005938	0.0006602	0.0007692	0.0006036	0.000778
Cr	0.01384	0.26498	0.2517	0.2934	0.26798	0.5932	0.8964	0.979	1.9408	2.1172	2.5026
Cu	0.25815	0.0048302	0.00035716	0.0000186	0.016192	0.01282	0.015722	0.020372	0.014002	0.013088	0.013646
Fe	0.235455	0.10884	0.12448	0.13858	0.32138	0.1944	0.20984	0.28122	0.29858	0.15864	0.21954
K	106.2	115.3314	113.2084	112.0696	99.38	98.64	102.54	99.16	104.74	107.14	108.6
Mg	163.3645	0.108372	0.125276	0.077096	BDL	BDL	BDL	0.203296	0.193492	BDL	BDL
Mn	0.001707	0.00045232	0.00062376	0.0011968	0.005656	0.0041404	0.00368	0.00584	0.007084	0.0039746	0.0046032
Mo	0.03927	0.2825	0.26584	0.28826	0.16782	0.18636	0.36128	0.36776	0.4206	0.5842	0.652
Na	4804.875	4130.78	3907.938	3912.916	4093.42	4224.36	4269.28	4131.74	4205.74	4494.96	4309.9
Ni	0.121	0.05358	0.0531	0.05404	0.06596	0.06536	0.06298	0.06868	0.06704	0.05378	0.05588
P	0.81575	BDL	BDL	BDL	1.2294	0.8454	0.9808	1.3384	1.0798	0.82	1.133
Pb	0.006504	0.002703	0.002489	0.0024702	0.004356	0.005446	0.003821	0.003797	0.008758	0.003665	0.003693
Se	0.004985	0.04618	0.04664	0.038712	0.054664	0.0157688	0.018162	0.037084	0.04336	0.0143	0.029716
Si	13.1144	0.37136	0.253446	0.275364	1.908128	0.548816	BDL	BDL	2.604194	BDL	BDL
Sr	3.055495	39.95296	37.06896	39.66934	31.03538	35.2122	40.03344	45.5484	56.9146	68.6974	74.2074
Ti	0.00069055	0.0012888	0.0015628	0.0018746	0.0050072	0.011046	0.00489	0.010304	0.0553	0.00735048	0.011722
V	0.019345	0.00902	0.00807	0.00853	0.004163	0.004482	0.009584	0.00903	0.013858	0.013078	0.011732
Zn	0.1309	0.022782	0.020398	0.020382	0.09572	0.06172	0.06852	0.10198	0.11626	0.07566	0.10586
pH	7.75	11.26	11.19	11.16	12.72	12.65	12.87	12.67	12.64	12.71	12.81
EC (mS/cm)	16.69	14.74	15.5	14.8	16.33	14.18	13.9	13.01	14.02	13.08	15.21
TDS (mg/L)	15400	7940	8360	7980	8810	7650	7500	7020	7580	7040	8200

Table A4: Concentration of species released in Secunda fly ash-brine batch reaction tests (main) at L/S 1.5:1 as a function of contact time (concentration in mg/L)

Parameter/ Reaction time (min)	Secunda fly ash-brine batch reaction at L/S 1.5:1										
	UB	5	10	20	30	60	240	480	840	1080	1440
Al	0.04941	0.04949	0.07172	0.07425	0.16226	0.17866	0.24972	0.21288	0.31126	0.18938	0.23354
As	0.00681	0.00190	0.00202	0.00262	BDL	BDL	0.00058186	0.00051732	0.0013682	0.000197776	0.00050846
B	2.23900	0.13317	0.11884	0.06532	2.5764	2.21	1.267	0.6532	0.4232	0.5248	0.34412
Ba	0.05707	0.49640	0.51107	0.56933	0.28236	0.32246	0.463	0.38668	0.34672	0.3151	0.26624
Ca	106.99650	1972.95333	2010.25467	1964.46000	2107.878	1992.736	1268.084	1172.65	1059.37	1082.014	1035.396
Cd	0.00017	BDL	BDL	BDL	0.00034804	0.0003013	0.000245298	0.00008476	0.00050466	0.0004608	0.000158646
Co	0.01421	0.00006	0.00019	0.00002	0.0006164	0.000662	0.0005056	0.0007454	0.0008068	0.0005286	0.0006258
Cr	0.01384	0.16265	0.17003	0.19164	0.19566	0.2186	0.6162	0.6904	1.4388	1.5982	1.7976
Cu	0.25815	0.00134	0.00162	0.00363	0.013914	0.014242	0.013506	0.013766	0.04137	0.014322	0.01537
Fe	0.23546	0.10767	0.09935	0.12297	0.17786	0.21026	0.23318	0.25336	0.32762	0.21646	0.19722
K	106.20000	121.42653	110.63640	110.79467	103.18	103.1	108.18	103.14	115.56	118.66	117.26
Mg	163.36450	0.09336	0.12786	0.17193	BDL	BDL	BDL	0.19392	BDL	BDL	BDL
Mn	0.00171	0.00074	0.00029	0.00140	0.0029552	0.0029608	0.002454	0.003435	0.004788	0.0039252	0.003403
Mo	0.03927	0.18436	0.18897	0.20808	0.14234	0.14994	0.26638	0.27492	0.35768	0.4654	0.5058
Na	4804.87500	4099.06667	3883.51733	3813.44400	4494.06	4425.42	4531.22	4317.9	4293.88	4461.56	4443.24
Ni	0.12100	0.07220	0.07144	0.07733	0.0733	0.07162	0.07656	0.07608	0.0801	0.07316	0.07282
P	0.81575	BDL	BDL	BDL	0.7318	0.7866	0.7782	1.0802	1.2162	1.0128	1.0118
Pb	0.00650	0.00222	0.00279	0.00309	0.003521	0.0035808	0.0040502	0.0039414	0.009204	0.003959	0.005206
Se	0.00499	0.07189	0.06199	0.05147	0.0498	0.028196	0.027664	0.01592	0.01485	0.075	0.013424
Si	13.11440	0.35091	0.32053	0.43519	BDL	BDL	BDL	BDL	BDL	1.163756	BDL
Sr	3.05550	28.99745	29.16923	29.64189	25.72146	29.37558	30.6897	38.52508	46.3066	52.167	54.7008
Ti	0.00069	0.00226	0.00257	0.00287	0.0043476	0.015204	0.0047072	0.004622	0.011936	0.0017416	0.0023504
V	0.01935	0.00831	0.00862	0.00974	0.0034366	0.0041674	0.009846	0.008926	0.012046	0.013316	0.013338
Zn	0.13090	0.01560	0.02896	0.01747	0.06542	0.06024	0.06106	0.06144	0.10566	0.07236	0.1412
pH	7.75	11.36	11.27	11.47	12.75	12.57	12.88	12.55	12.69	12.66	12.81
EC (mS/cm)	16.69	14.71	16.52	15.74000	16.79000	15.79000	16.04000	16.09	14.29	13.95	17
TDS (mg/L)	15400	7930	8900	8490	9020	8520	8640	8680	7720	7530	9190

Table A5: Concentration of species released in Secunda fly ash-brine batch reaction tests (main) at L/S 5:1 as a function of contact time (concentration in mg/L)

Parameter/ Reaction time (min)	Secunda fly ash-brine batch reaction at L/S 5:1										
	UB	5	10	20	30	60	240	480	840	1080	1440
Al	0.04941	0.02513	0.03790	0.03388	0.18452	0.09536	0.16828	0.12234	0.1596	0.117	0.11826
As	0.00681	0.00219	0.00238	0.00298	0.0006474	0.0006314	0.00050922	0.0004988	0.0009988	0.0013688	0.00084474
B	2.23900	0.56360	0.35493	0.50787	2.3014	2.3004	2.1656	1.872	1.79	1.6796	1.3754
Ba	0.05707	0.29349	0.32332	0.43320	0.2832	0.2389	0.31778	0.29368	0.27384	0.2879	0.301
Ca	106.99650	1581.06667	1684.75467	1813.82133	1676.618	1890.756	1620.02	1804.46	1550.678	1671.264	1705.272
Cd	0.00017	BDL	BDL	BDL	0.000221407	0.00013144	0.00013552	0.00009608	0.00019208	0.0002139	0.00073728
Co	0.01421	0.00086	0.00038	0.00020	0.0016436	0.000982	0.0008798	0.0008192	0.000925	0.0008134	0.0008462
Cr	0.01384	0.06696	0.08205	0.07013	0.26796	0.10182	0.16514	0.19666	0.37768	0.25662	0.3143
Cu	0.25815	0.00689	0.00617	0.00720	0.022188	0.01881	0.022956	0.019334	0.02323	0.021496	0.025366
Fe	0.23546	0.11145	0.14601	0.06200	0.29266	0.1907	0.19446	0.24434	0.23022	0.23718	0.22304
K	106.20000	109.35800	113.32733	110.22893	114.8	115.12	113.16	113.42	112.16	102.38	116.08
Mg	163.36450	0.08661	0.10397	0.08341	BDL	BDL	BDL	BDL	0.284324	BDL	BDL
Mn	0.00171	0.00093	0.00107	BDL	0.0041746	0.0024448	0.0041304	0.00353	0.0027606	0.004139	0.003877
Mo	0.03927	0.07781	0.07981	0.08341	0.10032	0.08494	0.10352	0.11076	0.13254	0.12464	0.13864
Na	4804.87500	3918.43333	4007.76000	4026.45467	4498.46	4533.42	4406.46	4433.22	4297.18	4294.22	4377.26
Ni	0.12100	0.10084	0.10224	0.09645	0.11816	0.10922	0.10776	0.1021	0.10426	0.09686	0.09582
P	0.81575	BDL	BDL	BDL	0.9324	0.8768	0.7886	0.762	0.7602	0.4844	0.9958
Pb	0.00650	0.00184	0.00174	0.00196	0.0040098	0.0030122	0.0039248	0.0035442	0.005886	0.0039296	0.005898
Se	0.00499	0.04955	0.05497	0.05039	0.03117	0.035988	0.0452	0.018306	0.0112968	0.012496	0.02897
Si	13.11440	1.22188	1.15613	1.04764	BDL	1.168086	1.927624	BDL	BDL	BDL	1.671704
Sr	3.05550	14.29381	15.64148	16.39416	14.27386	15.11428	14.36168	19.86502	19.0106	17.90592	21.4322
Ti	0.00069	0.00359	0.00161	0.00203	0.0049486	0.00069888	0.0008498	0.0042208	0.0013826	0.0028212	0.0015336
V	0.01935	0.00934	0.01117	0.01188	0.0032238	0.0037402	0.009784	0.006264	0.009066	0.010154	0.009586
Zn	0.13090	0.01291	0.01124	0.01107	0.06542	0.04874	0.0519	0.06214	0.08094	0.0579	0.07346
pH	7.75	11.4	11.33	11.32	12.64	12.55	12.74	12.6	12.56	12.53	12.66
EC (mS/cm)	16.69	27.12	28.84	29.24	28.4	30.52	29.2	31.44	29.32	29.8	31.84
TDS (mg/L)	15400	14640	15560	15800	15360	16480	15840	16960	15960	16120	17160

Table A6: Concentration of species released in Tutuka fly ash-brine batch reaction tests (main) at L/S 1:1 as a function of contact time (concentration in mg/L)

Parameter/ Reaction time (min)	Tutuka fly ash-brine batch reaction at L/S 1:1										
	UB	5	10	20	30	60	240	480	840	1080	1440
Al	0.04941	0.37414	0.6692	0.464	0.9894	2.7064	1.7694	3.9182	4.2006	2.3196	1.8676
As	0.0068105	0.010906	0.008656	0.009204	0.012388	0.011258	0.013558	0.01534	0.014498	0.016324	0.015554
B	2.239	0.6382	0.18776	0.13946	1.382	1.3296	1.3298	0.5172	0.4408	1.0268	1.1964
Ba	0.057065	0.22412	0.23128	0.25316	0.3595	0.27618	0.26928	0.25922	0.22142	0.19504	0.17694
Ca	106.9965	196.7556	208.706	209.6716	220.0268	244.8212	298.6346	218.0452	184.6988	229.6902	243.918
Cd	0.00016935	BDL	BDL	BDL	0.0006074	0.00058878	0.0005436	0.00042582	0.0006628	0.000269598	0.00040668
Co	0.014205	0.00553	0.004556	0.005434	0.010026	0.007684	0.006372	0.005902	0.0040364	0.004216	0.003761
Cr	0.01384	2.7402	1.9248	1.9646	2.2742	2.5708	3.2808	2.6486	2.6164	3.2252	3.348
Cu	0.25815	0.021392	0.017596	0.022842	0.05282	0.04372	0.033924	0.041908	0.032788	0.034194	0.035712
Fe	0.235455	0.1461	0.11506	0.0969	0.21384	0.23604	0.26204	0.3138	0.2032	0.26758	0.29756
K	106.2	140.1616	134.3546	134.601	139.9	144.5	145.84	146.2	141.1	145.12	147.1
Mg	163.3645	16.02868	4.81036	9.03558	5.55194	0.548968	1.642318	BDL	BDL	BDL	0.396896
Mn	0.001707	0.00082898	0.0007692	0.000639	0.004702	0.005222	0.008392	0.004962	0.009962	0.005155	0.005938
Mo	0.03927	0.9866	0.765	0.7976	0.8374	0.9508	1.0974	0.9706	0.9152	1.0698	1.1162
Na	4804.875	3357.516	3280.268	3424.714	3764.622	3768.572	3866.506	3657.042	3615.974	3785.756	3852.134
Ni	0.121	0.09374	0.08168	0.088	0.0991	0.1024	0.10206	0.10078	0.09408	0.10656	0.10688
P	0.81575	BDL	BDL	BDL	0.33102	0.40778	0.3083	0.50926	0.6856	0.42548	0.70636
Pb	0.006504	0.0011544	0.0007616	0.0011446	0.0024838	0.002233	0.0025678	0.0023676	0.0019858	0.0021144	0.0019314
Se	0.004985	0.031966	0.01864	0.02446	0.022874	0.020288	0.03509	0.029898	0.037882	0.04147	0.028464
Si	13.1144	5.44738	6.35644	6.13854	7.6263	8.55024	9.53098	8.36188	11.37152	12.53012	12.61206
Sr	3.055495	8.7743	9.4201	9.30744	9.86448	10.1285	10.89088	9.60616	8.6889	9.5372	10.08368
Ti	0.00069055	0.0030326	0.0040844	0.0028258	0.00321	0.0028876	0.030146	0.0030878	0.006552	0.003793	0.00269
V	0.019345	0.33646	0.3407	0.33128	0.35654	0.4434	0.4824	0.5058	0.5582	0.621	0.6116
Zn	0.1309	0.019786	0.010232	0.01047	0.07866	0.05672	0.05644	0.0542	0.0599	0.0694	0.09594
pH	7.75	9.49	9.54	9.57	10.91	11.21	11.16	11.6	11.5	11.43	11.52
EC (mS/cm)	16.69	10.55	10.29	8.5	7.5	7.5	7.55	5.93	6.2	6.11	6.8
TDS (mg/L)	15400	5400	5570	4540	4000	4060	4110	3200	3350	3310	3680

