

## Chemical, mineralogical and morphological changes in weathered coal fly ash: A case study of a brine impacted wet ash dump

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### Abstract

The mobility of species in coal fly ash (FA), co-disposed with brine using a wet ash handling system, from a coal fired power generating utility has been investigated. The study was conducted in order to establish if the wet ash dump could act as a salt sink. The ash was dumped as a slurry with 5:1 brine/ash ratio and the dam was in operation for 20 years. Weathered FA samples were collected along three cores at a South African power station's wet ash dump by drilling and sampling the ash at 1.5 m depth intervals. A fresh FA sample was collected from the hoppers in the ash collection system at the power station. Characterization of both fresh FA and weathered FA obtained from the drilled cores S1, S2 and S3 was done using X-ray diffraction (XRD) for mineralogy, X-ray fluorescence (XRF) for chemical composition and scanning electron microscopy (SEM) for morphology. Analysis of extracted pore water and moisture content determination of the fresh FA and the weathered FA obtained from the drilled cores S1, S2 and S3 was done in order to evaluate the physico-chemical properties of the FA. The XRD analysis revealed changes in mineralogy along cores S1, S2 and S3 in comparison with the fresh FA. The SEM analysis revealed spherical particles with smooth outer surfaces for the fresh FA while the weathered ash samples obtained from cores S1, S2 and S3 consisted of agglomerated, irregular particles appearing to be encrusted, etched and corroded showing that weathering and leaching had occurred in the ash dump. The moisture content (MC) analysis carried out on the fresh FA (1.8%) and the weathered FA obtained from the drilled cores S1 (41.4-73.2%), S2 (30.3-94%) and S3 (21.7-76.2%) indicated that the ash dump was water logged hence creating favourable conditions for leaching of species. The fresh fly ash ( $n = 3$ ) had a pH of  $12.38 \pm 0.15$ , EC value of  $4.98 \pm 0.03$  mS/cm and TDS value of  $2.68 \pm 0.03$  g/L, the pH of the drilled core S1 ( $n = 45$ ) was  $10.04 \pm 0.50$ , the EC value was  $1.08 \pm 0.14$  mS/cm and the TDS value was  $0.64 \pm 0.08$  g/L. Core S2 ( $n = 105$ ) had pH of  $10.04 \pm 0.23$ ; EC was  $1.08 \pm 0.06$  mS/cm and TDS was  $0.64 \pm 0.04$  g/L, while core S3 ( $n = 66$ ) had pH of  $11.04 \pm 0.09$ ; EC was  $0.99 \pm 0.03$  mS/cm and TDS was  $0.57 \pm 0.01$  g/L. The changes in pH values

can be attributed to the dissolution and flushing out of alkaline oxides like CaO and MgO from the dumped ash. The variations in pH values shows that the fly ash is acidifying over time and metal mobility can be expected under these conditions. The large decrease of EC in the drilled ash cores S1, S2 and S3 compared to the fresh ash indicated a major loss of ionic species over time in the ash dump. The XRF analysis showed the progressive dissolution of the major alumi-nosilicate ash matrix which influenced the release of minor and trace elements into the pore water enhancing their mobility as the ash dam acidified over time. Brine co-disposal on the ash may have been responsible for the slight enrichment of some species such as Na (0.27-0.56%), SO<sub>4</sub> (0.06-0.08%), Mg (0.57-0.96 %) and K (0.02-0.34%) in the disposed weathered FA. However, there was no significant accumulation of these species in the disposed FA despite continuous addition of large volumes of highly saline brine over the 20 year period that the dump existed, indicating that the ash dam was incapable of holding salts and continually released elements to the environment over the lifetime of the dam.

## 1. Introduction

South Africa (SA) has abundant coal reserves which are utilized to generate electricity and petrochemical related products. Sasol, which is one of Africa's major producers of chemicals and liquid fuels, and Eskom, the major power utility company in SA are the biggest consumers of coal in the country. The Sasol complex located at Secunda in SA operated by Sasol Synfuels (Pty) Ltd is the world's largest commercial coal-to-liquids (CTL) facility (Mangena, 2009). Sasol Secunda utilizes low rank bituminous coal in its gasification and combustion processes to produce synthesis gas and steam respectively. Sasol Secunda utilizes approximately 28 million tons of coal annually, out of which 70% (coarse coal) is used as feedstock for its gasification process while the remaining 30% (finer coal fraction) is used in steam and electric power production. A mixture of coarse and fine ash particles is produced as a by-product of the gasification process and FA as the by-product of the combustion process (Matjie et al., 2005; Hlatshwayo et al., 2009).

FA is the fine particulate waste product that results during the combustion of pulverised coal to generate electricity. FA travels with the flue gases and is removed from the flue gas stream using either electrostatic precipitators or bag filters to avoid release into the atmosphere. FA consists of inorganic and organic components (Liu et al., 2005; Vassilev and Vassileva, 2005). The mineral components in FA have natural and anthropogenic origins and can be classified as primary, secondary and tertiary. The primary mineral phases originate from the parent coal and do not undergo phase transformation during coal combustion; the secondary mineral phases are formed during coal combustion while the tertiary mineral phases are formed during the handling and storage of the FA (Vassilev and Vassileva, 2005).

SA generated about 30 million tons of FA in 2003 of which only about 1.2 million tons was beneficiated (Potgieter, 2003). However, in 2009, Eskom alone generated nearly 36.7 million tons of FA from coal combustion, of which only 5.7% was beneficiated ([www.eskom.co.za](http://www.eskom.co.za)). Thus the bulk of the FA generated is disposed in ponds or dry surfaces. FA is mainly disposed using either the dry or wet disposal method. In the dry disposal method, the FA is transported by truck, chute or conveyor at the power plant and disposed by constructing a dry embankment; the ash heap is then irrigated with brine for dust suppression. In the wet disposal method, the FA is blended with brine and is then transported as slurry with liquid: solid ratio of 1:5 through pipes and disposed in an impoundment referred to as ash pond or dam (Akinyemi, 2011).

Various environmental risks are associated with FA disposal, these include air pollution, loss of arable land and surface and ground water contamination due to the leaching of toxic and non-degradable metals, and other chemical species from the ash dump (Vadapalli et al., 2010; Potgieter-Vermaak et al., 2005). The management and long term disposal of FA is a major concern and requires the proper understanding of the weathering trends of FA. The huge amount of FA that is disposed cannot be separated from nature's weathering cycle as the FA dumps are exposed to ash disposal water, air and rainfall. The weathering of FA results in changes in the physical, chemical and mineralogical properties such as the formation of secondary mineral phases (Yeheyis et al., 2009), decrease in the pH and EC of the pore water in the FA (Ward et al., 2009; Baba et al., 2008; Gitari et al., 2009; Ugurlu, 2004) and reduction of soluble salt content (Brower, 1985) which may have a significant effect on the leaching and mobilization of the FA species (Zevenbergen et al., 1999; Yeheyis et al., 2009). Understanding the changes in the chemical, physical, morphological properties and phase transformation of FA is vital in predicting the environmental impact associated with FA disposal.

This study focuses on the changes in the chemical, physical, morphological properties and mineral phase transformation that occurred during the disposal or storage of the brine impacted coal FA. The design and operation of the ash dump is based on the assumption that presupposed that the dumped FA may act as a sink for the salts which mainly originated from the brines generated during desalination procedures used at the power station. This study aims at understanding the weathering patterns of the disposed FA in the wet ash handling system over time and understanding the environmental impact associated with the FA disposal technique in order to ascertain whether the ash dump could act as a sustainable salt sink.

## 2. Materials and methods

### 2.1. Sampling

The FA samples used in this study were collected from an ash dump at a petrochemical utility station in the Mpumalanga province in SA. The ash dump consisted of 87% FA from the combustion of pulverised coal to produce steam and electric power and 13% fine ash from coal gasification processes. The particle size of the fine ash ranged between  $20 \leq 50 \mu\text{m}$  as given by the scientific officer at the petrochemical utility plant. The samples obtained from the ash dump were wet and required drying and milling hence it was not possible to determine the original particle size due to the disposal method used in the dump. The ash disposed at the dump was pumped as a slurry of 5:1 water/ash ratio using the high saline stream (brine) that was generated from the water treatment processes in the power station. The dump site was created in 1989 and dumping stopped in 2009. The oldest layer at the bottom of the ash dump was 20 years old while the youngest layer at the top of the ash dump was 1 year old. The geophysics electrical resistivity survey profile (Fig. 1) shows the position of the three cores drilled at the FA dump. Core S1 was drilled at 960 m (Lat 26.560411, long 29.119348) while core S2 was drilled at 800 m (Lat 26.559099, long 29.119039). Core S3 was drilled at 600 m (Lat 26.557826, long 29.118943). The positions of cores S1 and S2 were selected based on the moisture content levels, with the latter core showing slightly lower moisture content compared to core S1. The position of core S3 was selected because of the geological fault line visible in the geophysics profile (Fig. 1). A combination of air flush coring and standard percussion drilling was used to drill the cores from the ash dump. During the coring process of core S1, the drilling stopped at 22.5 m due to an unknown obstruction in the dump that prevented the auger from proceeding further. The drilling of cores S2 and S3 stopped at 51 m and 31.5 m respectively. The fresh FA samples used for comparative analysis in this study were collected from the hoppers inside the ash collection system at the coal burning power station of the petrochemical facility.

### 2.2. Experimental procedures

#### 2.2.1. X-ray fluorescence (XRF)

The bulk chemical composition of the fresh FA sample and the drilled cores S1, S2 and S3 were determined using XRF spectrometry. The samples for XRF analysis were taken at 1.5 m depth intervals along the drilled cores. The core ash samples were oven-dried at  $100 \text{ }^{\circ}\text{C}$  for 12 h to remove adsorbed water prior to analysis, and milled to a uniform size grained powder. The powder samples were then mixed with a binder (ratio of 1:9). The powder mixture was then pelletized at a pressure of 15 Kbars. Loss on ignition (LOI) experiment was performed prior to major element analysis and for accuracy of the analytical results. A Phillips PAN-alytical pw1480 X-ray fluorescence spectrometer using a rhodium tube as the X-ray source was used. The

technique reports concentration as % oxides for major elements and ppm for trace elements. Elements reported as % oxides were converted to % elements using element conversion software downloaded from <http://www.marscigrp.org/oxtoel.html>. All the samples were analysed in triplicates.