Table A7: Concentration of species released in Tutuka fly ash-brine batch reaction tests (main) at L/S 1.5:1 as a function of contact time (concentration in mg/L)

Parameter/ Reaction time (min)	Tutuka fly ash-brine batch reaction at L/S 1.5:1										
	UB	5	10	20	30	60	240	480	840	1080	1440
Al	0.04941	0.39983	0.40500	0.45600	0.6694	1.0762	1.0738	3.2102	3.7668	3.0154	1.3466
As	0.00681	0.01454	0.01240	0.01266	0.01258	0.011604	0.01207	0.013132	0.013478	0.014038	0.015474
B	2.23900	0.50560	0.41892	0.56613	1.795	1.9048	2.0854	1.2624	1.0004	1.064	2.1754
Ba	0.05707	0.29360	0.28397	0.29867	0.417	0.3046	0.26656	0.26526	0.2429	0.23128	0.19056
Ca	106.99650	174.98053	187.05000	201.40080	231.0846	266.6404	284.9832	289.1774	249.8996	252.665	320.2634
Cd	0.00017	BDL	BDL	BDL	0.00013816	0.0001617	0.00019592	0.00031784	0.0003018	0.00029088	0.000452
Co	0.01421	0.00641	0.00626	0.00632	0.0117	0.00956	0.006754	0.005108	0.0038682	0.0037534	0.0036326
Cr	0.01384	1.50907	1.46400	1.54147	1.9298	1.9318	2.2502	1.935	1.9298	2.0104	2.5178
Cu	0.25815	0.03636	0.03121	0.02814	0.06336	0.04896	0.045	0.04962	0.035038	0.036018	0.038244
Fe	0.23546	0.10147	0.10644	0.20803	0.2942	0.24828	0.20774	0.25528	0.23298	0.4848	0.26222
K	106.20000	134.41013	132.47307	134.52173	141.22	140.04	138.32	142.26	136.88	142.44	143.64
Mg	163.36450	47.38373	33.78160	25.55997	30.44508	8.23842	3.406394	0.526012	0.465176	0.380054	0.705382
Mn	0.00171	0.00055	0.00068	0.00244	0.004958	0.004288	0.0036606	0.00473	0.004924	0.0043042	0.0036436
Mo	0.03927	0.61480	0.58680	0.61747	0.716	0.694	0.7706	0.692	0.6904	0.6948	0.8208
Na	4804.87500	3659.05600	3610.72933	3620.41600	4232.06	4107.32	4063.2	4143.82	3840.126	3994.758	4140.46
Ni	0.12100	0.09643	0.09445	0.09476	0.11548	0.10476	0.1045	0.11004	0.10374	0.10998	0.1122
P	0.81575	BDL	BDL	BDL	0.598	0.4268	0.40134	0.3968	0.5636	0.4404	0.5286
Pb	0.00650	0.00090	0.00127	0.00208	0.0023748	0.002266	0.002721	0.0018766	0.002003	0.002004	0.001538
Se	0.00499	0.01319	0.01730	0.01970	0.023206	0.0323	0.041582	0.030728	0.036004	0.025276	0.030512
Si	13.11440	4.69976	4.89477	5.41501	7.57098	6.2846	8.0689	8.6611	9.83428	11.95758	11.20332
Sr	3.05550	8.08105	8.58720	8.70267	9.74446	10.30668	10.50722	10.3926	9.68072	9.87236	11.22978
Ti	0.00069	0.00315	0.00248	0.00209	0.002759	0.0020466	0.004888	0.004822	0.00637	0.0025882	0.0009446
V	0.01935	0.29120	0.29731	0.29600	0.3227	0.36072	0.4054	0.4386	0.4614	0.4844	0.5226
Zn	0.13090	0.03939	0.03092	0.03468	0.09948	0.06812	0.06148	0.05918	0.05594	0.06258	0.07386
pH	7.75	9.42	9.46	9.57	10.6	10.77	11.06	11.49	11.41	11.48	11.3
EC (mS/cm)	16.69	15.68	15.83	15.41	7.76	9.32	10.17	6.58	7.98	7.3	7.72
TDS (mg/L)	15400	8470	8560	8390	4170	4940	5490	3540	4270	3890	4160

Table A8: Concentration of species released in Tutuka fly ash-brine batch reaction tests (main) at L/S 5:1 as a function of contact time (concentration in mg/L)

Parameter/ Reaction time (min)	Tutuka fly ash-brine batch reaction at L/S 5:1										
	UB	5	10	20	30	60	240	480	840	1080	1440
Al	0.04941	0.33643	0.36669	0.42893	0.20454	0.28862	0.431	0.34498	0.5902	0.5102	0.35222
As	0.00681	0.02163	0.02137	0.02252	0.022828	0.021728	0.021154	0.021534	0.019144	0.017816	0.022604
B	2.23900	0.49933	0.57413	0.65800	1.9094	2.0162	2.0398	2.204	2.1576	2.167	2.1938
Ba	0.05707	0.50373	0.52987	0.52160	0.551	0.5618	0.4328	0.29572	0.3334	0.23684	0.19072
Ca	106.99650	158.93613	163.18173	166.82787	192.7996	219.5816	206.0606	173.6978	207.4158	190.9584	196.7426
Cd	0.00017	BDL	BDL	BDL	BDL	0.0006376	0.00014508	BDL	0.00004084	0.00020028	0.00000436
Co	0.01421	0.00784	0.00758	0.00767	0.013126	0.013076	0.012596	0.011986	0.012018	0.01207	0.01115
Cr	0.01384	0.50587	0.54093	0.54413	0.607	0.667	0.7136	0.6276	0.6946	0.659	0.8294
Cu	0.25815	0.09579	0.09224	0.09091	0.12266	0.11794	0.10192	0.08936	0.08492	0.08516	0.08278
Fe	0.23546	0.14235	0.25669	0.14069	0.20408	0.19962	0.20174	0.21792	0.20154	0.23114	0.20546
K	106.20000	121.07427	121.07733	123.87787	117.9	120.82	118.48	118.78	120.08	120.64	121.4
Mg	163.36450	120.38493	118.16880	116.63920	124.6502	115.0824	110.311	95.425	95.8214	86.717	84.6484
Mn	0.00171	0.00191	0.00560	0.00257	0.0042458	0.004634	0.0046442	0.0038074	0.005092	0.00554	0.004228
Mo	0.03927	0.22005	0.23253	0.23648	0.2426	0.26616	0.2683	0.24722	0.25678	0.24196	0.29132
Na	4804.87500	4084.34667	4030.50000	4067.99333	4300.12	4407.2	4292.9	4288.54	4317.82	4233.46	4303.92
Ni	0.12100	0.10649	0.10995	0.11284	0.11556	0.11964	0.11628	0.11778	0.11718	0.11718	0.12108
P	0.81575	BDL	BDL	BDL	0.76	0.6352	0.5542	0.12956	0.27166	0.35366	0.3374
Pb	0.00650	0.00128	0.00244	0.00211	0.001793	0.0020126	0.002131	0.00171	0.0017868	0.0017688	0.0021516
Se	0.00499	0.01037	0.00651	0.01248	0.02207	0.021768	0.020638	0.025996	0.024226	0.019852	0.024146
Si	13.11440	6.28788	6.21971	5.96944	7.16766	6.34216	4.98836	4.93178	4.40726	5.36302	5.28016
Sr	3.05550	6.03188	6.11833	6.18709	6.5918	7.31904	6.74112	6.33956	6.73154	6.42182	6.5661
Ti	0.00069	0.00407	0.00388	0.00362	0.0026608	0.000567	0.0010722	0.0016156	0.002644	0.0034456	0.0005912
V	0.01935	0.14792	0.15785	0.16120	0.16044	0.18262	0.20006	0.2005	0.21156	0.21484	0.25238
Zn	0.13090	0.07212	0.07523	0.07313	0.12312	0.12114	0.09858	0.10888	0.0956	0.07522	0.0748
pH	7.75	8.99	8.85	9.08	9.72	9.98	9.92	10.01	9.95	9.98	10.26
EC (mS/cm)	16.69	16.8	16.68	17.03	16.64	16.7	17.68	16.54	17.04	16.83	17.2
TDS (mg/L)	15400	9080	9060	9210	9040	9030	9560	8950	9210	9130	9300

Table A9: Summary of the calculated saturation indices (SI) for the mineral phases controlling the concentrations of species in Secunda fly ash-brine batch reaction tests at L/S 1:1 as a function of contact time

Phase/Reaction time (min)	5	10	20	30	60	240	480	840	1080	1440
Anhydrite (CaSO4)	0.13	0.12	0.1	0.27	0.02	-0.14	-0.21	-0.23	-0.17	-0.21
Ba3(AsO4)2	12.31	11.96	12.46	10.07	7.63	8.19	10.91	11.95	10.97	11.65
Barite (BaSO4)	2.11	2.08	2.08	1.85	1.87	1.95	1.85	1.81	1.68	1.64
Birnessite (MnO2)	-0.16	-0.27	-0.09	4.34	4.15	4.2	4.32	4.38	4.19	4.32
Bixbyite (Mn2O3)	5.47	5.38	5.8	11.54	11.3	11.16	11.6	11.79	11.25	11.32
Brucite (Mg(OH)2)	-1.03	-1.1	-1.38	0.43	-0.66	-0.49	1.67	1.61	0.43	0.56
Calcite (CaCO3)	3.51	3.52	3.52	2.99	3.11	2.83	3.08	3.06	2.76	2.73
CaMoO4	-0.41	-0.43	-0.4	-0.42	-0.58	-0.39	-0.43	-0.42	-0.21	-0.18
Cd(OH)2				-3.48	-4.02	-3.47	-2.82	-3.24	-3.06	-3.33
Celestite (SrSO4)	0.56	0.52	0.54	0.45	0.47	0.48	0.52	0.63	0.72	0.74
Chrysotile (Mg3Si2O5(OH)4)	2.43	2.04	1.35	4.99	0.84			9.02		
Co3O4	6.28	4.09	0.09	10.26	9.45	9.67	9.84	10.03	9.7	10.03
Co(OH)2	-2.92	-3.61	-4.92	-2.57	-2.79	-2.8	-2.68	-2.59	-2.75	-2.71
CoFe2O4	22.03	21.57	20.45	20.39	19.86	19.71	20.28	20.46	19.64	19.76
Cu(OH)2	-0.77	-1.84	-3.1	-2.16	-2.09	-2.18	-1.9	-2.01	-2.17	-2.3
Cupricferrite (CuFe2O4)	10.27	9.42	8.35	6.89	6.66	6.41	7.14	7.13	6.31	6.25
Diaspore (AlOOH)	-1.07	-0.64	-1.21	-1.76	-1.72	-1.59	-1.63	-1.17	-1.76	-1.61
Dolomite (CaMg(CO3)2)	3.14	3.23	3.01	0.43	-0.08	-0.61	2.3	2.31	0.32	0.2
Fe(OH)2.7Cl.3	3.77	3.89	3.99	2.31	2.17	2.06	2.31	2.36	2.02	2.02
Ferrihydrite (Fe(OH)3)	1	1.11	1.2	0	-0.15	-0.23	0	0.04	-0.29	-0.25
Gibbsite (Al(OH)3)	-2.46	-2.03	-2.6	-3.15	-3.11	-2.98	-3.02	-2.56	-3.15	-3
Goethite (FeOOH)	3.75	3.86	3.96	2.76	2.6	2.53	2.75	2.8	2.47	2.51
Gypsum (CaSO4:2H2O)	0.41	0.4	0.38	0.55	0.3	0.14	0.07	0.05	0.11	0.07
Halite (NaCl)	-3.82	-3.85	-3.88	-3.88	-3.88	-3.87	-3.9	-3.9	-3.85	-3.9
Hematite (Fe2O3)	9.88	10.09	10.29	7.88	7.58	7.42	7.88	7.97	7.31	7.39
Lepidocrocite (FeOOH)	3.13	3.24	3.33	2.13	1.98	1.9	2.13	2.17	1.84	1.88
Maghemite (Fe2O3)	2.62	2.83	3.03	0.62	0.31	0.16	0.62	0.71	0.05	0.13
Magnesioferrite (Fe2MgO4)	7.26	7.42	7.33	6.73	5.33	5.35	7.97	7.99	6.16	6.36
Magnetite (Fe3O4)	7.18	7.57	7.89	2.72	2.33	1.99	2.77	2.93	1.87	1.89
Manganite (MnOOH)	3.14	3.09	3.3	6.17	6.05	5.98	6.2	6.3	6.03	6.06
Mg(OH)2(active)	-2.5	-2.57	-2.85	-1.04	-2.13	-1.96	0.2	0.14	-1.04	-0.91
Ni(OH)2	-0.87	-0.82	-0.79	-2.13	-2.06	-2.18	-2.04	-2.03	-2.19	-2.27
Nsutite (MnO2)	0.43	0.31	0.5	4.92	4.73	4.78	4.9	4.97	4.77	4.91
Pb(OH)2	-0.35	-0.31	-0.29	-2.86	-2.57	-2.94	-2.72	-2.3	-2.83	-3.03
Strontianite (SrCO3)	2.47	2.45	2.48	1.7	2.08	1.99	2.32	2.44	2.18	2.2
Zn(OH)2	-2.86	-2.82	-1.71	-3.59	-4.68	-3.76	-3.39	-4.33	-3.7	-4.71

Table A10: Summary of the calculated saturation indices (SI) for the mineral phases controlling the concentrations of species in Tutuka fly ash-brine batch reaction tests at L/S 1:1 as a function of contact time

Phase/Reaction time (min)	5	10	20	30	60	240	480	840	1080	1440
Anhydrite (CaSO4)	-0.61	-0.59	-0.58	-0.57	-0.52	-0.43	-0.57	-0.64	-0.55	-0.52
Aragonite (CaCO3)*	0.9	0.95	0.96	0.76	0.15	0.22	0.46	0.38	0.21	0.71
Atacamite (Cu2(OH)3Cl)*	-0.21	-0.31	-0.09	-1.06	-2.02	-2.1	-0.53	-0.52	-1.66	-0.47
Ba3(AsO4)2	11.88	11.85	12.02	14.26	13.92	13.99	13.83	13.48	13.69	13.25
Barite (BaSO4)	1.96	1.97	2.02	2.14	2.05	2.04	2.02	1.95	1.87	1.86
Birnessite (MnO2)	-6.77	-6.6	-6.57	-0.41	0.77	0.77	-1.61	-1.69	-0.03	-1.86
Bixbyite (Mn2O3)	-4.22	-3.97	-3.98	5.66	7.42	7.53	3.89	3.92	6.25	3.55
Brochantite (Cu4(OH)6SO4)*	0.36	0.12	0.55	-1.64	-3.56	-3.73	-0.57	-0.56	-2.87	-0.5
Brucite (Mg(OH)2)	-2.29	-2.71	-2.38	0.09	-0.34	0.03	-3.28	-3.47	-2.48	-1.85
Calcite (CaCO3)	1.09	1.15	1.16	0.95	0.35	0.41	0.66	0.58	0.41	0.91
CaMoO4	-0.66	-0.73	-0.73	-0.67	-0.58	-0.44	-0.62	-0.71	-0.55	-0.52
Cd(OH)2				-2.5	-2.5	-2.58	-3.17	-3.1	-2.99	-3.31
Celestite (SrSO4)	0.04	0.06	0.06	0.07	0.09	0.13	0.07	0.02	0.06	0.09
Chrysotile (Mg3Si2O5(OH)4)	3.68	2.53	3.46	9.11	7.35	8.65	-0.33	-0.49	1.66	4.44
Co(OH)2	-2.3	-2.29	-2.18	-1.09	-1.21	-1.29	-1.34	-1.52	-1.47	-1.54
Co3O4	4.6	4.74	5.12	11.07	11.32	10.99	9.71	8.96	10.12	8.93
CoFe2O4	26.39	26.12	25.98	25.13	24.53	24.62	25.84	25.47	24.79	25.73
Cu(OH)2	0.4	0.36	0.48	0.61	0.28	0.21	0.72	0.67	0.35	0.7
Cupricferrite (CuFe2O4)	15.17	14.86	14.73	12.92	12.11	12.2	13.99	13.76	12.7	14.06
Diaspore (AlOOH)	1.63	1.84	1.64	0.64	0.77	0.64	1.54	1.67	0.92	1.3
Dolomite (CaMg(CO3)2)	1.4	0.96	1.25	0.58	-1.69	-1.17	-2.73	-2.82	-3.27	-0.69
FeCr2O4*	4.58	3.79	3.44	-11.78	-15.22	-14.38	-7.76	-6.75	-12.45	-6.63
Fe(OH)2.7Cl.3	6.09	5.94	5.82	4.47	4.14	4.25	5.05	4.99	4.47	5.13
Ferrihydrite (Fe(OH)3)	2.86	2.72	2.6	1.63	1.39	1.47	2.11	2.02	1.65	2.16
Gibbsite (Al(OH)3)	0.24	0.45	0.26	-0.75	-0.61	-0.75	0.16	0.29	-0.47	-0.09
Goethite (FeOOH)	5.62	5.48	5.36	4.39	4.15	4.23	4.86	4.77	4.41	4.91
Gypsum (CaSO4:2H2O)	-0.32	-0.3	-0.3	-0.29	-0.24	-0.15	-0.29	-0.36	-0.27	-0.24
Halite (NaCl)	-4.13	-4.12	-4.09	-3.94	-3.94	-3.91	-3.95	-3.95	-3.93	-3.91
Hematite (Fe2O3)	13.61	13.33	13.09	11.14	10.66	10.83	12.1	11.92	11.18	12.2
Kaolinite (Al2Si2O5(OH)4)*	1.42	1.93	1.49	-2.27	-2.48	-2.56	0.19	0.89	-1.45	0.2
Lepidocrocite (FeOOH)	5	4.85	4.73	3.76	3.52	3.6	4.24	4.15	3.78	4.29
Maghemite (Fe2O3)	6.35	6.07	5.83	3.88	3.4	3.57	4.84	4.66	3.92	4.94
Magnesioferrite (Fe2MgO4)	9.74	9.04	9.12	9.65	8.74	9.28	7.24	6.86	7.11	8.77
Magnetite (Fe3O4)	14.54	14.07	13.68	9.43	8.4	8.7	11.17	11	9.39	11.4
Malachite (Cu2(OH)2CO3)*	1.03	0.89	1.09	-1.58	-3.49	-3.54	2.35	2.36	3.53	2.18
Manganite (MnOOH)	-1.71	-1.58	-1.59	3.23	4.11	4.17	2.35	2.36	3.58	2.18
Mg(OH)2(active)	-3.76	-4.18	-3.85	-1.38	-1.81	-1.44	-4.75	-4.94	-3.95	-3.32
MgCr2O4*	4.36	3.34	3.48	-6.97	-10.29	-9.22	-7.09	-6.29	-10.14	-4.68
Ni(OH)2	-1.01	-0.98	-0.91	-0.35	-0.55	-0.51	-0.21	-0.21	-0.36	-0.15
Nsutite (MnO2)	-6.19	-6.01	-5.98	0.18	1.35	1.36	-1.02	-1.11	0.56	-1.27
Pb(OH)2	-0.46	-0.6	-0.41	0.2	-0.24	-0.11	0.44	0.38	0.02	0.37
Sepiolite (Mg2Si3O7.5OH:3H2O	1.22	0.54	1.11	3.43	1.85	2.88	-2.33	-2.06	-1.32	1.26
Strontianite (SrCO3)	0.26	0.32	0.33	0.12	-0.52	-0.51	-0.18	-0.23	-0.46	0.04
Zn(OH)2	-0.87	-1.12	-0.93	-0.81	-1.4	-1.3	-0.69	-0.57	-0.96	-0.38

Appendix B: Long-term fly ash-brine interaction experiments and the acid neutralization capacity (ANC) tests.

Table B1: Concentration and percentage of species removed or leached into the excess brine solution decanted from the Secunda solid residues after the long-term fly ash-brine interactions experiment; (concentration in mg/L; negative (-) values means concentration or % of species leached)

		SAC(L)		SBC(L)		SCC(L)		SDC(L)	
Element	Unreacted brine (UB)	Conc. removed/ leached	% removed /leached	Conc. removed/ leached	% removed /leached	Conc. removed/ leached	% removed /leached	Conc. removed/ leached	% removed /leached
Al	0.016	-0.04	-256.3	-104.9	-655525	-141.5	-884275	-132.1	-825838
As	0.0036	0.002	58.3	-0.02	-650	-0.04	-1122.2	-0.097	-2705.6
B	1.39	1.39	100	0.8	58.3	1.39	100	-2.08	-149.6
Ba	0.029	-0.19	-658.6	-0.14	-486.2	-0.065	-224.1	-0.008	-27.6
Ca	101.27	-876.3	-865.3	-144.3	-142.5	96.03	94.8	93.21	92.04
Co	0.0072	0.007	100	0.0059	81.9	0.0072	100	0.0046	63.9
Cr	0.0063	-1.5	-24503.2	-1.3	-20376.2	-0.37	-5931.7	-0.15	-2455.6
Cu	0.1004	0.1	100	0.095	94.6	0.095	95.1	0.092	91.4
Fe	0.043	-0.06	-127.9	-0.2	-458.1	-0.061	-141.9	-0.507	-1179.1
K	56.37	-87.6	-155.3	-125.23	-222.2	-175.73	-311.7	-187.79	-333.1
Mg	75.44	75.3	99.9	75.31	99.8	75.41	99.9	75.44	100
Mn	0.043	0.04	98.9	0.037	85.8	0.0404	94	0.026	60.5
Mo	0.019	-0.4	-1900	-0.65	-3426.3	-1.26	-6636.8	-1.591	-8373.7
Na	4475.07	64.1	1.4	103.02	2.3	816.71	18.3	1539.87	34.4
Ni	0.057	0.01	19.3	-0.005	-8.8	0.026	45.6	0.017	29.8
Pb	0.00093	0.00056	60.2	0.00027	29	0.00058	62.4	0.0007	75.3
Si	7.27	6.7	92.3	-63.84	-878.1	-40.93	-563	-392.3	-5396.1
Sr	2.93	-47.7	-1626.3	-7.82	-266.9	0.97	33.1	2.77	94.5
Zn	0.051	0.04	74.5	0.024	47.1	0.003	5.9	0.029	56.9
Cl	2424	335	13.8	474	19.6	694	28.6	644	26.6
SO4	8858	4022.8	45.4	7858	88.7	8206	92.6	8152.67	92

Table B2: Concentration and percentage of species removed or leached into the excess brine solution decanted from the Tutuka solid residues after the long-term fly ash-brine interactions experiment; (concentration in mg/L; negative (-) values means concentration or % of species leached)

		TAC(L)		TBC(L)		TCC(L)		TDC(L)	
Element	Unreacted brine (UB)	Conc. removed/ leached	% removed /leached	Conc. removed/ leached	% removed /leached	Conc. removed/ leached	% removed /leached	Conc. removed/ leached	% removed /leached
Al	0.016	-0.4	-2588	-4.7	-29463	-3.27	-20463	-6.41	-40088
As	0.0036	-0.0051	-141.7	-0.011	-316.7	-0.011	-316.7	-0.0094	-261.1
B	1.39	1.25	89.9	0.55	39.6	1.39	100	0.59	42.4
Ba	0.029	-0.14	-486.2	-0.131	-451.7	-0.091	-313.8	-0.151	-520.7
Ca	101.27	-93.45	-92.3	27.4	27.1	-8.9	-8.8	5.95	5.9
Co	0.0072	0.0044	61.1	0.0045	62.5	0.0054	75	0.0052	72.2
Cr	0.0063	-2.08	-33027	-2.69	-42757.1	-2.6	-40535	-1.52	-24186
Cu	0.1004	0.085	85.1	0.084	84.1	0.093	93	0.082	82.1
Fe	0.043	-0.024	-55.8	-0.247	-574.4	-0.087	-202.3	0.001	2.3
K	56.37	-91.51	-162.3	-90.99	-161.4	-98.18	-174.2	-89.52	-158.8
Mg	75.44	73.97	98	75.3	99.8	75.31	99.8	75.4	99.9
Mn	0.043	0.042	98.1	0.039	90	0.042	98.3	0.042	97.2
Mo	0.019	-0.771	-4057.9	-0.961	-5057.9	-1.015	-5342.1	-1.18	-6215.8
Na	4475.07	835.78	18.7	1201.5	26.8	867.29	19.4	1234.66	27.6
Ni	0.057	-0.034	-59.6	-0.053	-92.9	-0.03	-52.6	-0.039	-68.4
Pb	0.00093	0.00008	8.6	0.00029	31.18	0.00068	73.1	0.00003	3.2
Si	7.27	-1.74	-23.9	-9.51	-130.8	-13.71	-188.6	-19.39	-266.7
Sr	2.93	-6.123	-208.9	-1.54	-52.6	-4.46	-152.2	-2.86	-97.6
Zn	0.051	0.041	80.4	0.02	39.2	0.035	68.6	0.04	78.4
Cl	2424	815.92	33.7	564	23.3	626.49	25.8	656	27.1
SO4	8858	2696.17	30.4	3470	39.2	3087.59	34.9	3746	42.3