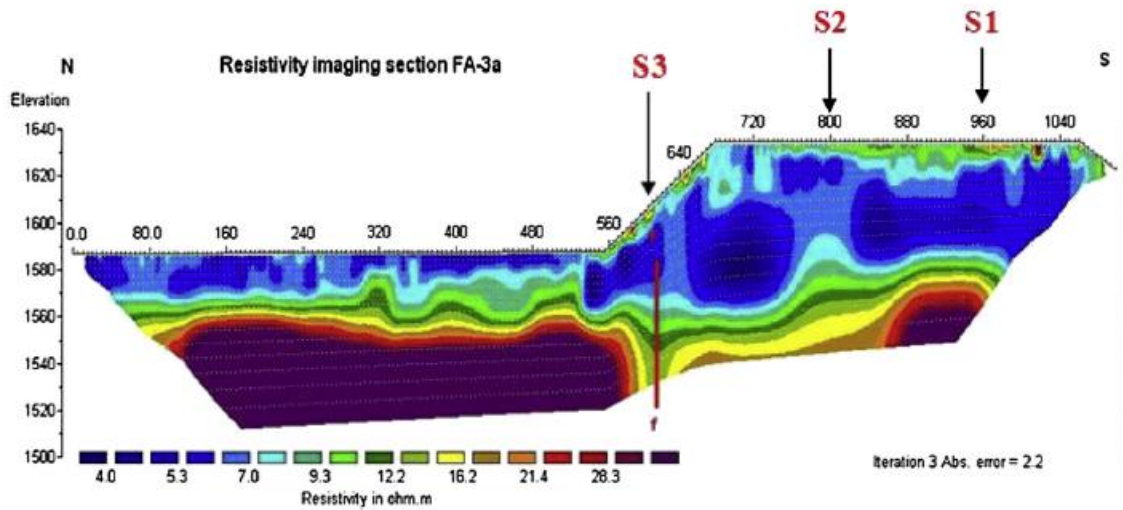


Fig. 1. Resistivity mapping of the wet disposed ash dump showing positions for cores S1, S2 and S3.

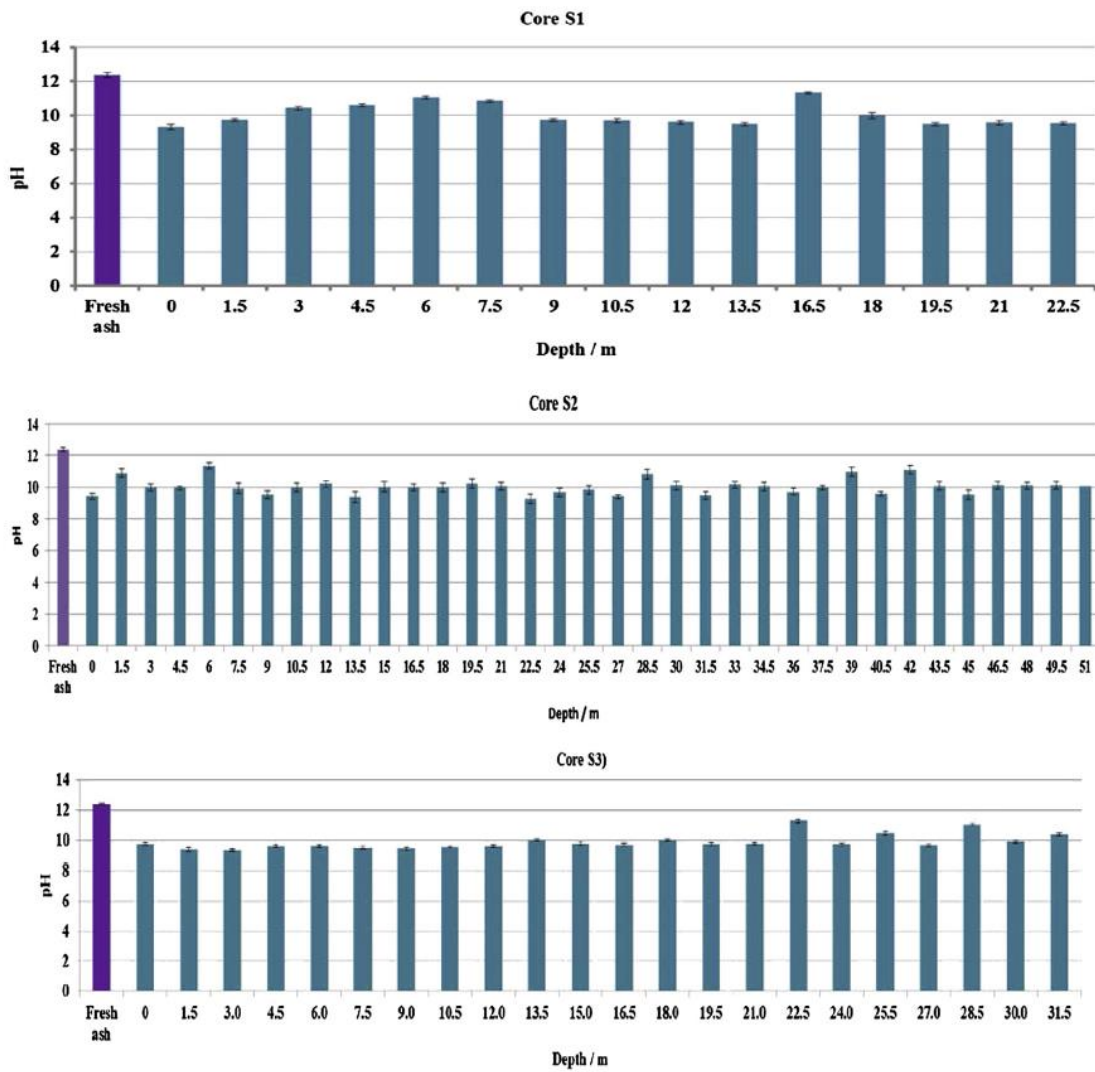


Fig. 2. pH of the fresh FA sample and the samples from weathered drilled cores S1, S2 and S3 [number of determinations for fresh ash, S1, S2 and S3 are 3, 45, 105 and 44 respectively].

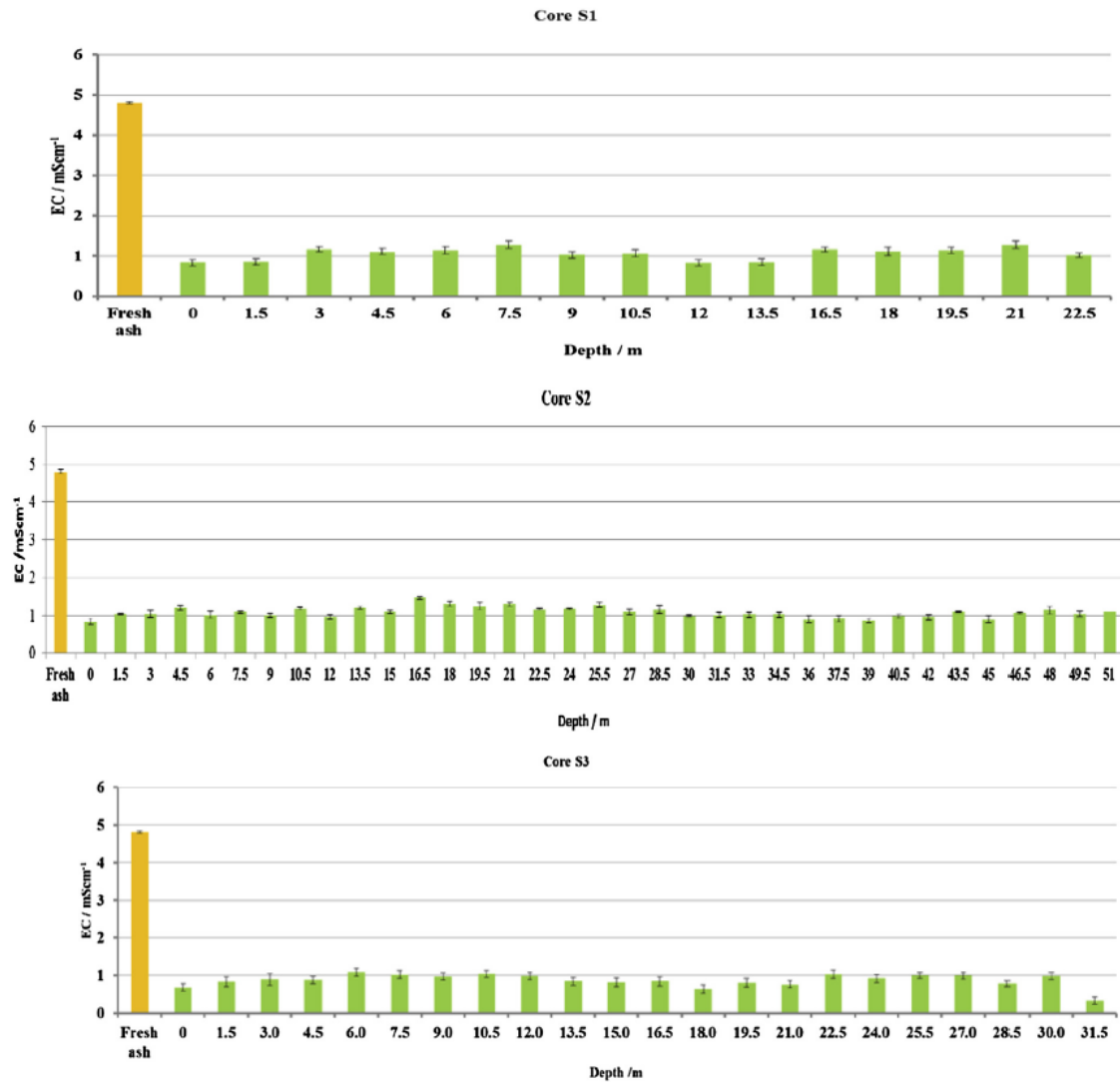


Fig. 3. EC of the fresh FA sample and the samples from weathered drilled cores S1, S2 and S3 [number of determinations for fresh ash, S1, S2 and S3 are 3, 45, 105 and 44 respectively].