Table B3: Chemical compositions (mg/kg) of Secunda fresh fly ash and solid residues from fly ash-brine long-term interactions experiments (n=3)

Element (mg/kg)	SFA	SAC	SBC	SCC	SDC
Al	137751	133993	133041	133517	132353
As*	33.86	40.48	36.95	37.99	40.09
Ba	2291.99	1767.86	1775.3	1790.37	1777.97
Ca	66467	66110	65824	65895	65824
Cl	73.89	1798.18	1599.80	1644.77	1571.23
Co	10.48	11	10.56	10.54	10.31
Cr	129.76	142.49	148.05	156.94	148.38
Cu	37	46.8	47.5	50.49	32.6
Fe	16506	16576	16436	16366	16646
K	6724	6641	6558	6558	6641
Mg	13572	13331	13331	13150	13270
Mn	387	310	387	387	387
Mo*	5.83	10.48	9.93	9.97	10.13
Na	4525	6083	6009	6603	7270
Ni	58.46	55.48	58.98	56.52	58.86
P	3884	3710	3622	3622	3666
Pb	41.04	47.46	49.19	44.27	45.86
S	1378.35	4616.29	3961.2	3271.17	6816.65
Si	231787	220052	217481	218416	216733
Sr	3268.09	3553.69	3556.4	3549.3	3534.61
Ti	9472	9052	8933	8933	8873
Zn	32.09	30.68	31.56	30.76	30.12

* Data from total acid digestion tests

Table B4: Chemical compositions (mg/kg) of Tutuka fresh fly ash and residues from fly ash-brine long-term interactions (n=3)

Element (mg/kg)	TFA	TAC	TBC	TCC	TDC
Al	129495	128701	128066	130501	127114
As*	44.79	42.41	41.96	42.83	44.15
Ba	983.74	919.81	895.52	885.88	883.84
Ca	42096	42167	41953	42310	41310
Cl	730.26	893.52	2125.17	3370.14	4600.15
Co	21.02	22.44	23.05	22.19	21.41
Cr	145.33	148.58	159.84	187.84	151.84
Cu	32.81	47.58	54.23	45.15	46.58
Fe	37907	37418	36579	37068	36229
K	6890	6973	6890	7139	7222
Mg	8204	8204	8204	8445	8023
Mn	387	387	387	387	387
Mo*	8.30	7.67	8.99	11.82	11.29
Na	2151	3709	4154	4303	4896
Ni	62.22	63.6	61.21	63.96	65.43
P	2095	1964	1964	2051	2008
Pb	50.33	64.35	61.56	67.73	66.39
S	7025.05	4928.46	6072.96	6437.70	10281.20
Si	242352	234592	233002	236321	234685
Sr	1164.44	1312.07	1308.75	1302.88	1297.83
Ti	8693	8693	8633	8753	8633
Zn	48.53	48.6	49.77	49.61	49.78

*Data from total acid digestion tests

Table B5: Concentration of species released from the solid residues recovered from Secunda long-term fly ash-brine interaction experiments for a period of 1 week (SAC) as a function of pH (concentration in mg/L)

pH/Element	12		10		9		8		6		4	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	8.0598	0.0446	0.3601	0.0304	0.2388	0.0534	0.0886	0.0135	0.2596	0.0248	67.0396	2.2863
As	0.0024	0.0001	0.0048	0.0001	0.0105	0.0009	0.0520	0.0005	0.0366	0.0011	0.0265	0.0010
B	0.4040	0.0235	7.6195	0.3328	9.3795	1.0484	13.7428	0.2777	16.7959	0.0557	18.3568	0.1116
Ba	0.1947	0.0055	0.3545	0.0092	0.3125	0.0323	0.3026	0.0034	0.3589	0.0018	0.6131	0.0080
Ca	68.7241	0.7407	1121.2067	37.4266	1337.3493	101.2196	2152.8787	49.9708	3045.3933	89.9676	4047.9333	23.4393
Cd	0.0200	0.0009	0.0077	0.0003	0.0126	0.0018	0.0123	0.0004	0.0085	0.0006	0.0173	0.0005
Co	0.0001	0.0000	0.0004	0.0000	0.0009	0.0001	0.0049	0.0002	0.0487	0.0006	0.0819	0.0013
Cr	0.4297	0.0078	1.5376	0.0361	1.6379	0.1749	2.0353	0.0248	1.4300	0.0069	0.5360	0.0137
Cu	0.0025	0.0004	0.0008	0.0001	0.0103	0.0009	0.0178	0.0016	0.0236	0.0030	0.3373	0.0100
Fe	0.0212	0.0038	0.0151	0.0027	0.0320	0.0082	0.0439	0.0182	0.0580	0.0073	0.1039	0.0166
K	11.3492	0.0651	11.2158	0.3979	9.7425	0.9273	13.1188	0.2043	12.2937	0.1659	17.6038	0.6618
Mg	0.0538	0.0019	122.4173	2.2980	211.5520	18.4813	308.5765	6.1875	408.4133	3.5401	671.3947	0.8173
Mn	0.0015	0.0002	0.0011	0.0002	0.0042	0.0004	0.6394	0.0017	6.4268	0.0411	13.0201	0.2878
Mo	0.0766	0.0020	0.1904	0.0063	0.1992	0.0198	0.2312	0.0017	0.1695	0.0023	0.0159	0.0002
Na	235.4368	4.6878	256.1272	7.2623	211.7708	20.4502	278.2071	6.9810	233.7391	6.2289	186.3333	3.8026
Ni	0.0044	0.0004	0.0052	0.0007	0.0140	0.0012	0.0645	0.0017	0.3070	0.0040	0.4498	0.0114
Pb	0.0007	0.0000	0.0002	0.0000	0.0005	0.0001	0.0005	0.0001	0.0007	0.0003	0.0012	0.0001
Se	0.0123	0.0016	0.0187	0.0002	0.0212	0.0016	0.0412	0.0048	0.0456	0.0003	0.1697	0.0042
Si	7.4671	0.0884	3.9856	0.0780	4.7325	0.4355	9.7475	0.2060	27.3181	0.3593	196.6072	0.9215
Sr	4.1234	0.0127	25.0352	0.5920	28.6934	2.6392	39.7140	0.7207	62.8571	0.2570	64.2275	1.1922
Ti	0.0050	0.0026	0.0041	0.0018	0.0120	0.0027	0.0057	0.0008	0.0215	0.0048	0.0046	0.0019
V	0.0819	0.0011	0.4671	0.0133	0.5689	0.0480	1.0402	0.0047	1.3029	0.0039	0.3790	0.0115
Zn	0.0939	0.0445	0.0180	0.0019	0.0664	0.0078	0.1104	0.0128	0.1919	0.0171	0.4295	0.0086
Cl	194.8485	44.1087	194.7283	52.1560	149.7673	61.9539	185.9547	45.5541	130.7164	47.2633	149.3333	19.7315
SO4	167.1942	22.4847	376.3189	29.4169	605.3701	24.7366	711.7057	45.6233	766.3895	49.9124	1164.0000	358.0168

Table B6: Concentration of species released from the solid residues recovered from Secunda long-term fly ash-brine interaction experiments for a period of 1 month (SBC) as a function of pH (concentration in mg/L)

pH/Element	12		10		9		8		6		4	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	15.8992	0.1324	0.2067	0.0142	0.0693	0.0041	0.0800	0.0155	0.0259	0.0028	72.8297	1.4572
As	0.0013	0.0001	0.0069	0.0002	0.0152	0.0010	0.0283	0.0005	0.0137	0.0002	0.0259	0.0011
B	1.1463	0.0666	5.0086	0.0444	7.8643	0.1591	12.4780	0.3233	19.6861	0.3536	17.1759	0.7507
Ba	0.1200	0.0018	0.2638	0.0015	0.3867	0.0122	0.4498	0.0029	0.5690	0.0043	0.6312	0.0215
Ca	66.9457	4.5804	1263.6120	13.4098	1808.6080	25.9764	2730.9600	58.2039	4166.5467	93.8898	4049.0307	75.8686
Cd	0.0085	0.0006	0.0088	0.0002	0.0081	0.0004	0.0051	0.0005	0.0074	0.0001	0.0015	0.0001
Co	0.0001	0.0001	0.0002	0.0000	0.0005	0.0000	0.0019	0.0001	0.0296	0.0003	0.1295	0.0024
Cr	0.4203	0.0025	1.0350	0.0077	1.3416	0.0614	1.6768	0.0137	1.8251	0.0074	0.9628	0.0206
Cu	0.0009	BDL	0.0004	0.0002	0.0033	0.0017	0.0057	0.0001	0.0041	0.0001	0.1073	0.0020
Fe	0.0492	0.0079	0.0250	0.0104	0.0179	0.0026	0.0180	0.0015	0.0141	0.0032	0.0919	0.0050
K	16.1698	0.2859	28.8308	0.5434	30.3352	1.4857	33.2009	0.6764	38.4519	0.3183	63.6432	0.8528
Mg	0.9636	0.3407	119.2860	0.9144	198.7807	2.3726	320.1461	9.7817	468.0427	10.0859	635.2280	23.6546
Mn	0.0096	0.0004	0.0026	0.0005	0.0253	0.0016	0.3692	0.0064	5.0967	0.0268	12.9228	0.2560
Mo	0.0430	0.0008	0.1429	0.0004	0.1773	0.0094	0.2115	0.0006	0.1976	0.0018	0.0185	0.0008
Na	177.5689	5.5674	231.6805	0.8302	255.9717	4.9345	272.2749	16.1647	295.5757	3.9054	186.5039	8.0972
Ni	0.0030	0.0009	0.0041	0.0006	0.0098	0.0004	0.0342	0.0003	0.3073	0.0044	0.6629	0.0152
Pb	0.0003	0.0001	0.0002	0.0002	0.0002	0.0001	0.0003	0.0001	0.0002	0.0000	0.0061	0.0002
Se	0.0075	0.0035	0.0212	0.0032	0.0331	0.0046	0.0323	0.0024	0.0387	0.0018	0.1599	0.0060
Si	4.1464	0.1610	3.9983	0.1344	5.8482	0.1773	8.2389	0.1342	22.8123	0.2956	128.7951	4.2180
Sr	4.3947	0.1286	22.4576	0.2805	31.5148	0.9826	47.1793	3.9287	71.5559	1.9578	64.3612	2.0195
Ti	0.0230	0.0004	0.0039	0.0031	0.0028	0.0013	0.0042	0.0014	0.0036	0.0021	0.0078	0.0033
V	0.0833	0.0028	0.2940	0.0022	0.3035	0.0173	0.3901	0.0031	0.4368	0.0039	0.1390	0.0050
Zn	0.0281	0.0040	0.0194	0.0013	0.0203	0.0012	0.0332	0.0013	0.0534	0.0019	0.7246	0.0201
Cl	148.8163	62.5207	122.0303	12.5243	166.4709	36.0429	139.1580	34.0290	151.2241	30.4309	128.0000	8.0000
SO4	287.2645	5.6909	670.7548	31.1673	675.4135	55.2099	749.4503	17.3875	814.4857	12.5018	1148.0000	70.4518

Table B7: Concentration of species released from the solid residues recovered from Secunda long-term fly ash-brine interaction experiments for a period of 6 months (SCC) as a function of pH (concentration in mg/L)

pH/Element	12		10		9		8		6		4	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	16.5901	0.2463	0.5276	0.0393	0.1224	0.0253	0.0689	0.0135	0.0537	0.0171	27.2927	0.1915
As	0.0019	0.0001	0.0062	0.0002	0.0196	0.0004	0.0286	0.0015	0.0107	0.0003	0.0222	0.0004
B	1.5992	0.0343	7.8530	0.4520	11.6561	0.4876	13.8205	0.4502	16.7094	0.5985	16.7659	0.4078
Ba	0.0593	0.0026	0.2812	0.0125	0.3342	0.0089	0.4031	0.0192	0.5021	0.0047	0.5252	0.0085
Ca	80.4815	5.2077	1334.6653	84.8354	1947.8720	79.7289	2571.5547	127.7293	3522.0160	72.2322	4021.5987	78.4395
Cd	0.0021	0.0001	0.0020	0.0002	0.0032	0.0001	0.0022	0.0003	0.0008	0.0001	0.0085	0.0002
Co	0.0000	0.0000	0.0005	0.0001	0.0014	0.0001	0.0039	0.0003	0.0333	0.0002	0.1189	0.0006
Cr	0.1956	0.0077	1.2660	0.0390	1.4292	0.0351	1.5365	0.0577	1.2164	0.0103	0.5847	0.0078
Cu	0.0003	0.0002	0.0028	0.0012	0.0083	0.0011	0.0055	0.0007	0.0092	0.0013	0.2179	0.0018
Fe	0.0238	0.0045	0.0302	0.0200	0.0236	0.0035	0.0865	0.0894	0.0309	0.0013	0.1141	0.0827
K	9.7450	0.2681	13.4059	0.6290	14.0883	0.4462	14.8105	0.8944	16.4251	0.4003	27.7375	0.1238
Mg	0.6863	0.3356	172.2393	8.6759	285.1281	11.5641	428.9213	26.0428	558.7053	8.4882	646.5080	13.0391
Mn	0.0038	0.0005	0.0024	0.0001	0.1270	0.0039	0.8991	0.0292	5.3818	0.0293	13.1691	0.1143
Mo	0.0740	0.0035	0.1860	0.0048	0.2013	0.0065	0.2176	0.0088	0.1871	0.0019	0.0166	0.0003
Na	258.7199	8.1692	259.0071	17.8697	305.0223	17.6983	240.2040	15.9694	232.9515	13.3382	216.8039	4.1738
Ni	0.0041	0.0001	0.0076	0.0005	0.0222	0.0007	0.0638	0.0037	0.2848	0.0012	0.5631	0.0023
Pb	0.0004	0.0000	0.0004	0.0001	0.0011	0.0002	0.0005	0.0002	0.0009	0.0004	0.0018	0.0000
Se	0.0114	0.0016	0.0218	0.0009	0.0272	0.0033	0.0331	0.0042	0.0286	0.0061	0.1328	0.0108
Si	5.3903	0.1296	2.1316	0.2214	5.7755	0.3386	8.3311	0.4351	17.1362	0.2532	97.0376	1.9996
Sr	2.8313	0.0240	26.8458	0.9979	37.6547	1.9413	43.7855	1.5477	58.7664	2.8257	68.6732	0.4291
Ti	0.0069	0.0025	0.0036	0.0017	0.0018	0.0011	0.0047	0.0017	0.0073	0.0012	0.0063	0.0025
V	0.1542	0.0052	0.3633	0.0137	0.4227	0.0132	0.6163	0.0254	0.6208	0.0030	0.1486	0.0009
Zn	0.0414	0.0151	0.0391	0.0213	0.1271	0.0061	0.0440	0.0044	0.0810	0.0059	2.9412	0.0082
Cl	153.9107	57.6615	142.2460	29.0208	124.2910	0.4266	122.9889	14.6498	117.4326	7.1934	148.0000	8.0000
SO4	333.0241	14.8659	700.5533	53.5853	747.9058	21.1158	774.6293	2.4610	773.8724	1.4023	1032.0000	167.0449