### 2.2.2. Pore water analysis

The pH, electrical conductivity (EC) and total dissolved solids (TDS) of the interstitial/pore water was determined using a solid: water ratio of 1:10. 10 g of the fresh FA sample and each of the FA samples extracted from cores S1, S2 and S3 at 1.5 m intervals down the profile of the ash dump were weighed and put in beakers and each suspended in 100 ml of ultra-pure water. The samples were then agitated thoroughly for 30 min and allowed to settle for 15 min. The pH, EC and TDS of the supernatants were recorded at room temperature. A portable, waterproof [Hanna](http://www.hannaist.com) pH meter series HI 991301N was used. The meter reports EC in mS/cm and TDS in ppt (g/L) ([www.hannaist.com](http://www.hannaist.com)).

### 2.2.3. Moisture content determination

The moisture content of the fresh FA sample and the drilled cores S1, S2 and S3 was carried out by drying 5 g of each FA sample in an oven at 105 °C for 24 h.

The samples were then allowed to cool down and weighed again. The percentage moisture content was then calculated from the difference in weight of each sample (Standards Association of Australia, 1977) as shown below:

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

#### **2.2.4. Scanning electron microscopy (SEM)**

The scanning electron microscopy analysis was carried out on the fresh FA sample and the samples from the drilled cores S1, S2 and S3 using a Nova Nano SEM 230 equipped with an Oxford X-max detector. The FA samples were oven-dried at 105 °C for 12 h in preparation for the analysis. The dried samples were speckled on special glue mixed with carbon graphite. Each sample was then mounted into specimen holders and the morphology and texture determined.

#### **2.2.5. X-ray diffraction (XRD)**

The fresh FA sample and the samples taken from the drilled cores S1, S2 and S3 were analysed for consistent mineral phases using XRD. A Philips PANalytical instrument with a pw3830 X-ray generator operated at 40 kV and 25 mA was used. The samples were step-scanned from 5 to 85° 2 theta scale at intervals of 0.02° and counted for 0.5 s per step.



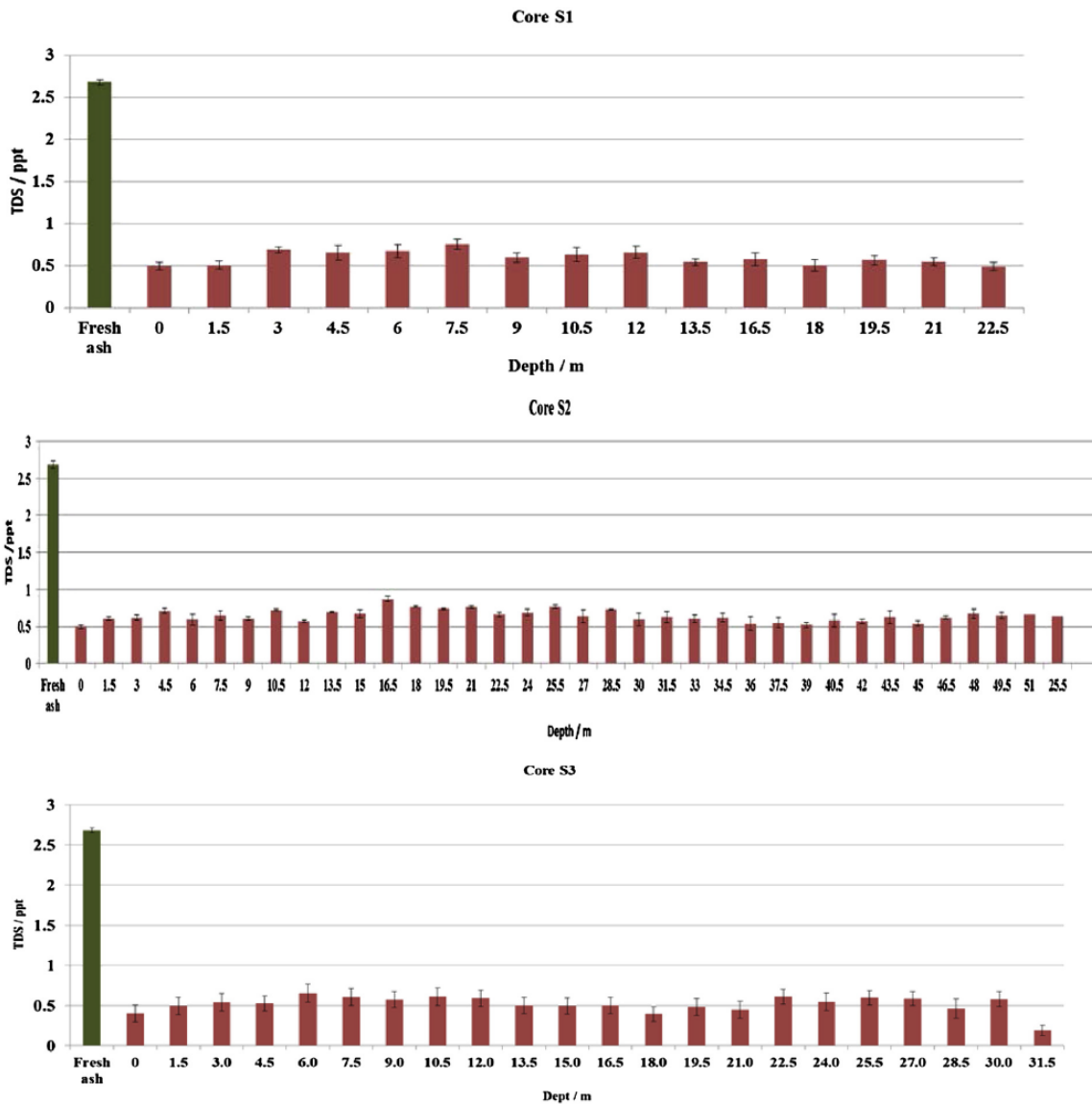


Fig. 4. TDS of the fresh FA sample and the weathered drilled cores S1, S2 and S3 [number of determinations for fresh ash, S1, S2 and S3 are 3, 45, 105 and 44 respectively].

### 3. Results and discussion

#### 3.1. pH

Fig. 2 shows the pH profile of the fresh FA sample and the samples taken from the weathered drilled cores S1, S2 and S3 as a function of depth. The pH analysis (Fig. 2) shows that the fresh FA sample had a pH of 12.38. For the samples taken from drilled core S1, the pH was between 9.33 at the surface and 11.32 at 16.5 m (Fig. 2). The pH for core S2 was between 9.29 at 22.5 m and 11.36 at 6 m while the pH for core S3 was between 9.32 at 3 m and 11.27 at 22.5 m (Fig. 2). The pH values show that the FA samples are alkaline. There is a significant decrease in pH in the drilled cores S1, S2 and S3 compared to the fresh FA. These variations in pH show that the dumped FA is acidifying over time, therefore metal mobility in the ash dump can be expected under these conditions. The acidification of the dumped weathered ash could be attributed

to the chemical interactions of the ash with the co-disposed brine as well as with the atmospheric CO<sub>2</sub> and percolating rain water, leading to the dissolution and consequent reduction of the alkaline materials such as CaO present in the FA (Saikia et al., 2006). Eqs. (1)e(3) illustrate how CaO is lost from the dumped FA through conversion into soluble calcium bicarbonate.

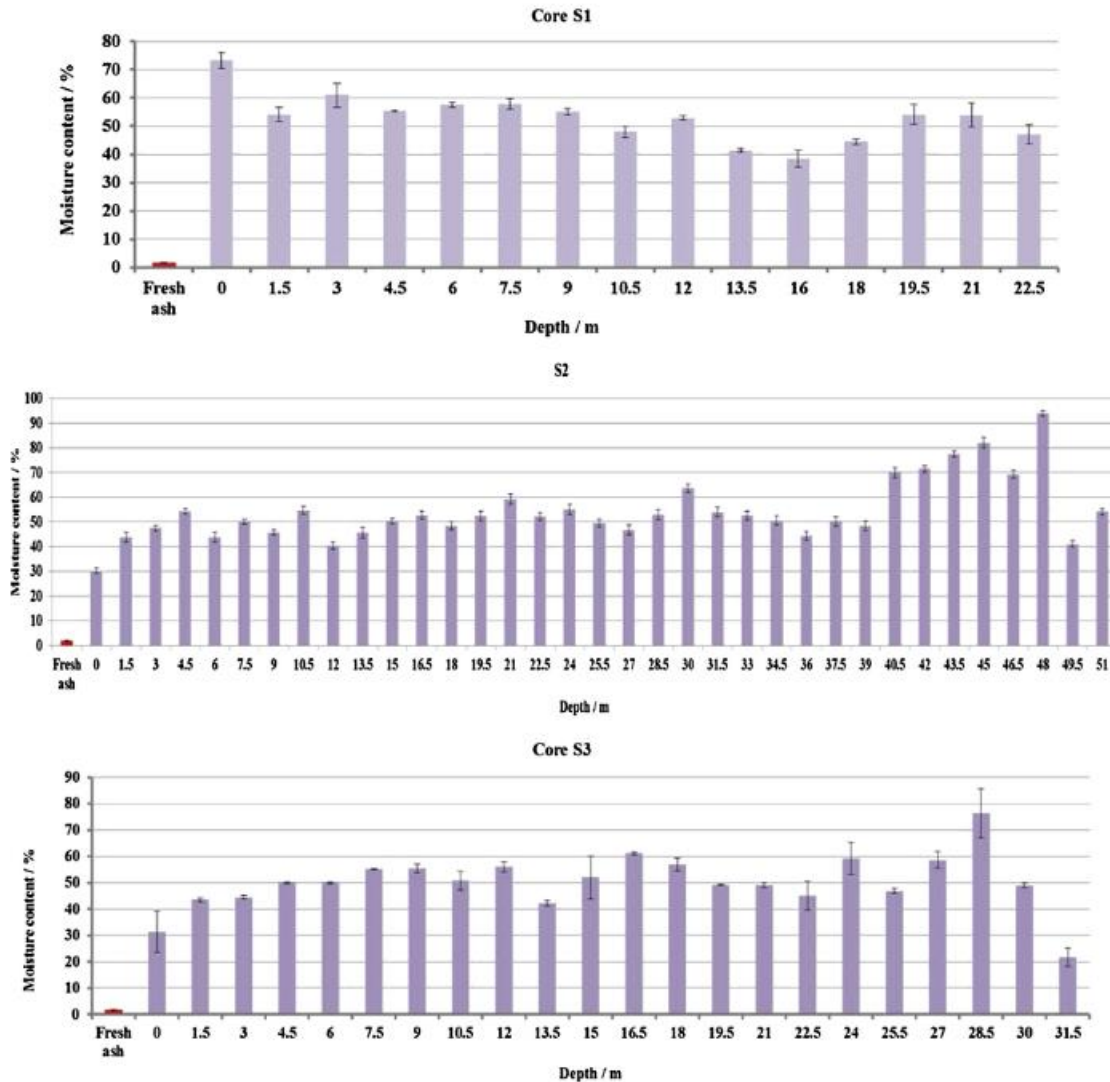
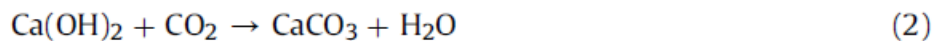
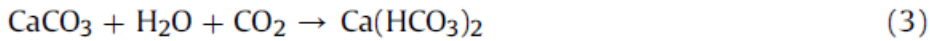


Fig. 5. Moisture content profile of the fresh FA sample and the samples from the weathered drilled cores S1, S2 and S3 [number of determinations for fresh ash, S1, S2 and S3 are 3, 45, 105 and 44 respectively].

hydration of lime in the FA into calcium hydroxide suspension as a result of brine and infiltrating rain water in the ash dam



carbonation of calcium hydroxide, by ingressed carbon dioxide in the ash dam, into calcium carbonate



reaction of calcium carbonate with water and carbon dioxide in the ash dam to form soluble calcium bicarbonate.

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

### 3.2. Electrical conductivity (EC)

Fig. 3 shows the EC profile of the fresh FA sample and the weathered drilled cores S1, S2 and S3 as a function of depth. The EC of the fresh FA sample was observed to be 4.92 mS/cm (Fig. 3). For the drilled core S1, the EC was between 0.83 mS/cm at the surface and 1.28 mS/cm at 7.5 m while the EC for core S2 was between 0.85 mS/cm at the surface and 1.46 mS/cm at 16.5 m. The EC for core S3 was between 0.32 mS/cm at 31.5 m and 1.08 mS/cm at 6 m (Fig. 3). The EC is governed by the amount of ions present in the extracted pore water. Therefore, high EC observed in the fresh FA indicates the release of more ionisable species from the FA into the solution while the lower EC observed in the core samples means lesser amount of ions are present in the aqueous extract. The lower EC observed in the drilled cores S1, S2 and S3 compared to the fresh FA indicates a significant loss of ionic species from the dumped weathered ash. This observation may be as a result of leaching of the ash through infiltrating brine and rainwater, leading to loss of the ionic species from the disposed ash into the ground water (Bhattacharyya et al., 2009; Petrik et al., 2010).

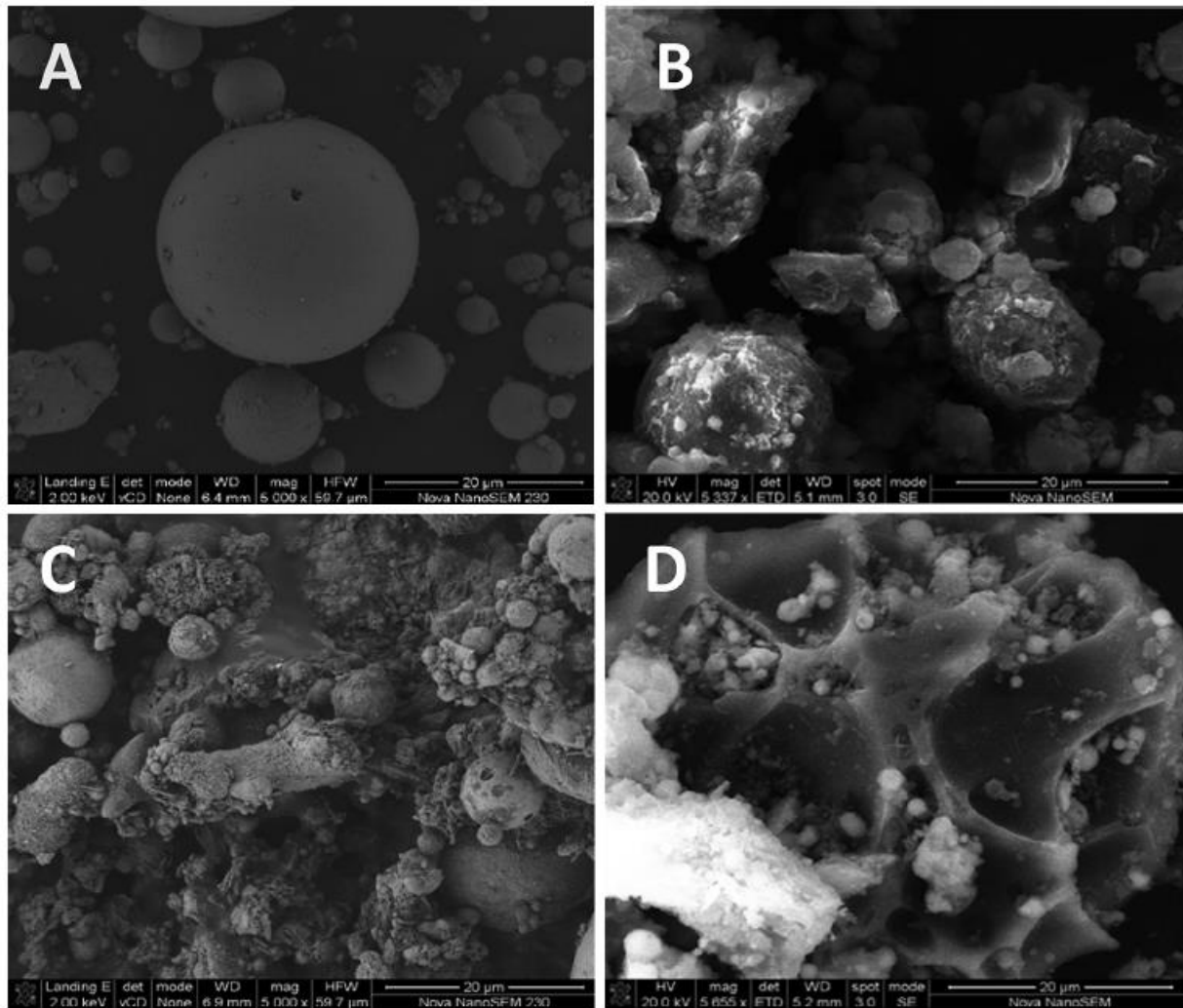


Fig. 6. SEM micrographs of ash samples: A for fresh, B, C, D for cores S1, S2 and S3 respectively.

### 3.3 Total dissolved solids (TDS)

Fig. 4 shows the TDS profile of the fresh FA sample and the weathered drilled cores S1, S2 and S3 as a function of depth. The TDS of the fresh FA sample was 2.68 g/L (Fig. 4). For the drilled core S1, the TDS was between 0.49 g/L at 22.5 m and 0.76 g/L at 7.5 m while the TDS for core S2 was between 0.5 g/L at the surface and 0.87 g/L at 16.5 m. The TDS for core S3 was between 0.19 g/L at 31.5 m and 0.68 g/L at 6 m (Fig. 4). The TDS data were indicative of the relative release and entrapment of various elements during weathering. The TDS essentially followed the same trend as that observed for the EC. The TDS profiles of the drilled cores S1, S2 and S3 show a significant decrease in comparison to the fresh FA (Fig. 4). This decrease indicates the extent of leaching and poor salt sink capacity of the FA dump since the TDS would have been considerably higher in the drilled cores S1, S2 and S3 if the FA dump was holding salts.

### 3.4 Moisture content (MC)

Fig. 5 shows the moisture content of the fresh FA sample and the moisture profile of samples from the weathered drilled cores S1, S2 and S3 as a function of depth. The MC of the fresh FA sample was 1.8% (Fig. 5). For the samples taken from the drilled core S1, the MC ranged between 41.4% and 73.2% while the MC for core S2 ranged between 30.3% and 94% (Fig. 5). The MC for core S3 ranged between 21.7% and 76.2% (Fig. 5). The high MC of the dumped weathered ash (cores S1, S2 and S3) resulted from the wet disposal method used at the petrochemical power utility station which involved mixing the FA with brine and transporting it to the dump in slurry form. This observed high MC could be attributed to seepage of rain water and ash transport water through the dump by natural hydraulic transport. Every time a new layer of ash slurry is placed on top of the dam, more ash transport water must percolate through the dam. The fluctuating trend in the MC in the drilled cores at different depths could be due to different dumping conditions i.e. dumping being done on sunny or rainy days or varying ash layer thickness arising from inconsistent ash placement conditions. The high water content in the ash dam may exacerbate the leaching of soluble species in the FA and increase the risk of the ash dump slumping with time, much like the Kingston fossil plant coal fly ash slurry spill in Tennessee in 2008, due to the high moisture content of the ash layers packed on top of each other during wet dumping.

### 3.5 Morphological analysis

The surface morphologies of the fresh FA sample and the weathered FA samples taken from cores S1, S2 and S3 are shown in the SEM micrographs (Fig. 6). The changes in surface morphology between the fresh FA and the weathered FA are evident from the SEM micrographs. The fresh FA mainly consisted of spherical particles with smooth outer surfaces (Fig. 6A) while the weathered FA from the drilled cores S1, S2 and S3 (Fig. 6BeD respectively) appeared to be encrusted, etched and corroded. Fig. 6D shows a fractured sphere of the weathered FA showing the vesicular interior. The spherical shape of the fresh FA is an indication that the particles were formed under un-crowded free fall conditions and a relatively sudden cooling, which helped to maintain the spherical shape; while the agglomerated nature of some particles is an indication that the particles were produced due to high temperature sintering reactions (Saikia et al., 2006). According to Seames (2003), the smooth outer surfaces of the fresh FA particles are assumed to be mainly aluminosilicate structures. The changes in morphology (encrustations, etchings and corrosion) observed on the surface of the weathered FA samples taken from the drilled cores S1, S2 and S3 is as a result of leaching (Praharaj et al., 2002), or the presence of secondary mineral phases such as calcite formed via carbonation process involving the reaction of carbon dioxide with the alkaline materials present in the FA (Yeheyis et al., 2009).