Table B8: Concentration of species released from the solid residues recovered from Secunda long-term fly ash-brine interaction experiments for a period of 12 months (SDC) as a function of pH (concentration in mg/L)

pH/Element	12		10		9		8		6		4	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	17.7016	0.4868	0.7256	0.0179	0.1626	0.0018	0.0631	0.0148	0.0415	0.0161	7.3930	0.1111
As	0.0023	0.0002	0.0053	0.0001	0.0102	0.0001	0.0199	0.0003	0.0063	0.0003	0.0161	0.0007
B	2.0574	0.0969	6.7991	0.3338	9.1269	0.3007	12.5422	0.3322	15.6000	0.1685	17.2898	0.2009
Ba	0.0397	0.0016	0.3441	0.0009	0.3715	0.0051	0.3966	0.0023	0.5291	0.0051	0.5407	0.0027
Ca	87.4600	9.4342	1595.4533	21.8182	2156.2453	26.3725	2744.8667	128.6057	3578.9347	59.3720	4153.2933	42.2635
Cd	0.0020	0.0002	0.0025	0.0002	0.0059	0.0005	0.0034	0.0002	0.0052	0.0001	0.0009	0.0002
Co	0.0003	0.0002	0.0005	0.0000	0.0009	0.0001	0.0034	0.0004	0.0283	0.0005	0.1166	0.0026
Cr	0.1569	0.0037	1.1181	0.0114	1.2581	0.0191	1.2868	0.0088	1.0150	0.0143	0.4293	0.0063
Cu	BDL	BDL	0.0019	0.0007	0.0023	0.0004	0.0059	0.0003	0.0015	0.0011	0.0474	0.0010
Fe	0.0190	0.0062	0.0244	0.0058	0.0148	0.0034	0.0190	0.0025	0.0189	0.0079	0.0478	0.0065
K	15.2178	0.3411	18.7377	0.1417	19.1063	0.4370	19.4690	0.0660	21.3700	0.3022	34.8571	0.8972
Mg	1.2236	1.2014	179.9869	5.0906	305.8248	6.8421	425.3027	14.2362	545.7600	10.1280	660.1987	2.5730
Mn	0.0031	0.0003	0.0036	0.0008	0.0458	0.0017	0.6295	0.0068	5.2778	0.0636	13.3943	0.2090
Mo	0.1010	0.0015	0.1822	0.0015	0.2044	0.0020	0.2005	0.0021	0.1783	0.0026	0.0217	0.0002
Na	215.6540	1.8366	240.8031	6.9529	238.0585	2.5461	232.1695	13.1918	220.0969	4.7660	248.1385	4.6310
Ni	0.0058	0.0034	0.0066	0.0006	0.0137	0.0010	0.0441	0.0006	0.2596	0.0044	0.5945	0.0054
Pb	0.0002	0.0000	0.0005	0.0003	0.0002	0.0000	0.0002	0.0000	0.0002	0.0001	0.0006	0.0001
Se	0.0135	0.0032	0.0180	0.0009	0.0237	0.0029	0.0285	0.0012	0.0221	0.0012	0.1004	0.0112
Si	4.3640	0.0480	1.5177	0.0250	3.2378	0.1387	6.7298	0.2318	14.4973	0.2077	68.7944	0.6690
Sr	1.7820	0.0271	26.1099	0.4515	33.2727	1.2352	42.6387	1.9268	57.7243	0.5495	72.5625	1.2520
Ti	0.0038	0.0021	0.0019	0.0007	0.0002	0.0000	0.0026	0.0009	0.0058	0.0022	0.0029	0.0020
V	0.2361	0.0066	0.2861	0.0019	0.3135	0.0027	0.4137	0.0051	0.4156	0.0060	0.1390	0.0021
Zn	0.0202	0.0012	0.0315	0.0192	0.0150	0.0001	0.0246	0.0007	0.0707	0.0480	0.4171	0.0078
Cl	101.4626	9.8759	139.2600	5.8368	109.5486	0.0000	88.9758	4.3703	83.8641	3.2303	164.0000	31.7490
SO4	299.4161	9.9412	639.8179	17.3152	710.5328	0.0000	770.2467	2.9838	849.0758	0.0000	940.0000	29.6637

Table B9: Concentration of species released from the solid residues recovered from Tutuka long-term fly ash-brine interaction experiments for a period of 1 week (TAC) as a function of pH (concentration in mg/L)

pH/Element	10.5		8.5		7.5		6.5		5.5		4	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	2.2546	0.0913	0.1922	0.0225	0.0897	0.0079	0.0752	0.0159	0.0971	0.0183	53.1752	3.2262
As	0.0060	0.0003	0.0412	0.0015	0.0672	0.0027	0.0292	0.0007	0.0193	0.0015	0.0139	0.0008
B	2.2816	0.3689	3.8597	0.0800	5.5697	0.4607	6.6592	0.4058	7.3256	0.0516	7.9509	0.6505
Ba	0.0896	0.0037	0.1512	0.0110	0.2190	0.0101	0.2619	0.0094	0.2507	0.0054	0.3745	0.0072
Ca	68.9563	2.1768	788.6900	36.7470	1264.6733	39.8465	1743.1900	83.8138	2101.7833	75.6877	2236.0817	184.3611
Cd	0.0063	0.0004	0.0128	0.0008	0.0065	0.0003	0.0037	0.0000	0.0022	0.0002	0.0084	0.0001
Co	0.0051	BDL	0.0000	0.0000	0.0005	0.0001	0.0082	0.0001	0.0203	0.0005	0.1162	0.0009
Cr	0.4338	0.0106	0.6442	0.0174	0.7506	0.0288	0.6418	0.0034	0.5443	0.0027	0.1150	0.0025
Cu	BDL	BDL	0.0011	0.0010	0.0012	0.0005	0.0013	0.0005	BDL	BDL	0.0479	0.0010
Fe	0.0716	0.0314	0.0468	0.0020	0.0653	0.0411	0.0420	0.0087	0.0620	0.0104	0.6923	0.0085
K	12.1798	0.0973	15.0291	0.2565	16.6049	0.5167	19.1328	0.3110	22.2461	0.3556	27.3076	0.5925
Mg	0.4931	0.0095	64.7672	0.4903	101.9827	1.6318	171.7320	7.0616	207.7388	8.9933	252.3232	20.9915
Mn	0.0017	0.0003	0.0096	0.0007	0.0597	0.0015	1.3073	0.0289	2.4862	0.0337	5.8517	0.3665
Mo	0.0879	0.0014	0.1467	0.0028	0.1775	0.0043	0.1615	0.0037	0.1462	0.0022	0.0116	0.0000
Na	181.3875	7.2386	167.7383	9.6435	154.8517	2.4809	141.4153	1.7928	154.4255	10.4621	131.6247	11.2093
Ni	0.0033	0.0033	0.0040	0.0009	0.0072	0.0036	0.0701	0.0006	0.1182	0.0007	0.3803	0.0042
Pb	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0047	0.0002
Se	0.0157	0.0024	0.0393	0.0033	0.0448	0.0036	0.0490	0.0036	0.0437	0.0096	0.0789	0.0021
Si	7.5874	0.2408	4.2739	0.0353	8.1095	0.3175	23.0204	0.4522	33.0184	0.8426	146.9677	9.3758
Sr	1.4083	0.0213	5.8096	0.3282	8.0456	0.2902	11.3005	0.1657	13.3318	0.7409	14.2544	1.0977
Ti	0.0115	0.0045	0.0058	0.0020	0.0048	0.0030	0.0033	0.0010	0.0059	0.0026	0.0346	0.0087
V	0.2153	0.0035	0.2042	0.0056	0.2404	0.0108	0.2607	0.0051	0.2207	0.0018	0.0650	0.0023
Zn	0.0101	0.0014	0.0241	0.0017	0.0253	0.0007	0.0359	0.0022	0.0496	0.0005	0.6496	0.0147
Cl	102.5000	3.5355	100.0000	0.0000	100.0000	7.0711	95.0000	7.0711	92.5000	3.5355	102.5000	10.6066
SO4	397.5000	38.8909	625.0000	0.0000	722.5000	10.6066	732.5000	24.7487	900.0000	49.4975	1195.0000	63.6396

Table B10: Concentration of species released from the solid residues recovered from Tutuka long-term fly ash-brine interaction experiments for a period of 1 month (TBC) as a function of pH (concentration in mg/L)

pH/Element	10.5		8.5		7.5		6.5		5.5		4	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	1.5511	0.0209	0.0953	0.0140	0.1055	0.0041	0.0649	0.0148	0.1323	0.0097	60.0987	0.5613
As	0.0040	0.0003	0.0686	0.0023	0.0851	0.0051	0.0299	0.0009	0.0174	0.0003	0.0143	0.0004
B	2.2129	0.1735	4.3862	0.1763	6.0224	0.2038	7.0644	0.4083	7.2094	0.3748	7.6850	0.5430
Ba	0.0674	0.0037	0.1052	0.0025	0.1870	0.0096	0.2441	0.0070	0.2329	0.0025	0.2983	0.0129
Ca	154.0740	5.2637	875.0800	48.1275	1400.9167	36.8503	2002.7317	13.9669	2227.1300	88.8149	2639.2150	122.6545
Cd	BDL	BDL	BDL	BDL	0.0000	BDL	0.0001	BDL	0.0039	0.0002	0.0094	0.0011
Co	BDL	BDL	0.0006	0.0002	0.0009	0.0001	0.0051	0.0002	0.0165	0.0002	0.1138	0.0057
Cr	0.4393	0.0222	0.5822	0.0168	0.7274	0.0283	0.6226	0.0120	0.3906	0.0050	0.1223	0.0042
Cu	0.0035	0.0011	0.0008	0.0004	0.0018	0.0006	0.0009	0.0001	BDL	BDL	0.0165	0.0015
Fe	0.0338	0.0083	0.0333	0.0047	0.0403	0.0058	0.0514	0.0318	0.0529	0.0127	1.1977	0.0609
K	13.8588	0.7627	17.7240	0.4806	21.7896	1.0134	25.9033	0.2824	27.8590	0.2605	33.9722	1.7510
Mg	0.7379	0.1963	43.4782	3.9801	80.9405	0.7290	148.1142	6.7208	197.2597	6.7914	294.5657	8.1903
Mn	0.0021	0.0003	0.0215	0.0010	0.1163	0.0039	1.3780	0.0267	3.0027	0.0299	7.3825	0.1585
Mo	0.1221	0.0040	0.1729	0.0034	0.2147	0.0114	0.1865	0.0019	0.1520	0.0011	0.0124	0.0005
Na	132.0632	3.0149	154.3740	31.9578	177.3978	3.6608	168.2520	11.3695	189.1100	14.9525	198.2982	4.2355
Ni	BDL	BDL	BDL	BDL	0.0023	0.0002	0.0474	0.0012	0.1066	0.0009	0.3646	0.0225
Pb	BDL	BDL	BDL	BDL	0.0002	0.0001	BDL	BDL	BDL	BDL	0.0041	0.0002
Se	0.0202	0.0065	0.0525	0.0006	0.0675	0.0065	0.0509	0.0078	0.0464	0.0026	0.0864	0.0062
Si	3.3976	0.0305	5.3318	0.4785	11.7720	0.0337	25.3391	0.7522	39.6950	1.9461	171.1187	2.8886
Sr	1.4233	0.0611	4.5397	1.0371	7.8200	0.1506	11.0325	0.8392	14.2638	1.2877	17.7185	0.4678
Ti	0.0036	0.0016	0.0049	0.0030	0.0050	0.0011	0.0056	0.0011	0.0036	0.0008	0.0078	0.0020
V	0.1746	0.0092	0.2086	0.0052	0.2687	0.0128	0.2248	0.0011	0.1826	0.0027	0.0583	0.0039
Zn	0.1558	0.0105	0.1492	0.0026	0.1530	0.0083	0.0516	0.0030	0.0836	0.0075	0.4265	0.0262
Cl	122.5000	3.5355	122.5000	3.5355	105.0000	0.0000	117.5000	17.6777	122.5000	3.5355	130.0000	0.0000
SO4	575.0000	56.5685	772.5000	17.6777	750.0000	14.1421	800.0000	35.3553	975.0000	28.2843	1437.5000	38.8909