### 3.6. Bulk chemical analysis

**Table 1** presents the bulk chemical composition based on XRF analysis of the fresh FA sample and the weathered FA samples taken from cores S1, S2 and S3. The composition of the major elements is reported as weight percentage (wt. %) while the trace elements are reported in parts per million (mg/kg). The concentrations of the major and trace elements in the fresh FA sample were compared to the mean concentrations of the major and trace elements in the samples of the weathered ash taken from drilled cores S1, S2 and S3. The fresh FA sample generally contained the same major and trace elements as the samples from the weathered drilled cores S1, S2 and S3 (**Table 1**).

**Table 1**

Chemical composition of the fresh FA sample and the weathered drilled cores S1, S2 and S3 [number of determinations for fresh ash, S1, S2 and S3 are 3, 45, 105 and 44 respectively].

Major elements	Fresh ash (wt %)	S1 (mean) (wt %)	S2 (mean) (wt %)	S3 (mean) (wt %)
SiO <sub>2</sub>	50.86	43.46	46.24	46.61
Al <sub>2</sub> O <sub>3</sub>	25.52	23.05	24.87	22.43
CaO	8.95	8.01	8.51	8.94
Fe <sub>2</sub> O <sub>3</sub>	2.26	3.67	3.39	3.90
Na <sub>2</sub> O	2.20	2.47	2.49	2.76
MgO	1.87	2.44	2.65	2.83
TiO <sub>2</sub>	1.78	1.70	1.75	1.90
K <sub>2</sub> O	0.95	0.97	1.04	1.29
P <sub>2</sub> O <sub>5</sub>	0.71	0.67	0.73	0.77
MnO	0.05	0.07	0.07	0.08
SO <sub>3</sub>	0.03	0.11	0.09	0.09
LOI	4.78	13.45	8.16	8.32
Sum	99.96	100.07	99.98	99.93
SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	1.99	1.89	1.86	2.08
Trace elements	Fresh ash (mg/kg)	S1 (mean) (mg/kg)	S2 (mean) (mg/kg)	S3 (mean) (mg/kg)
Sr	4160	4456	4490	4864
Ba	2749	2682	2804	3014
Th	1922	2075	2096	2283
Zr	664	667	676	720
Ce	177	184	173	202
Y	156	166	164	171
Nb	109	126	123	141
As	61	91	61	89
Co	32	33	33	34
Pb	28	37	37	34
Ni	23	29	29	32
Rb	16	16	21	25
V	15	77	70	71

nd = not detected.

**Table 2**  
Enrichment/depletion of the major and trace elements in core S1 based on XRF analysis.

Majors	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	TiO <sub>2</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	SO <sub>3</sub>	Traces	Sr	Ba	Th	Zr	Ce	Y	Nb	As	Co	Pb	Ni	Rb	V
Fresh ash	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Surface	0.92	0.95	0.69	1.98	1.09	1.41	0.98	0.95	0.76	1.21	1.84	0.81	0.76	0.85	0.77	0.85	0.88	0.97	0.95	1.21	0.82	1.04	1.03	1.93	6.22
1.5 m	0.98	0.99	0.76	1.64	1.05	1.24	0.87	0.79	0.73	0.99	3.24	0.85	0.77	0.85	0.85	0.88	0.89	0.98	0.96	0.80	1.10	1.52	1.18	2.02	6.90
3 m	0.94	1.00	0.86	1.02	1.14	0.25	1.02	1.12	1.15	1.06	4.42	1.14	1.11	1.16	1.16	1.02	0.99	1.11	1.36	1.08	0.98	1.35	1.10	0.29	6.06
4.5 m	0.94	1.00	0.92	1.27	1.15	1.42	1.02	1.01	1.07	1.31	4.43	1.09	1.04	1.10	1.10	1.03	0.89	1.08	1.10	0.98	1.10	1.62	1.22	0.81	5.53
6 m	0.92	0.98	0.96	1.31	1.22	1.54	1.05	1.05	1.09	1.28	4.95	1.10	1.09	1.11	1.09	1.01	1.09	1.11	1.28	1.16	1.18	1.72	1.27	0.32	4.38
7.5 m	0.91	0.97	0.98	1.74	1.16	1.41	0.98	0.99	1.03	1.42	4.85	1.04	0.94	1.04	1.04	1.01	0.83	1.05	0.98	1.06	0.63	1.46	1.27	1.91	4.58
9 m	0.91	0.98	0.96	1.42	1.20	1.41	1.00	1.03	1.04	1.42	4.27	1.07	0.97	1.07	1.01	1.01	0.90	1.06	1.07	1.18	1.23	1.54	1.20	0.96	5.40
10.5 m	0.84	0.88	0.95	1.30	1.12	1.28	0.98	1.02	0.96	1.29	4.41	1.12	1.01	1.13	1.13	1.07	1.12	1.11	1.31	1.50	0.92	1.35	1.22	0.29	4.93
12 m	0.88	0.92	0.97	1.89	1.18	1.42	1.00	1.00	0.97	1.46	4.79	1.07	0.98	1.08	1.08	1.04	1.10	1.08	1.23	1.24	0.88	1.38	1.54	0.53	4.60
13.5 m	0.85	0.89	1.10	2.90	1.14	1.38	0.56	1.04	0.93	1.59	4.65	1.02	0.93	1.02	1.02	0.97	1.01	0.96	0.97	1.23	1.13	1.10	1.43	2.26	2.66
16.5 m	0.86	0.92	1.02	1.89	1.12	1.36	1.00	1.11	1.01	1.43	4.40	1.12	0.99	1.13	1.03	1.03	1.13	1.06	1.04	1.34	0.96	1.18	1.28	1.30	3.59
18 m	0.68	0.74	0.81	1.59	1.06	0.98	0.86	1.01	0.80	1.21	4.42	1.14	0.98	1.16	1.02	1.02	1.37	1.07	1.22	2.60	1.08	1.04	1.35	0.77	4.65
19 m	0.81	0.86	0.84	1.33	1.11	1.22	0.95	1.14	0.97	1.16	3.99	1.17	1.05	1.20	1.03	1.03	1.07	1.11	1.32	1.73	0.82	1.24	1.36	0.81	7.37
21 m	0.73	0.79	0.82	1.49	1.04	1.14	0.86	1.01	0.89	1.14	4.30	1.13	1.02	1.15	1.03	1.03	1.07	1.08	1.26	2.16	1.01	1.23	1.34	0.27	4.99
22.5 m	0.65	0.69	0.77	1.44	0.99	0.95	0.81	0.96	0.77	1.09	4.32	1.19	1.00	1.20	1.00	1.00	1.19	1.08	1.31	3.03	1.56	0.95	1.24	0.77	4.65

The concentrations of Si and Al in the fresh FA were observed to be higher than those of samples taken from the drilled cores S1, S2 and S3 (Table 1). The decrease in the concentration (calculated difference in concentrations of the elements in fresh FA samples and samples from the weathered drilled cores) of SiO<sub>2</sub> (7.45%, 4.62% and 4.30% in core S1, S2 and S3 respectively) and Al<sub>2</sub>O<sub>3</sub> (2.47%, 0.65% and 3.09% in core S1, S2 and S3 respectively) compared to the fresh FA sample could be attributed to the weathering process which may have led to the dissolution of the ash matrix and the release of these major elements from the core samples over time. According to Zevenbergen et al. (1999), the leaching of Si and Al increases with weathering. The case was different for elements such as Mn, Fe, Na, Mg and S where the concentrations of these elements in the core samples were slightly higher than those observed in the fresh FA (Table 1). The slight overall increase in the concentrations of Na (a difference of 0.26% in core S1, 0.29% in core S2 and 0.55% in core S3); Mg (0.37% in core S1, 0.78% in core S2 and 0.96% in core S3) and S (0.08% in core S1, 0.06% in core S2 and 0.06% in core S3) in the drilled core samples compared to the fresh FA could be as a result of co-disposal with brine, while the increase in the concentration of Fe (1.40% in core S1, 1.13% in core S2 and 1.63% in core S3) compared to the fresh FA could be attributed to the disposal of spent Fe-catalysts on the ash dump where the drilled core samples were collected. According to Nyamhingura (2009), brine from Sasol Secunda power station contains elements such as Na, Cl, Ca, K and Mg in high concentrations. Therefore, the slight overall increase in the concentrations of these species in the drilled core samples could be attributed to the FA and brine interaction at the dump. However, considering the high volumes of brine (5 times more than the ash) disposed over 20 years of operation of the ash disposal site one would have expected much higher salt content than what was found, had the dump actually captured the salts.

The loss on ignition (LOI) which is an indication of unburnt carbon or organic content was 4.78% for the fresh FA and 13.45%, 8.16% and 8.32% for the taken from drilled cores S1, S2 and S3 respectively. The LOI of the samples obtained from the three drilled cores S1, S2 and S3 was observed to be enriched in the weathered FA when compared to that of the fresh FA. The higher LOI observed for the drilled cores compared to the fresh FA could indicate high hydrocarbon content in the ash dump because of the co-disposal practice at the power station where hydrocarbon waste is included in the brine stream for disposal on the ash which is the most probable explanation given the water quality. The enrichment in LOI could otherwise be due to changes in burner conditions over time resulting in more or less carbon in the disposed ash, or due to the structural incorporation of H<sub>2</sub>O into secondary mineral phases formed in the disposal of the FA (Yeheyis et al., 2009).



### 3.5.1 Classification of the FA

According to the American Society for Testing and Materials (ASTM C 618-92a), FA can be classified as class F or C based on the sum of the oxides of aluminium, silicon and iron in the FA. Class F FA is characterised by (i) the sum of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ ,  $\text{Fe}_2\text{O}_3 > 70\%$ , (ii)  $\text{SO}_3 < 5\%$ , (iii) moisture content  $< 3\%$ , (iv) loss on ignition (LOI)  $< 6\%$  and (v)  $\text{CaO} < 20\%$ . The fresh FA and the weathered FA obtained from sampling the three drilled cores S1, S2 and S3 was classified as Class F. The sum of the mean concentrations of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{Fe}_2\text{O}_3$  was 78.67%, 70.19%, 74.50% and 72.94% for the fresh FA, core S1, core S2 and core S3 respectively (Table 1). The fresh FA contained 8.95% CaO while the average percentages contained in samples from cores S1, S2 and S3 were 8.01%, 8.51% and 8.95% CaO respectively (Table 1). The CaO concentration for the different FA samples was in the mid-range among Class F FA that usually has low calcium content (Vassilev and Vassileva, 2007). The average concentrations of trace elements such as As, Ce, Co, Cu, Nb, Ni, Pb, Rb, V and Y were observed to be slightly higher in the drilled core samples than in the fresh FA sample (Table 1). This observation could be attributed to the contact of the FA with brine since these trace elements are present in the brine being used for ash transport at the power station as reported by Nyamhingura (2009). XRF technique was used in the analysis of the trace elements instead of ICP-MS technique due to cost constraints.

### 3.5.2 Enrichment and depletion of major and trace elements

The enrichment/depletion factors of major and trace elements in the samples taken from cores S1, S2 and S3 were determined in order to understand the changes in the chemical compositions of the drilled core samples as a function of depth at the dump. To calculate the enrichment/depletion factors, the XRF data of the drilled cores S1, S2 and S3 were normalized with that of the fresh FA, based on a modified formula used by Ogugbuaja and James (1995). The enrichment/depletion factors were calculated as shown in Eq. (4):

The results showing the enrichment/depletion factors of the major and trace elements in the fresh FA and the drilled core S1, S2 and S3 samples are presented in Tables 2e4. The values below 1.0 represent relative depletion in relation to the fresh ash while values above 1.0 represent relative enrichment in relation to the fresh ash. The enrichment/depletion factors showed the mobility patterns of the species as a result of the dissolution of the ash matrix and soluble salts contained in the ash. The concentrations of Si and Al were depleted in the ash samples from the drilled cores S1, S2 and S3 relative to the fresh FA. The enrichment/depletion trends of Si and Al were somewhat similar in the three drilled cores. Si was consistently depleted down the three drilled cores relative to the fresh FA, except for slight accumulation observed at the bottom of core S3. Al was generally depleted down the three

drilled cores relative to the fresh FA, although the concentration of Al remained unchanged at 3 m, 4.5 m in core S1; 1.5 m, 4.5 m, 25.5 m in core S3; 18 m, 21 m, 24 m, 25.5 m, 51 m in core S2, with slight accumulation at 3 m, 36 m, 42 m and 43.5 m in core S2. The depletion of Si and Al indicates that these species were continuously leached from the ash as a result of weathering and it is noteworthy as earlier mentioned that the leaching of Si and Al from FA increases with weathering. Since Si and Al form the major matrix of the ash, the progressive leaching of these major elements will lead to the release of other components locked in the ash matrix and indicates the long term instability of the fly ash matrix.

The concentration of Fe, Mn, Na, K, Mg and S were observed to be somewhat enriched consistently in the drilled cores S1, S2 and S3. The slight enrichment in the concentration of S and Na maybe as a result of the FA interactions with the co-disposed brine that has a substantial concentration of these species (Mooketsi et al., 2007)

$$\text{Enrichment/Depletion} = \frac{\text{wt. \% of element in drilled core samples at specific depth}}{\text{wt \% of the element in fresh fly ash sample}} \quad (4)$$

**Table 3**  
Enrichment/depletion of the major and trace elements in core S2 based on XRF analysis.

Majors	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	TiO <sub>2</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	SO <sub>3</sub>	Traces	Sr	Ba	Th	Zr	Ce	Y	Nb	As	Co	Pb	Ni	Rb	V
Fresh ash	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Surface	0.96	0.96	0.84	1.90	1.04	1.37	0.95	0.79	0.75	1.24	2.28		0.82	0.70	0.81	0.91	0.61	0.90	0.96	0.78	1.05	1.48	1.05	2.15	5.73
1.5 m	0.92	0.92	1.06	2.71	1.11	1.27	0.98	0.81	0.80	1.40	3.33		0.85	0.71	0.84	0.97	0.99	0.95	0.90	1.17	1.19	1.20	1.62	2.01	5.48
3 m	0.96	1.01	0.89	1.22	1.10	1.37	1.00	0.92	0.96	1.09	2.87		0.97	0.88	0.97	0.94	0.92	1.02	1.14	0.86	0.76	1.41	1.18	nd	6.04
4.5 m	0.86	0.91	1.11	1.78	1.17	1.35	1.02	1.05	0.96	1.40	4.09		1.06	1.00	1.07	1.00	0.98	1.01	1.04	1.31	0.58	1.39	1.33	1.70	1.91
6 m	0.90	0.94	1.09	1.99	1.12	1.49	0.97	0.99	0.95	1.59	2.94		1.05	0.95	1.06	1.03	1.10	1.03	1.02	0.84	1.44	1.02	1.21	1.75	4.14
7.5 m	0.91	0.99	0.99	1.27	1.24	1.59	0.99	0.98	1.02	1.52	2.96		1.07	0.92	1.08	1.04	1.03	1.11	1.15	1.07	1.08	1.96	1.34	0.93	7.44
9 m	0.88	0.94	1.03	1.64	1.14	1.52	0.96	0.96	0.98	1.46	3.40		1.04	0.96	1.05	1.04	0.92	1.07	1.00	1.05	1.29	1.42	1.39	1.08	3.83
10.5 m	0.85	0.91	1.01	1.84	1.19	1.46	0.96	1.04	0.96	1.59	3.55		1.03	0.88	1.04	1.00	1.01	1.04	0.95	1.33	0.95	1.71	1.31	2.56	4.46
12 m	0.90	0.97	0.97	2.09	1.15	1.49	0.98	1.16	1.02	1.50	2.67		1.08	0.98	1.10	1.01	0.98	0.95	1.04	0.95	0.76	1.42	1.26	2.44	3.63
13.5 m	0.92	0.97	0.96	1.42	1.16	1.45	1.03	1.19	1.07	1.29	3.52		1.08	0.98	1.09	1.00	0.99	1.08	1.18	1.10	0.87	1.55	1.21	0.93	5.08
15 m	0.92	0.99	0.93	1.39	1.15	1.43	0.99	1.18	1.02	1.26	3.21		1.08	1.00	1.09	1.02	0.92	1.07	1.20	0.98	0.79	1.44	1.26	0.57	4.88
16.5 m	0.90	0.98	1.05	1.52	1.19	1.41	1.04	1.18	1.11	1.38	4.25		1.13	1.02	1.15	1.03	0.96	1.06	1.12	1.02	1.19	1.52	1.25	2.11	5.47
18 m	0.92	1.00	0.90	1.41	1.13	1.41	1.01	1.14	1.06	1.32	3.48		1.10	1.05	1.12	1.01	1.01	1.08	1.10	0.99	1.14	1.51	1.19	1.03	3.49
19.5 m	0.89	0.99	0.91	1.70	1.14	1.40	0.99	1.16	1.11	1.35	3.35		1.14	1.06	1.15	1.01	1.22	1.10	1.12	1.17	0.91	1.15	1.23	0.44	4.20
21 m	0.90	1.00	0.91	1.45	1.16	1.38	0.99	1.20	1.08	1.22	3.33		1.09	1.06	1.11	1.00	0.93	1.07	1.10	0.99	0.62	1.33	1.35	1.01	5.74
22.5 m	0.90	0.98	0.93	1.49	1.14	1.39	1.02	1.11	1.06	1.28	3.47		1.11	1.02	1.13	1.04	1.09	1.09	1.23	1.16	1.08	1.32	1.30	0.73	5.15
24 m	0.90	1.00	0.90	1.45	1.14	1.34	1.00	1.19	1.13	1.26	3.09		1.16	1.21	1.18	1.03	0.90	1.11	1.32	1.13	1.32	1.30	1.37	0.65	2.88
25.5 m	0.93	1.00	0.86	1.26	1.13	1.33	0.99	1.23	1.03	1.18	3.28		1.13	1.02	1.15	0.98	0.84	1.07	1.30	0.88	0.70	1.16	1.21	0.43	4.38
27 m	0.93	0.97	0.90	1.50	1.11	1.40	0.97	1.24	1.02	1.23	3.12		1.04	1.02	1.05	0.98	0.92	1.01	1.12	0.92	1.02	1.44	1.24	1.43	5.52
28.5 m	0.90	0.96	0.93	2.09	1.12	1.37	0.96	1.18	1.05	1.39	3.10		1.04	1.06	1.05	0.98	0.81	0.97	1.01	1.01	1.12	1.31	1.43	2.34	4.87
30 m	0.92	0.98	0.88	1.35	1.10	1.37	0.98	1.21	1.10	1.24	2.92		1.07	1.10	1.08	1.01	1.13	1.05	1.29	1.01	1.23	1.28	1.34	0.05	4.77
31.5 m	0.91	0.97	0.92	1.63	1.14	1.37	0.98	1.20	0.99	1.31	3.08		1.08	1.04	1.09	1.01	0.87	1.04	1.02	1.10	1.38	1.53	1.40	2.21	3.78
33 m	0.90	0.97	0.95	1.62	1.13	1.37	1.00	1.16	1.04	1.37	2.98		1.06	1.03	1.06	1.04	0.97	1.04	1.05	1.11	1.18	1.49	1.54	1.16	5.26
34.5 m	0.92	0.96	0.91	1.63	1.10	1.43	0.99	1.23	0.99	1.27	2.92		1.12	1.01	1.14	1.04	1.04	1.04	1.18	1.01	1.08	1.16	1.34	1.51	2.18
36 m	0.94	1.01	0.88	1.32	1.06	1.35	1.01	1.17	1.09	1.29	2.70		1.09	1.04	1.10	1.06	0.96	1.07	1.25	1.03	1.35	1.38	1.24	nd	4.06
37.5 m	0.90	0.95	0.90	1.23	1.05	1.37	0.96	1.24	1.01	1.20	2.67		1.13	1.04	1.14	1.05	1.06	1.08	1.14	1.11	0.79	1.44	1.24	0.67	5.45
39 m	0.90	0.95	1.04	1.44	1.09	1.42	0.96	1.18	1.04	1.46	2.67		1.06	1.03	1.07	1.05	1.07	1.03	0.96	1.09	0.85	1.07	1.23	2.00	2.42
40.5 m	0.93	0.98	0.92	1.17	1.11	1.46	0.98	1.21	1.04	1.25	2.76		1.07	1.02	1.08	1.02	0.97	1.07	1.19	0.70	0.79	0.88	1.28	0.67	6.51
42 m	0.96	1.01	0.82	1.09	1.08	1.49	0.90	1.13	0.96	1.25	2.24		1.04	1.04	1.04	1.01	1.02	1.03	1.20	0.66	1.28	1.04	1.21	0.51	3.91
43.5 m	0.93	1.01	0.95	0.95	1.15	1.46	1.01	1.10	1.10	1.25	2.76		1.23	1.16	1.26	1.04	0.91	1.12	1.19	0.79	0.60	1.07	1.30	1.09	4.14
45 m	0.92	0.99	0.98	1.12	1.16	1.40	1.02	1.08	1.08	1.34	2.64		1.13	1.10	1.15	1.05	0.92	1.04	1.18	0.97	0.78	1.37	1.35	2.77	5.52
46.5 m	0.90	0.98	0.91	1.22	1.14	1.49	0.97	1.03	1.07	1.27	2.83		1.11	1.11	1.12	1.05	1.06	1.06	1.11	0.84	0.75	1.17	1.33	1.22	4.02
48 m	0.84	0.97	1.02	1.28	1.16	1.52	0.88	0.89	1.09	1.26	2.77		1.24	1.19	1.26	1.03	1.01	1.15	1.18	0.90	1.13	1.24	1.42	0.49	3.93
49.5 m	0.90	0.99	0.97	1.15	1.13	1.48	1.00	0.84	1.15	1.37	3.02		1.13	1.14	1.14	1.11	0.92	1.13	1.06	0.91	1.46	1.18	1.31	0.48	5.16
51 m	0.87	1.00	1.03	1.15	1.15	1.46	0.99	0.85	1.32	1.27	2.87		1.12	1.17	1.14	1.05	1.16	1.10	1.37	1.04	1.12	1.60	1.45	0.42	3.89