Table B11: Concentration of species released from the solid residues recovered from Tutuka long-term fly ash-brine interaction experiments for a period of 6 months (TCC) as a function of pH (concentration in mg/L)

pH/Element	10.5		8.5		7.5		6.5		5.5		4	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	1.2083	0.0392	0.0927	0.0159	0.1016	0.0352	0.0571	0.0286	0.0568	0.0092	47.4826	3.7057
As	0.0106	0.0008	0.0783	0.0015	0.0908	0.0020	0.0360	0.0011	0.0231	0.0010	0.0143	0.0008
B	2.3115	0.0480	4.9395	0.1850	6.2461	0.5020	6.8124	0.5971	7.4693	0.3084	7.8905	0.5542
Ba	0.0545	0.0034	0.1072	0.0041	0.2007	0.0083	0.2186	0.0057	0.1830	0.0048	0.2789	0.0129
Ca	176.0958	1.8442	927.6467	21.6492	1350.1850	57.6666	1962.4133	69.4783	2013.5450	79.5523	2412.4250	110.5802
Cd	0.0009	0.0005	0.0037	0.0002	0.0087	0.0006	0.0042	0.0002	0.0047	0.0006	0.0099	0.0006
Co	BDL	BDL	0.0000	0.0000	0.0009	0.0002	0.0079	0.0003	0.0183	0.0003	0.1196	0.0040
Cr	0.3652	0.0161	0.6405	0.0111	0.7621	0.0125	0.6926	0.0213	0.5581	0.0125	0.1063	0.0049
Cu	BDL	BDL	BDL	BDL	0.0080	0.0090	0.0044	0.0006	0.0008	0.0004	0.0375	0.0018
Fe	0.0449	0.0221	0.0373	0.0060	0.0416	0.0121	0.0324	0.0027	0.0423	0.0110	0.6468	0.0245
K	13.1144	0.6387	16.9506	0.1467	19.7405	0.2347	22.0863	0.4767	23.4513	0.1977	29.6510	0.9646
Mg	2.9276	0.2030	68.9132	0.8245	104.3677	3.1475	177.1168	4.3795	196.3873	8.5708	285.2828	9.2750
Mn	0.0016	0.0014	0.0308	0.0013	0.1689	0.0010	1.4308	0.0369	2.5383	0.0166	6.4647	0.0636
Mo	0.0938	0.0056	0.1688	0.0015	0.2011	0.0066	0.1783	0.0056	0.1589	0.0024	0.0105	0.0007
Na	178.7008	1.4542	180.4922	1.7484	183.1863	2.2025	177.2365	5.7440	171.0598	7.7150	164.8500	6.5647
Ni	0.0007	BDL	0.0032	0.0016	0.0135	0.0031	0.0753	0.0029	0.1211	0.0032	0.3849	0.0125
Pb	BDL	BDL	BDL	BDL	0.0000	BDL	0.0003	0.0003	0.0000	BDL	0.0044	0.0001
Se	0.0223	0.0029	0.0610	0.0029	0.0661	0.0038	0.0546	0.0054	0.0509	0.0048	0.0745	0.0094
Si	4.2010	0.1459	6.8021	0.0736	11.4259	0.3922	23.3227	0.3977	30.9346	1.5118	147.0645	3.7124
Sr	1.6104	0.0458	5.7161	0.0662	8.0672	0.5150	11.8708	0.3687	12.5829	0.7114	15.5648	0.4422
Ti	0.0015	0.0005	0.0012	0.0013	0.0033	0.0018	0.0044	0.0029	0.0008	0.0006	0.0061	0.0021
V	0.1892	0.0101	0.2338	0.0043	0.3218	0.0012	0.2897	0.0085	0.2293	0.0048	0.0534	0.0017
Zn	0.0132	0.0014	0.0122	0.0042	0.0716	0.0032	0.2800	0.0173	0.1865	0.0059	0.6427	0.0339
Cl	127.5000	3.5355	127.5000	3.5355	125.0000	0.0000	122.5000	10.6066	130.0000	14.1421	130.0000	7.0711
SO4	725.0000	14.1421	865.0000	21.2132	872.5000	10.6066	875.0000	35.3553	882.5000	3.5355	1307.5000	45.9619

Table B12: Concentration of species released from the solid residues recovered from Tutuka long-term fly ash-brine interaction experiments for a period of 12 months (TDC) as a function of pH (concentration in mg/L)

pH/Element	10.5		8.5		7.5		6.5		5.5		4	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	2.6103	0.0229	0.2031	0.0298	0.0787	0.0047	0.0481	0.0052	0.0664	0.0148	54.7513	0.4825
As	0.0068	0.0004	0.0427	0.0014	0.0613	0.0013	0.0253	0.0006	0.0170	0.0007	0.0152	0.0005
B	1.7363	0.1327	3.7742	0.1314	5.3294	0.0539	6.8911	0.5053	7.2483	0.2064	7.4718	0.4066
Ba	0.0517	0.0022	0.1250	0.0021	0.2063	0.0065	0.1882	0.0037	0.1758	0.0071	0.2860	0.0073
Ca	69.8027	5.1195	722.4150	104.0842	1122.7267	65.2069	1769.8850	112.2363	1854.6383	46.9059	2257.7833	103.6952
Cd	0.0018	0.0005	0.0007	0.0005	0.0005	0.0004	0.0020	0.0001	0.0022	0.0001	0.0089	0.0004
Co	0.0001	BDL	BDL	BDL	0.0003	0.0003	0.0061	0.0002	0.0148	0.0007	0.1219	0.0016
Cr	0.2764	0.0024	0.4767	0.0210	0.5948	0.0098	0.5078	0.0153	0.3621	0.0104	0.1098	0.0009
Cu	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0344	0.0011
Fe	0.0251	0.0049	0.0305	0.0057	0.0366	0.0087	0.0373	0.0034	0.0512	0.0078	1.0650	0.0271
K	17.6715	0.1181	20.6409	0.8560	22.3388	0.3149	24.9820	0.9472	26.0269	0.6948	32.2549	0.2531
Mg	0.6287	0.4021	46.0926	7.7027	75.1670	5.3037	147.9857	8.9542	168.7577	8.2264	252.1775	6.7774
Mn	0.0014	0.0004	0.0096	0.0009	0.0643	0.0016	1.3518	0.0402	2.5085	0.0562	6.2866	0.0706
Mo	0.1135	0.0016	0.1600	0.0065	0.1886	0.0046	0.1705	0.0047	0.1543	0.0052	0.0120	0.0004
Na	154.2098	6.4423	152.5472	26.1590	146.8688	12.4931	163.6118	9.3783	159.8907	7.3996	171.8047	7.1538
Ni	0.0009	BDL	0.0019	0.0004	0.0064	0.0013	0.0699	0.0022	0.1153	0.0034	0.3882	0.0039
Pb	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0053	0.0001
Se	0.0151	0.0037	0.0402	0.0031	0.0489	0.0061	0.0421	0.0042	0.0421	0.0039	0.0799	0.0042
Si	5.5702	0.2180	2.9745	0.4246	5.8393	0.2550	19.8162	0.8510	24.5165	0.9827	141.7872	1.5479
Sr	0.8555	0.0210	4.5101	0.5876	6.4832	0.7488	11.0061	0.6997	11.8348	0.6324	15.0361	0.1089
Ti	0.0007	BDL	0.0031	BDL	0.0022	0.0013	0.0046	0.0016	0.0065	0.0006	0.0089	0.0052
V	0.2392	0.0017	0.1935	0.0103	0.2306	0.0061	0.2254	0.0072	0.1894	0.0070	0.0595	0.0007
Zn	0.0126	0.0028	0.0064	0.0030	0.0121	0.0051	0.0118	0.0012	0.0173	0.0013	0.5044	0.0084
Cl	127.5000	3.5355	125.0000	14.1421	115.0000	7.0711	122.5000	3.5355	130.0000	0.0000	132.5000	3.5355
SO4	532.5000	17.6777	792.5000	3.5355	807.5000	10.6066	875.0000	134.3503	982.5000	159.0990	1222.5000	95.4594

Appendix C: Up-flow percolation tests

Table C1: pH and EC of Secunda up-flow percolation tests

Cummulative L/S ratio	Fly ash-brine pH	Fly ash-brine EC (mS/cm)	Fly ash-brine-antiscalant pH	Fly ash-brine-antiscalant EC (mS/cm)
0.1	13.21	34.75	13.82	31.7
0.2	13.6	34.25	13.6	35.2
0.5	13.67	33	13.73	35.75
1	11.95	26.5	12.02	26.75
2	11.56	27.65	11.91	27.35
5	12.73	25.65	12.6	24.35
10	11.34	18.62	11.2	18.05
20	10.79	18.13	11.02	17.86
35	10.61	15.48	11.03	15.61
55	9.38	17.1	9.45	16.85
80	9.24	17.01	9.14	17.11

Table C2: pH and EC of Tutuka up-flow percolation tests

Cummulative L/S ratio	Fly ash-brine pH	Fly ash-brine EC (mS/cm)	Fly ash-brine-antiscalant pH	Fly ash-brine-antiscalant EC (mS/cm)
0.1	7.83	5.6	11.72	7.34
0.2	12.44	13.23	12.16	13.6
0.5	12.49	13.73	12.32	13.64
1	10.86	13.97	11	13.81
2	11.62	14.36	11.74	14.5
5	11.59	14.57	11.61	15.46
10	10.55	17.43	9.58	17.43
20	9.55	17.67	9.69	17.57
35	9.36	15.45	9.58	15.6
55	8.71	17.33	8.48	17
80	8.74	17.05	8.92	17.13

Table C3: Concentration of species released into Secunda fly ash-brine up-flow percolation systems as a function of L/S ratio (concentration in mg/L)