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**Table 4**  
Enrichment/depletion of the major and trace elements in core S3 based on XRF analysis.

Majors	SiO <sub>2</sub>	Al <sub>2</sub> O <sub>3</sub>	CaO	Fe <sub>2</sub> O <sub>3</sub>	Na <sub>2</sub> O	MgO	TiO <sub>2</sub>	K <sub>2</sub> O	P <sub>2</sub> O <sub>5</sub>	MnO	SO <sub>3</sub>	Traces	Sr	Ba	Th	Zr	Ce	Y	Nb	As	Co	Pb	Ni	Rb	V
Fresh ash	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00		1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
0 m	0.91	0.92	0.94	1.40	1.07	1.77	1.07	1.20	1.17	1.36	1.67		1.15	1.14	1.16	1.09	1.07	1.11	1.34	1.56	1.15	1.17	1.21	0.73	3.18
1.5 m	0.93	1.01	0.90	1.20	1.11	1.48	1.03	1.15	1.06	1.16	4.00		1.15	1.13	1.17	1.07	0.90	1.11	1.32	0.74	0.85	1.06	nd	4.79	
3 m	0.93	0.97	0.91	1.37	1.16	1.36	1.07	1.28	1.00	1.36	3.00		1.10	1.02	1.11	1.06	1.06	1.05	1.29	1.25	1.01	1.21	1.26	1.43	7.49
4.5 m	0.93	1.00	0.83	1.26	1.16	1.39	0.98	1.31	1.04	1.16	3.00		1.08	1.12	1.09	0.97	0.92	1.01	1.27	0.99	1.16	1.49	1.30	1.48	4.92
6 m	0.89	0.96	0.99	1.54	1.26	1.38	1.07	1.30	1.10	1.16	3.33		1.21	1.15	1.23	1.06	0.99	1.10	1.32	1.51	1.02	1.49	1.24	0.83	7.73
7.5 m	0.89	0.93	0.96	2.19	1.18	1.37	0.98	1.21	1.01	1.16	4.00		1.05	1.02	1.06	1.04	0.95	1.04	1.03	1.18	0.73	1.22	1.29	1.13	3.82
9 m	0.90	0.81	1.11	1.89	1.36	1.48	1.18	1.36	1.14	1.55	3.67		1.31	1.16	1.35	1.17	1.40	1.19	1.45	1.70	1.19	1.60	1.33	1.07	5.98
10.5 m	0.94	0.87	1.00	1.39	1.29	1.56	1.15	1.41	1.15	1.16	3.33		1.26	1.17	1.29	1.12	1.19	1.17	1.47	1.50	0.85	1.21	1.40	1.18	4.63
12 m	0.98	0.83	0.95	1.49	1.31	1.60	1.17	1.46	1.17	1.16	3.33		1.15	1.13	1.17	1.10	1.28	1.12	1.35	1.30	1.27	1.23	1.47	1.85	5.39
13.5 m	0.81	0.84	1.03	4.58	1.14	1.37	0.95	1.03	0.94	1.94	3.00		1.17	0.97	1.17	1.08	1.40	0.96	1.04	1.82	0.82	0.86	1.33	2.06	3.56
15 m	0.90	0.93	0.87	2.24	1.08	1.30	0.98	1.21	1.00	1.16	2.67		1.13	0.98	1.13	1.04	1.23	1.08	1.20	1.31	1.60	1.29	1.01	0.58	4.07
16.5 m	0.90	0.84	0.98	1.85	1.20	1.47	1.06	1.30	1.06	1.55	3.00		1.21	1.09	1.22	1.13	1.13	1.13	1.23	1.29	1.18	1.32	1.26	1.59	3.98
18 m	0.94	0.88	0.97	1.46	1.30	1.55	1.11	1.33	1.18	1.16	3.00		1.25	1.18	1.28	1.14	1.15	1.18	1.44	1.37	1.07	1.23	1.37	1.36	8.10
19.5 m	0.94	0.90	1.04	1.40	1.23	1.50	1.11	1.32	1.07	1.55	3.00		1.17	1.06	1.19	1.13	1.12	1.13	1.21	1.28	0.99	0.90	1.27	1.84	4.20
21 m	0.95	0.88	1.07	1.29	1.27	1.55	1.17	1.27	1.14	1.55	3.00		1.16	1.13	1.18	1.16	1.26	1.14	1.36	1.34	0.82	1.26	1.32	0.70	2.75
22.5 m	0.80	0.91	1.16	2.42	1.27	1.46	1.01	0.95	1.13	1.74	3.33		1.20	1.11	1.23	1.11	0.94	1.12	1.44	1.26	0.57	1.17	1.33	0.14	5.67
24 m	0.92	0.83	1.11	1.09	1.37	1.66	1.19	1.16	1.18	1.55	3.33		1.38	1.13	1.41	1.12	1.27	1.21	1.46	1.77	0.97	1.15	1.71	nd	3.90
25.5 m	0.92	1.00	0.96	0.96	1.16	1.46	1.04	1.03	1.13	1.16	2.67		1.34	1.21	1.38	1.21	1.21	1.24	1.55	1.41	1.08	1.10	1.44	0.11	6.75
27 m	0.88	0.84	1.10	1.28	1.41	1.70	1.15	1.05	1.25	1.55	3.67		1.35	1.21	1.39	1.23	1.31	1.31	1.51	1.41	1.32	1.48	1.57	nd	4.64
28.5 m	0.88	0.79	1.26	1.28	1.43	1.77	1.19	0.92	1.34	1.74	3.00		1.34	1.26	1.38	1.25	1.23	1.30	1.49	1.50	1.13	1.09	1.59	nd	3.58
30 m	0.86	0.96	1.09	1.16	1.24	1.51	1.04	1.00	1.20	1.55	3.33		1.31	1.14	1.35	1.16	1.28	1.19	1.40	1.27	0.87	1.14	1.40	nd	3.20
31.5 m	1.16	0.47	0.75	3.00	1.44	1.55	0.85	4.63	0.51	2.32	1.33		0.22	0.61	0.18	0.40	0.80	0.25	0.25	2.49	1.53	1.68	2.63	8.41	1.97

Though high enrichment of Na in the drilled cores would have been expected due to the large amount of salt laden brine disposed on the dump over 20 years, it is noteworthy that Na<sub>2</sub>O levels remained below 2 weight % in all samples showing that the dump is not holding or encapsulating Na to any significant extent. This shows that the salt holding capacity of the ash dump is very low which has a major implication for using it as a salt sink.

According to Lee and Spears (1997), the interaction of dumped FA with infiltrating pore water leads to the depletion of CaO as a result of leaching and weathering. This explains why Ca was depleted at most of the depths along the drilled cores S1, S2 and S3 compared to the fresh FA. The geophysics electrical resistivity survey profile (Fig. 1) indicated a fault line (crack) in the dump at the position of core S3 which reported the enrichment of Ca. This observed enrichment may have resulted due to the accumulation of brine components in preferential leaching pathways or the formation of some secondary mineral phases in the fault. This observation highlights the inhomogeneity of the ash dump.

The concentrations of trace elements in the samples obtained from the drilled cores S1, S2 and S3 were observed to have similar trends. In all the three cores, the concentrations of Pb, V, Zn, Cr, Ni and Co were observed to be somewhat enriched along the entire cores. Previous studies have reported the presence of the trace elements in the petrochemical power utility's brine (Mooketsi et al., 2007; Nyamhingura, 2009). Therefore, the slight enrichment of these trace elements in the drilled core samples could be due to the contact of the dumped FA with the co-disposed brine.

The inhomogeneous enrichment and depletion of elements observed along the entire length of the three drilled cores could be explained by the processes occurring in the dam involving the precipitation, dissolution versus flushing of the soluble salts bearing various elements as a result of rain water infiltration and the percolation of brine co-disposed with the FA. From the enrichment and depletion data (Tables 2e4), no significant enrichment or accumulation of any particular element was observed in samples taken from the three drilled cores S1, S2 and S3 compared to the fresh FA.

### 3.7. Mineralogical analysis

Fig. 7 shows the XRD patterns of the fresh FA and the drilled cores S1, S2 and S3. XRD was applied in order to identify the mineralogical phases present in the fresh FA and any changes taking place over time in the drilled cores at different depths. The XRD results revealed that the major crystalline mineral phases for the fresh FA samples were quartz (SiO<sub>2</sub>) and mullite (Al<sub>6</sub>Si<sub>2</sub>O<sub>13</sub>). Lime (CaO) was also identified in the fresh FA but was present in low amounts as can be seen from the relatively minor peaks when compared to those of

quartz and mullite. According to [Singh and Kolay \(2002\)](#), quartz and mullite are the major crystalline constituents of coal FA. Quartz is a hard mineral commonly found as cell and pore infillings in the organic matter of coal and is regarded as a primary mineral. It is basically considered as non-reactive in combustion processes due to its high fusion temperature ([Ward, 2002](#)). Mullite is a secondary mineral that is assumed to be formed during the thermal decomposition of kaolinite, an aluminosilicate mineral in the coal ([Koukouzas et al., 2009](#), [White and Case, 1990](#)). Lime, which is also a secondary mineral may have resulted from the decomposition of calcite or dolomite, which are the most important and common calcium-bearing minerals in coal.

Core S1 showed quartz and mullite as the major crystalline mineral phases from the surface down to the depth of 16.5 m ([Fig. 7](#)). Lime and calcite ( $\text{CaCO}_3$ ) were also identified in core S1 but as minor peaks ([Fig. 7](#)). Calcite is a secondary mineral formed by contact of lime ( $\text{CaO}$ ) contained in the FA with ingressed  $\text{CO}_2$  ([Vassilev and Vassileva, 1996](#)). At 22.5 m, apart from quartz and mullite, minor phases of kaolinite ( $\text{Al}_2(\text{Si}_2\text{O}_5)(\text{OH})_4$ ) and nitratine ( $\text{NaNO}_3$ ) were also identified in core S1. Nitratine is a tertiary mineral that may have resulted from the interaction of brine with the FA or may be due to the drying process in the sample preparation prior to analysis. The kaolinite identified at 22.5 m (bottom of core S1) may have been derived from the erosion of the rock and soil surrounding the ash dump. It could also have resulted from the alteration of the glass phase or weathering of the ash in the dump ([Ward et al., 2009](#)).

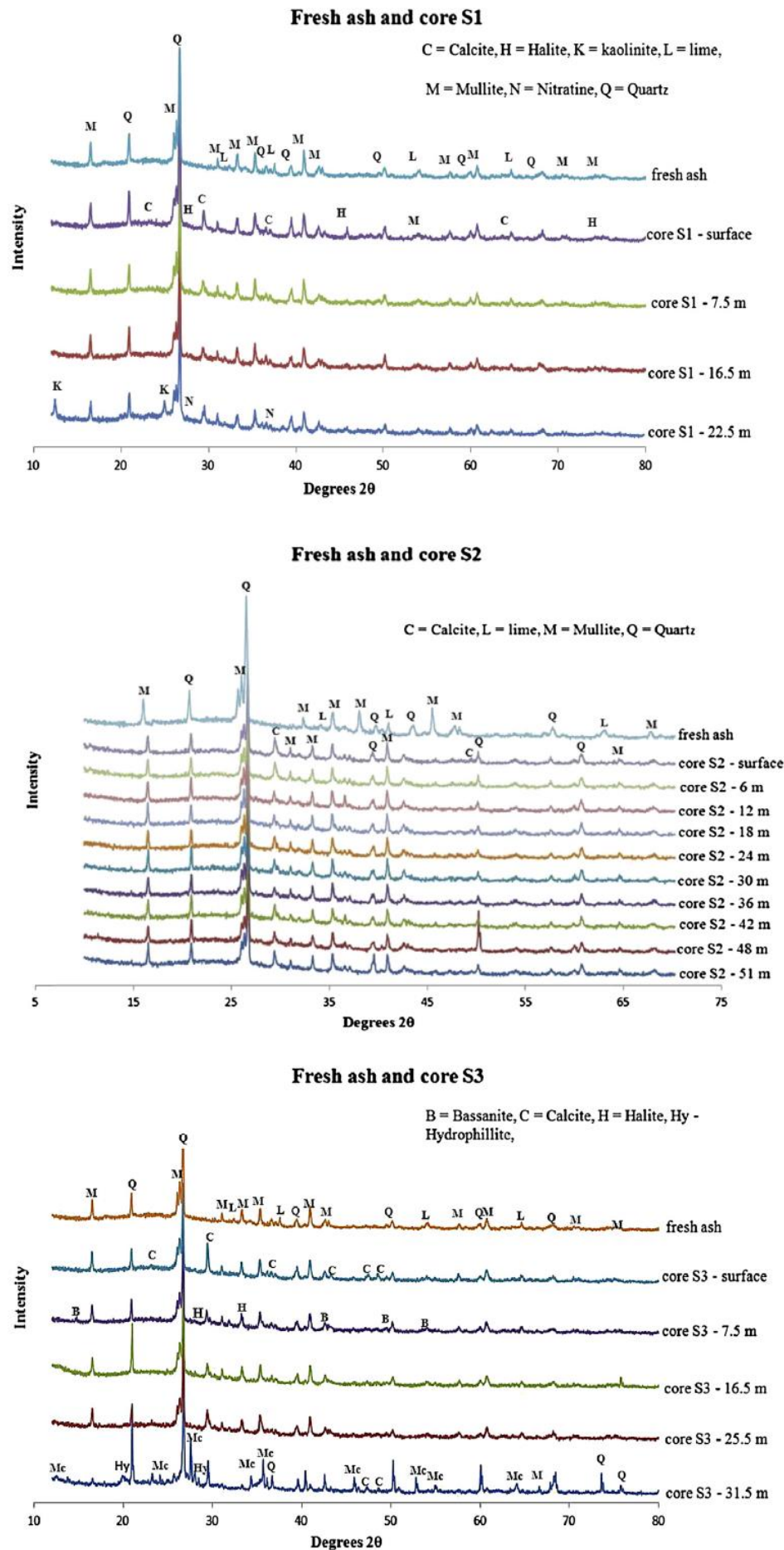


Fig. 7. XRD patterns for the fresh FA sample and the weathered drilled cores S1, S2 and S3 sampled at different depths.

Core S2 showed three crystalline mineral phases namely quartz, mullite and calcite (Fig. 7) which are common mineral phases found in weathered coal FA (Rao and Gluskoter, 1973). The XRD patterns showed a similar trend for core S2 from the surface sample, along the core down to the bottom of the ash dam. The three crystalline mineral phases identified in core S2 remained consistent at every sampling depth (Fig. 7). All the mineral phases detected by XRD in core S2 corresponded to the significant levels of Si, Al and Ca contained in the fresh FA and the weathered FA as reported by XRF analysis (Table 1). The lower levels of elements like Fe and Mg, for example, may have made it difficult to detect any mineral phases associated with them such as hematite ( $\text{Fe}_2\text{O}_3$ ) and enstatite ( $\text{Mg}_2\text{Si}_2\text{O}_6$ ) by the XRD. However, other mineral phases present in core S2 were not detected by XRD probably because they were in a transition/amorphous state, or present in very low thus undetectable levels. Core S2 did not show mineralogical inhomogeneity but rather gave a consistent trend from the top to the bottom of the core.

Core S3 showed quartz and mullite as the major crystalline mineral phases and calcite as the minor phase at the surface of the ash dump (Fig. 7). Core S3 presented a unique transformation in mineralogy down the depth of the ash dump. At 7.5 m, 16.5 m and 25.5 m, the major crystalline mineral phases were quartz and mullite with calcite, halite ( $\text{NaCl}$ ) and bassanite ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) showing up as minor phases (Fig. 7). At 31.5 m in core S3, quartz was the major phase. Other minerals also tentatively identified at this depth in minor quantities were calcite, microcline ( $\text{KAlSi}_3\text{O}_8$ ) and hydrophitte ( $\text{CaCl}_2$ ) (Fig. 7). Halite, bassanite, nitratine, hydrophitte, microcline and albite low are considered as transient minerals that may have formed from the interaction of brine with the FA. According to Alai et al. (2005), halite, bassanite and nitratine may form during brine evolution in complex aqueous systems at elevated temperatures.

The XRD spectra of the FA samples extracted at different depths of cores S1 and S3 were inconsistent in terms of secondary mineral phases although the major mineral components in all cases were quartz, calcite and mullite regardless of the sampling depth. The quartz peaks of the drilled core samples are quite prominent and have a tendency to obscure other less abundant or less crystalline mineral phases. This as well as the fact that samples cannot be analysed in situ without drying is one of the major limitations of XRD analysis. The geophysics electrical resistivity survey profile of the ash dump (Fig. 1) similarly provides clues to explaining the observed mineralogy in cores S1 and S3. Contact with rocks prevented coring to deeper depths in cores S1 and S3. Furthermore, the geophysics of core S3 also showed indication of a fault (crack) at a depth of 16.5 m which coincided with the point

where the new mineral phases were found. This may indicate a preferred flow pathway for the brine, resulting in a region with saturated conditions promoting the precipitation of various salts in a localized region of the dump.

#### **4. Conclusion**

The high volumes of brine that pass through the ash dump in the wet ash handling system present a great environmental concern, considering the fact that brine introduces salts and some toxic elements into the FA during co-disposal of the two wastes. The high moisture content associated with the wet ash handling system creates an environment that is more conducive to the release of species from the disposed ash. Leaching and weathering process led to the morphological changes observed on the surface of the weathered FA samples. The major mineral phases that were identified in the weathered ash were quartz, mullite and calcite. The transient minerals that were identified in the weathered ash may have been formed from the interaction of brine with the FA, or during sample preparation prior to XRD analysis. The decrease in pH in the ash dump led to the progressive weathering dissolution of the major aluminosilicate ash matrix which consequently influenced the release of other elements previously locked in the ash matrix. This establishes the role that pH plays in the mobility patterns of various species in the ash dump. Lower EC observed in the weathered ash compared to the fresh FA indicated a significant loss of ionic species from the dumped weathered ash. TDS followed the same trend as that observed for the EC. Low TDS observed in the weathered ash compared to the fresh FA suggested poor salt sink capacity of the FA dump since the TDS would have been considerably higher in the weathered ash if the FA dump was holding salts.

The slight enrichment of some species e.g. Mg, K, SO<sub>4</sub> and Na that was observed in the disposed weathered FA was attributed to the interaction of the fly ash with brine. However, there was no significant accumulation of the various species in the disposed FA despite continuous addition of large volumes of salt laden brine over the 20 year period that the dam existed, which meant that the ash dump did not sustainably accumulate salts but released these elements to the environment.

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