L/S ratio/ Element	UB		0.1		0.2		0.5		1		2		5		10		20		35		55		80	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	0.0111	0.0017	1.4623	0.0152	0.9313	0.0230	0.8260	0.0247	0.0940	0.0024	0.0856	0.0215	0.4235	0.0396	4.3510	0.1301	3.4305	0.0076	1.3837	0.0420	0.9738	0.0495	0.4352	0.0405
As	0.0070	0.0007	0.0022	0.0003	0.0024	0.0000	0.0026	0.0001	0.0027	0.0000	0.0025	0.0001	0.0032	0.0004	0.0079	0.0003	0.0053	0.0001	0.0053	0.0001	0.0065	0.0003	0.0058	0.0004
B	1.9840	0.1017	0.3107	0.0109	0.2556	0.0359	0.2004	0.0531	0.5079	0.0263	0.5458	0.0477	0.5100	0.0000	0.3783	0.0292	2.3214	0.0149	6.1170	0.0239	3.6976	0.1182	3.9982	0.3242
Ba	0.0579	0.0015	24.7125	0.7248	7.6900	2.0153	7.4350	0.3111	0.3221	0.0005	0.2695	0.0050	0.1921	0.0155	0.2886	0.0087	0.2912	0.0074	0.1985	0.0123	0.1179	0.0015	0.0741	0.0050
Ca	91.0120	0.7122	163.5855	5.2672	216.0933	2.4611	262.8900	3.3573	487.0300	1.2777	471.7395	1.3661	368.2488	5.0611	221.4510	4.2525	423.3910	0.5614	378.6023	5.7680	502.6997	3.2448	377.8077	2.5811
Cd	BDL	BDL	0.0004	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0002	0.0000	BDL	BDL	0.0003	0.0000	0.0002	0.0001
Co	0.0081	0.0006	BDL	BDL	BDL	BDL	0.0000	0.0000	BDL	BDL	BDL	BDL	BDL	BDL	0.0006	0.0001	0.0033	0.0001	0.0062	0.0006	0.0024	0.0001	0.0058	0.0005
Cr	0.0151	0.0015	1.1498	0.0081	1.9678	0.0308	2.8948	0.0350	1.1990	0.0064	0.1645	0.0018	0.0240	0.0031	0.0150	0.0001	0.0314	0.0008	0.0268	0.0010	0.0128	0.0010	0.0160	0.0033
Cu	0.1894	0.0077	1.3033	0.0067	1.1038	0.0223	0.9618	0.0103	0.5503	0.0046	0.2194	0.0034	0.1484	0.0101	0.0905	0.0005	0.0325	0.0000	0.0271	0.0007	0.0232	0.0004	0.0259	0.0015
Fe	0.1018	0.0075	0.1165	0.0000	0.0744	0.0000	0.1004	0.0071	0.1032	0.0000	0.0931	0.0116	0.1553	0.0104	0.1137	0.0054	BDL	BDL	0.1479	0.0061	0.0591	0.0544	0.0416	0.0133
K	106.2000	3.8432	202.5750	0.6010	159.0750	1.3789	147.2500	3.7477	132.9250	1.5910	138.6500	0.0707	144.4750	11.2784	118.7500	0.0000	102.4183	0.6304	96.9617	3.4070	97.4505	2.4477	101.5228	2.5137
Mg	147.5000	10.5674	0.2130	0.0086	0.0648	0.0173	0.0540	0.0006	0.0719	0.0135	0.0616	0.0004	0.0916	0.0120	0.1671	0.0026	0.3511	0.0088	0.8007	0.0206	1.4181	0.0063	10.6619	0.0461
Mn	0.0016	0.0002	0.0051	0.0008	0.0033	0.0002	0.0014	0.0000	0.0019	0.0001	0.0014	0.0004	0.0022	0.0002	0.0023	0.0003	0.0018	0.0001	0.0025	0.0004	0.0008	0.0004	0.0018	0.0003
Mo	0.0380	0.0024	1.3060	0.0028	1.3520	0.0375	1.4855	0.0191	0.4324	0.0064	0.2294	0.0015	0.1935	0.0179	0.0879	0.0025	0.0588	0.0010	0.0566	0.0008	0.1730	0.0028	0.0755	0.0048
Na	4323.2200	44.7672	4966.3075	4.1401	4491.6825	134.9902	4537.6275	25.1412	4415.7675	91.7506	4577.1200	33.2764	4342.9175	57.5903	4260.2875	15.6801	4225.2575	24.6179	4132.1317	41.9532	4283.7750	23.1329	4342.3517	53.2992
Ni	0.1197	0.0052	0.0139	0.0038	0.0069	0.0018	0.0110	0.0011	0.0122	0.0015	0.0821	0.0015	0.1104	0.0082	0.1279	0.0030	0.1275	0.0025	0.1168	0.0068	0.1342	0.0021	0.1321	0.0079
Pb	0.0067	0.0094	0.3211	0.0038	0.0488	0.0181	0.0545	0.0001	0.0766	0.0037	0.0586	0.0015	0.0290	0.0018	0.0021	0.0004	0.0011	0.0001	0.0006	0.0000	0.0037	0.0002	0.0014	0.0001
Se	0.0066	0.0008	0.0333	0.0001	0.0241	0.0060	0.0264	0.0011	0.0172	0.0001	0.0142	0.0042	0.0171	0.0002	0.0195	0.0060	0.0191	0.0010	0.0175	0.0005	0.0107	0.0018	0.0145	0.0022
Si	11.1022	0.0271	2.8157	0.0226	2.5985	0.1392	2.3725	0.0154	2.0486	0.0697	2.3389	0.1617	3.8066	0.0627	20.4064	0.3233	18.7492	0.1634	10.9755	0.0334	6.5341	0.1822	5.3733	0.0294
Sr	2.5908	0.0097	230.4898	2.1295	235.5348	2.3211	215.8225	0.9362	73.2865	1.0225	51.7525	0.0827	32.4175	0.2142	25.9394	0.0455	12.1951	0.0089	9.3394	0.1360	16.1138	0.2294	12.7018	0.0413
Ti	0.0009	0.0005	0.0034	0.0013	0.0029	0.0003	0.0035	0.0001	0.0010	0.0003	0.0000	0.0000	0.0008	0.0001	0.0015	0.0000	0.0075	0.0079	0.0046	0.0001	0.0019	0.0012	0.0014	0.0009
V	0.0174	0.0012	0.0110	0.0005	0.0075	0.0003	0.0028	0.0001	0.0150	0.0001	0.0159	0.0010	0.0525	0.0068	0.4758	0.0009	0.2793	0.0030	0.1981	0.0015	0.2984	0.0039	0.3008	0.0118
Zn	0.1104	0.0057	1.6188	0.0110	0.9768	0.0286	0.8560	0.0014	0.6888	0.0124	0.4194	0.0035	0.2393	0.0093	0.0421	0.0065	0.0055	0.0005	0.0066	0.0007	0.1385	0.0062	0.0602	0.0033
Cl	2424.0000	159.8061	1945.8000	89.0274	2019.2333	241.6727	1945.8167	262.7891	2217.5000	99.3292	2092.6667	212.4533	2173.4500	89.0274	1970.7833	136.9514	2028.0500	82.4696	2120.5667	44.3420	1778.6466	54.3106	1688.6562	45.2517
SO4	8858.0000	82.2258	49.2500	0.9179	199.2333	5.9591	639.5000	21.1465	3542.7500	70.9706	3779.0000	113.2312	3928.8167	45.7872	6854.3500	46.3734	7764.6000	37.8824	7761.8167	219.7336	7299.2284	254.0396	7256.2403	236.3505

Table C4: Concentration of species released into Secunda fly ash-brine-antiscalant up-flow percolation systems as a function of L/S ratio (concentration in mg/L)

L/S ratio/ Element	UB		0.1		0.2		0.5		1		2		5		10		20		35		55		80	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	0.0551	0.0320	0.8247	0.0696	1.2020	0.0755	1.2572	0.1201	0.1638	0.0265	0.0388	0.0050	3.7613	0.0583	1.8458	0.1949	3.3163	0.0993	1.2111	0.1297	0.6607	0.0051	0.2480	0.0240
As	0.0068	0.0006	0.0025	0.0007	0.0017	0.0010	0.0022	0.0006	0.0021	0.0002	0.0018	0.0002	0.0052	0.0004	0.0055	0.0006	0.0055	0.0003	0.0043	0.0002	0.0072	0.0005	0.0065	0.0001
B	2.2310	0.1681	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.7565	0.0031	3.1737	0.2062	2.1864	0.0775	2.2111	0.2628
Ba	0.0595	0.0045	10.3817	1.2401	31.0767	1.3431	29.8833	1.9543	0.8615	0.0845	0.3107	0.0128	0.4138	0.0220	0.3343	0.0186	0.2892	0.0083	0.0878	0.0032	0.1380	0.0038	0.1299	0.0038
Ca	90.7942	1.1557	136.8002	1.9616	187.8338	2.8313	194.1710	7.5629	401.5810	13.6880	416.2150	2.7993	160.2535	1.5528	251.7948	45.7836	304.4345	1.4941	324.5748	4.6603	255.4618	7.0705	266.1617	1.4610
Cd	0.0001	0.0000	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0002	0.0000	BDL	BDL	0.0003	0.0001	0.0001	0.0000
Co	0.0087	0.0006	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0006	0.0002	0.0020	0.0000	0.0022	0.0001	0.0070	0.0005	0.0063	0.0001
Cr	0.0165	0.0024	4.1933	0.5254	0.7440	0.0260	1.5607	0.1153	2.3723	0.0249	0.6383	0.0134	0.0885	0.0016	0.1730	0.0191	0.2593	0.0099	0.1800	0.0157	0.0386	0.0014	0.0437	0.0022
Cu	0.2060	0.0167	0.8447	0.1132	0.8802	0.0384	0.9157	0.0778	0.3660	0.0043	0.3173	0.0043	0.0877	0.0005	0.0399	0.0045	0.0372	0.0018	0.0299	0.0049	0.0474	0.0006	0.0487	0.0007
Fe	0.1118	0.0094	0.1426	0.0241	0.1091	0.0342	0.1185	0.0316	0.0788	0.0149	0.1012	0.0422	0.1381	0.0060	0.1175	0.0363	BDL	BDL	0.0969	0.0371	0.0237	0.0029	0.0339	0.0121
K	116.7000	5.2115	204.3833	18.7243	166.5000	7.2751	165.9000	7.3313	129.0667	3.2655	135.4000	0.9260	136.9667	2.7319	112.6557	0.8276	106.1083	1.6757	103.9824	7.5171	107.9377	2.8625	108.7628	0.6021
Mg	140.4883	1.6435	0.1787	0.0301	0.0881	0.0375	0.0905	0.0121	0.0966	0.0218	0.0927	0.0329	0.0801	0.0041	0.2135	0.0076	0.2529	0.0286	0.8164	0.0898	31.5887	0.9329	28.2645	0.2725
Mn	0.0018	0.0001	0.0003	0.0003	0.0006	BDL	0.0000	BDL	BDL	BDL	0.0003	BDL	0.0004	0.0002	0.0003	0.0003	0.0007	0.0004	0.0019	0.0010	0.0018	0.0003	0.0007	0.0002
Mo	0.0391	0.0034	1.7017	0.2486	0.7035	0.0305	1.1837	0.1009	0.7330	0.0144	0.2349	0.0031	0.1828	0.0032	0.0698	0.0058	0.0719	0.0013	0.0724	0.0065	0.0944	0.0035	0.0870	0.0009
Na	4327.6500	33.8152	4619.0800	103.5452	4336.6233	19.6945	4479.0700	364.2785	4269.7533	55.7205	4149.7417	31.2684	4025.2683	18.6808	4013.0967	93.5746	4348.9867	80.0378	4003.6933	68.0133	4244.2433	146.3676	4227.6133	19.4595
Ni	0.1226	0.0095	0.0165	0.0007	0.0113	0.0022	0.0115	0.0008	0.0121	0.0006	0.0677	0.0043	0.1055	0.0022	0.1201	0.0104	0.1221	0.0056	0.1189	0.0101	0.1263	0.0038	0.1236	0.0014
Pb	0.0032	0.0000	0.1943	0.0244	0.0894	0.0049	0.0885	0.0055	0.0306	0.0005	0.0241	0.0005	0.0155	0.0001	0.0023	0.0004	0.0011	0.0003	0.0012	0.0002	0.0012	0.0000	0.0012	0.0001
Se	0.0038	0.0019	0.0513	0.0105	0.0156	0.0026	0.0210	0.0093	0.0091	0.0088	0.0086	0.0027	0.0069	0.0055	0.0043	0.0053	0.0093	0.0019	0.0191	0.0044	0.0132	0.0034	0.0105	0.0051
Si	11.0566	0.1582	4.5619	1.7550	4.3141	0.1820	4.3305	0.5865	2.7213	0.0618	2.6617	0.1933	11.0911	0.1184	21.6996	4.7865	21.5999	0.1275	14.1509	0.3192	7.4344	0.2633	6.7385	0.0430
Sr	2.5996	0.0455	145.1383	1.5399	244.4795	1.6952	233.2030	0.3340	95.8187	1.1168	51.3907	0.4960	30.7257	0.0845	24.9815	1.8606	18.5077	0.1482	11.8309	0.1882	12.6370	0.3970	12.6816	0.0920
Ti	0.0033	0.0016	0.0047	0.0042	0.0011	0.0014	0.0007	0.0007	0.0014	0.0000	0.0007	0.0000	0.0020	0.0012	0.0029	0.0020	0.0013	0.0010	0.0014	0.0000	0.0017	0.0017	0.0012	0.0011
V	0.0188	0.0015	0.0151	0.0020	0.0084	0.0004	0.0083	0.0006	0.0128	0.0003	0.0156	0.0003	0.2175	0.0053	0.4431	0.0360	0.4499	0.0181	0.3201	0.0251	0.2925	0.0074	0.2842	0.0043
Zn	0.1179	0.0095	2.5692	0.3483	1.0805	0.0559	1.0782	0.0865	0.3176	0.0131	0.3239	0.0065	0.1180	0.0056	0.0077	0.0014	0.0070	0.0016	0.0040	0.0017	0.0283	0.0025	0.0254	0.0003
Cl	2424.0000	167.7791	2157.2833	152.3674	2041.2500	89.0274	2117.6333	5.0807	2116.1667	126.6312	2204.2833	58.6696	1934.0667	200.5844	2008.9667	33.2458	1934.0500	73.3162	2126.4500	53.8453	1889.7775	83.3898	1832.7426	0.2815
SO4	8858.0000	74.9402	271.4000	9.1095	31.9833	3.0432	90.8000	4.4584	3015.0000	103.7934	3721.1833	54.4828	4259.5833	63.7722	7385.8833	111.4358	7505.6667	219.2342	7561.8000	194.0638	6953.9350	14.3467	6978.9216	23.7021

Table C5: Concentration of species released into Tutuka fly ash-brine up-flow percolation systems as a function of L/S ratio (concentration in mg/L)

L/S ratio/ Element	UB		0.1		0.2		0.5		1		2		5		10		20		35		55		80	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	0.0111	0.0017	14.0650	0.5903	9.0250	0.3661	9.6733	0.3661	7.7500	0.5890	5.5867	0.6040	2.5600	0.1044	1.3700	0.1329	1.2079	0.3043	0.1609	0.0159	0.1316	0.0043	0.1434	0.0064
As	0.0070	0.0007	0.0115	0.0006	0.0157	0.0009	0.0174	0.0009	0.0135	0.0010	0.0138	0.0024	0.0136	0.0013	0.0133	0.0024	0.0123	0.0003	0.0357	0.0025	0.0511	0.0014	0.0516	0.0017
B	1.9840	0.1017	0.3777	0.0992	BDL	BDL	0.0872	BDL	0.7332	0.2141	1.6952	0.3304	2.0810	0.1902	2.5473	0.1328	3.3641	0.0009	4.2040	0.1526	2.9148	0.0817	2.8550	0.1416
Ba	0.0579	0.0015	0.3465	0.0327	0.2833	0.0240	0.2801	0.0240	0.2456	0.0093	0.2004	0.0140	0.1593	0.0090	0.1861	0.0167	0.1145	0.0025	0.0567	0.0026	0.0502	0.0012	0.0379	0.0025
Ca	91.0120	0.7122	92.9945	1.5558	194.8110	3.4681	203.4647	3.4681	291.7537	3.9985	335.9755	1.2339	339.7483	3.8521	323.1685	3.0368	227.7423	3.6308	143.9862	2.8664	115.9418	0.2104	115.0133	1.2667
Cd	BDL	BDL	0.0003	0.0004	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0002	0.0000	BDL	BDL	0.0001	0.0001	0.0001	0.0001
Co	0.0081	0.0006	0.0053	0.0003	0.0011	0.0002	0.0013	0.0002	0.0016	0.0003	0.0025	0.0003	0.0033	0.0002	0.0035	0.0005	0.0068	0.0002	0.0105	0.0010	0.0197	0.0004	0.0195	0.0004
Cr	0.0151	0.0015	9.8267	0.4394	0.9705	0.0544	0.9572	0.0544	0.2137	0.0232	0.2406	0.0232	0.2290	0.0086	0.2389	0.0247	0.1258	0.0030	0.1118	0.0052	0.0132	0.0012	0.0132	0.0008
Cu	0.1894	0.0077	0.1048	0.0072	0.0371	0.0055	0.0442	0.0055	0.0492	0.0029	0.0554	0.0062	0.0591	0.0022	0.0510	0.0057	0.0518	0.0015	0.0808	0.0059	0.0923	0.0018	0.0888	0.0015
Fe	0.1018	0.0075	0.1154	0.0088	0.2977	0.0528	0.1702	0.0528	0.1309	0.0483	0.0998	0.0302	0.1021	0.0200	0.1277	0.0469	0.0826	BDL	0.0911	0.0082	0.0397	0.0142	0.0283	0.0035
K	106.2000	3.8432	169.2667	5.1561	199.5333	3.4882	205.4500	3.4882	125.8167	4.8894	121.5667	9.4790	111.6167	2.8776	114.1167	4.8250	100.5343	1.5150	96.2406	4.7481	115.3965	4.5954	112.3888	0.7044
Mg	141.9607	0.6702	0.3127	0.0442	0.1179	0.0245	0.1091	0.0245	0.1036	0.0116	0.1078	0.0166	0.4925	0.0175	1.6337	0.0168	76.1457	0.2852	114.6287	1.9562	170.4352	2.4032	169.9397	0.6659
Mn	0.0016	0.0002	0.0020	0.0002	0.0025	0.0012	0.0024	0.0012	0.0022	0.0009	0.0021	0.0004	0.0013	0.0003	0.0019	0.0009	0.0017	0.0004	0.0029	0.0006	0.0051	0.0007	0.0022	0.0001
Mo	0.0380	0.0024	4.0853	0.2046	0.3204	0.0255	0.2993	0.0255	0.0755	0.0024	0.0872	0.0075	0.0846	0.0021	0.0930	0.0083	0.0674	0.0022	0.0624	0.0042	0.0423	0.0006	0.0411	0.0015
Na	4323.2200	44.7672	1322.6333	31.6522	3937.0133	50.6007	3962.1383	50.6007	4445.4467	77.7956	4429.4100	24.1664	4478.5483	94.7954	4268.8600	45.4877	4348.2967	46.4660	3942.6667	39.0483	4499.2933	16.8721	4462.6983	35.2746
Ni	0.1197	0.0052	0.0535	0.0021	0.1104	0.0086	0.1141	0.0086	0.1183	0.0078	0.1287	0.0097	0.1169	0.0025	0.1289	0.0111	0.1252	0.0050	0.1129	0.0042	0.1320	0.0048	0.1297	0.0029
Pb	0.0067	0.0094	0.0052	0.0002	0.0011	0.0005	0.0017	0.0005	0.0028	0.0016	0.0014	0.0003	0.0031	0.0031	0.0016	0.0002	0.0019	0.0006	0.0014	0.0002	0.0020	0.0005	0.0014	0.0000
Se	0.0066	0.0008	0.1295	0.0262	0.0189	0.0115	0.0135	0.0115	0.0091	0.0064	0.0188	0.0144	0.0218	0.0062	0.0325	0.0118	0.0406	0.0082	0.0218	0.0058	0.0147	0.0062	0.0154	0.0013
Si	11.1022	0.0271	7.1199	0.1441	5.5427	0.1566	5.4394	0.1566	6.2667	0.1058	6.3469	0.1662	8.5794	0.1940	9.6819	0.0425	5.3542	0.0578	3.4477	0.0837	3.2770	0.0231	3.2379	0.0787
Sr	2.5908	0.0097	5.7484	0.0148	10.9783	0.0679	11.3853	0.0679	17.4921	0.2123	13.0753	0.1051	7.8355	0.0605	7.2588	0.1066	4.3720	0.0533	3.4516	0.0198	3.1424	0.0188	3.1344	0.0360
Ti	0.0009	0.0005	0.0111	0.0037	0.0014	0.0007	0.0008	0.0007	0.0013	0.0016	0.0020	0.0004	0.0008	0.0000	0.0016	0.0020	0.0033	0.0011	0.0018	0.0002	0.0012	0.0007	0.0030	0.0006
V	0.0174	0.0012	0.8137	0.0352	0.8463	0.0373	0.8853	0.0373	0.4914	0.0254	0.2719	0.0258	0.3038	0.0143	0.3090	0.0254	0.1968	0.0007	0.1595	0.0092	0.0903	0.0011	0.0896	0.0018
Zn	0.1104	0.0057	0.0913	0.0043	0.0519	0.0031	0.0475	0.0031	0.0417	0.0022	0.0475	0.0062	0.0258	0.0004	0.0271	0.0048	0.0293	0.0059	0.0752	0.0013	0.1483	0.0072	0.1468	0.0044
Cl	2424.0000	159.8061	998.6167	89.0377	1820.9833	77.3635	1820.9833	121.3179	1821.0000	55.4416	1901.7667	67.2875	1894.4167	88.1250	1947.2833	43.4111	1951.6833	24.5251	2149.9333	46.6219	1817.3229	5.6280	1753.4385	25.2457
SO4	8858.0000	82.2258	1707.3667	53.3698	6561.6833	134.4359	6688.4833	98.1803	7358.7833	285.1893	7380.2333	9.6196	7483.6167	126.7613	7804.2000	70.5452	7767.6500	79.6445	7661.9500	166.8933	7347.9735	76.2775	7283.1330	98.8476

Table C6: Concentration of species released into Tutuka fly ash-brine-antiscalant up-flow percolation systems as a function of L/S ratio (concentration in mg/L)

L/S ratio/ Element	UB		0.1		0.2		0.5		1		2		5		10		20		35		55		80	
	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.	Ave	stdev.
Al	0.0551	0.0320	17.6800	1.8577	16.1617	1.2564	15.5767	1.2099	8.5117	0.3950	5.6802	0.7050	3.4273	0.2740	0.1236	0.0125	1.3321	0.0100	0.1451	0.0024	0.1711	0.0116	0.1194	0.0238
As	0.0068	0.0006	0.0113	0.0029	0.0164	0.0011	0.0149	0.0033	0.0141	0.0006	0.0130	0.0019	0.0136	0.0002	0.0128	0.0017	0.0173	0.0008	0.0471	0.0010	0.0542	0.0010	0.0615	0.0029
B	2.2310	0.1681	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.1203	BDL	0.6661	0.2593	0.9900	0.1873	2.9127	0.0432	3.0970	0.0497	4.0173	0.1769	2.9591	0.1840
Ba	0.0595	0.0045	0.4115	0.0464	0.3786	0.0164	0.3687	0.0194	0.1974	0.0095	0.2069	0.0186	0.1800	0.0046	0.2533	0.0312	0.1210	0.0042	0.1120	0.0002	0.0525	0.0014	0.0310	0.0008
Ca	90.7942	1.1557	148.2973	3.7346	195.9870	1.1701	192.5062	1.2114	238.6425	2.7330	279.3775	6.0096	322.6225	2.0739	182.5523	3.8990	220.3890	10.1069	155.6427	3.5074	146.1467	1.0894	117.4292	0.9389
Cd	0.0001	0.0000	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	BDL	0.0003	0.0000	0.0001	BDL	0.0005	0.0004	0.0001	0.0000
Co	0.0087	0.0006	0.0039	0.0002	0.0011	0.0002	0.0011	0.0002	0.0009	0.0001	0.0017	0.0002	0.0038	0.0004	0.0072	0.0011	0.0064	0.0003	0.0130	0.0004	0.0171	0.0001	0.0134	0.0003
Cr	0.0165	0.0024	7.4217	0.6817	0.9310	0.0796	0.8652	0.0431	0.2855	0.0093	0.3223	0.0317	0.2051	0.0219	0.1065	0.0066	0.1031	0.0038	0.0421	0.0036	0.0235	0.0010	0.0140	0.0004
Cu	0.2060	0.0167	0.0144	0.0038	0.0268	0.0023	0.0312	0.0023	0.0318	0.0015	0.0301	0.0037	0.0451	0.0033	0.0648	0.0076	0.0595	0.0026	0.1023	0.0079	0.0722	0.0044	0.1068	0.0012
Fe	0.1118	0.0094	0.1233	0.0497	0.0914	0.0117	0.1329	0.0200	0.1100	0.0205	0.1328	0.0410	0.1064	0.0279	0.0848	0.0137	BDL	BDL	0.1070	0.0155	0.0211	0.0059	0.0494	0.0137
K	116.7000	5.2115	194.6172	3.2882	208.3777	2.3236	201.6145	4.3221	131.9650	2.2534	116.4873	1.1505	116.0943	1.0101	112.3053	3.1628	100.3022	4.1590	92.0119	3.3376	112.1217	1.9248	109.5898	3.0159
Mg	140.4883	1.6435	0.1611	0.0118	0.1250	0.0203	0.1514	0.0144	0.1571	0.0241	0.2363	0.0184	0.3233	0.0097	92.7773	1.4323	81.8033	1.5147	136.3970	2.6668	145.0647	1.1332	160.6827	0.8378
Mn	0.0018	0.0001	0.0009	0.0002	0.0000	BDL	0.0004	0.0002	0.0004	0.0001	0.0010	0.0001	0.0012	0.0010	BDL	BDL	0.0014	0.0005	0.0065	0.0005	0.0011	0.0003	0.0077	0.0005
Mo	0.0391	0.0034	2.9560	0.3480	0.2602	0.0165	0.2424	0.0094	0.0875	0.0037	0.0995	0.0106	0.0794	0.0072	0.0573	0.0058	0.0654	0.0018	0.0428	0.0008	0.0455	0.0013	0.0409	0.0013
Na	4327.6500	33.8152	1901.4383	34.4655	3975.9400	34.9456	3939.5833	35.0058	4107.6333	47.7904	4131.6383	110.5340	4257.6625	13.0567	4172.2050	49.2946	4322.6017	53.7282	4091.1250	146.9543	4380.4150	3.0174	4304.1850	67.5539
Ni	0.1226	0.0095	0.0621	0.0102	0.1065	0.0057	0.1044	0.0044	0.1047	0.0012	0.1164	0.0103	0.1180	0.0083	0.1166	0.0104	0.1222	0.0053	0.1075	0.0018	0.1271	0.0015	0.1254	0.0039
Pb	0.0032	0.0000	0.0026	0.0004	0.0022	0.0006	0.0017	0.0002	0.0020	0.0002	0.0014	0.0003	0.0054	0.0040	0.0024	0.0007	0.0015	0.0002	0.0018	0.0001	0.0016	0.0002	0.0009	0.0000
Se	0.0038	0.0019	0.0734	0.0076	0.0083	BDL	0.0108	0.0089	0.0073	0.0080	0.0063	0.0066	0.0130	0.0081	0.0099	0.0056	0.0373	0.0025	0.0197	0.0022	0.0248	0.0048	0.0170	0.0033
Si	11.0566	0.1582	4.1818	0.0895	4.0988	0.0572	4.1601	0.1076	5.1705	0.0997	7.9795	0.1394	10.2653	0.1111	5.3316	0.0686	5.9247	0.1370	2.6464	0.1049	2.9816	0.0440	2.6946	0.1134
Sr	2.5996	0.0455	8.4011	0.1832	11.3069	0.1086	11.1638	0.0646	14.1362	0.1220	17.0051	0.2149	10.0690	0.0888	4.6485	0.0934	4.9915	0.0469	3.0618	0.1362	3.0806	0.0090	2.4446	0.0263
Ti	0.0033	0.0016	0.0065	0.0015	0.0006	0.0000	0.0011	0.0004	0.0006	0.0007	0.0020	0.0010	0.0014	0.0020	0.0007	0.0014	0.0015	0.0010	0.0016	0.0004	0.0010	0.0008	0.0027	0.0019
V	0.0188	0.0015	0.7808	0.0801	1.0995	0.0830	1.0337	0.0546	0.6297	0.0228	0.4639	0.0529	0.3368	0.0236	0.2067	0.0169	0.2225	0.0064	0.0842	0.0019	0.1589	0.0032	0.1035	0.0031
Zn	0.1179	0.0095	0.0359	0.0059	0.0227	0.0059	0.0232	0.0025	0.0231	0.0018	0.0158	0.0027	0.0188	0.0051	0.0534	0.0153	0.0393	0.0023	0.0882	0.0029	0.1191	0.0022	0.1059	0.0011
Cl	2424.0000	167.7791	1402.4500	47.5324	1937.0167	22.6067	2019.2500	157.0596	1989.8833	77.3611	2032.4667	78.9599	2055.9667	53.3018	1951.6833	183.1938	2023.6333	129.9669	2085.3333	36.6934	1752.5800	118.6552	1782.8311	95.6203
SO4	8858.0000	74.9402	2954.9167	95.9294	7050.5833	79.4054	7014.9833	81.9906	7543.3500	166.9616	7753.0667	53.4875	7857.4667	69.4515	7865.6667	129.7509	7803.0833	93.1895	7655.3333	110.1966	7163.0605	707.0776	7314.5819	1037.7687