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Chemical Weathering in a Hypersaline Effluent Irrigated Dry Ash Dump: An Insight from Physicochemical and Mineralogical Analysis of Drilled Cores

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Abstracts

Accumulation of high ionic strength effluents (brines) that require disposal in inland industries where water recycling is necessary due to scarcity is a major challenge. A coal combustion power utility in South Africa utilizing a dry ash disposal system produces 1.765 Mt of fly ash per annum and also employs the zero liquid effluent discharge policy (ZLED) to manage its liquid effluents. Fly ash is conditioned for dust suppression before being conveyed to the ash dumps with the high saline effluent. The saline effluents results from various processes employed for maximum utilization, upgrading and re-use of various mine water and industrial effluents such as RO, EDR, softening and ion exchange in an effort to adhere to ZLED policy. In the ash dumps it is further conditioned by irrigation with the high saline effluents, therefore the ash acts as a repository for the salts. This study is an attempt to understand the chemical weathering of the effluent conditioned fly ash and species mobility in a dry disposal scenario. A combination of leaching tests was performed for fresh ash and drilled cores to estimate the highly leachable species. Results from DIN-S4 tests of the fresh and weathered ash reveal that Ca, K, Na, Mg, Ba, SO₄²⁻, Se, Mo and Cr are highly leached. Leaching tests also revealed that major soluble components in the solution at equilibrium are Ca, Na, SO₄²⁻ and K. Weathering profiles of the ash dump cores were observed to follow a similar

trend. The greatest weathering was observed to take place at the top layer (0.55-3 m depth) in the weathered ash cores (15 years and older), showing that infiltration of rain water over time has a profound effect on the decrease of the pore water pH. Analysis of the extracted pore water in each of the different weathered ash cores by depth indicated the mobility of several elements through the ash. Increased cation exchange capacity at 4-5 m depth suggests a transient mineralization zone.

Key words: Weathered fly ash; Pore water; Ash dumps; Hypersaline effluents; X-ray diffraction analysis; DIN-S4 test; Cation exchange capacity

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INTRODUCTION

As the world population increases, demand for energy supply increases proportionally. Many countries depend on their vast coal deposits for cheap generation of electricity (He and Qin, 2006; Klass, 2003) Combustion of coal for energy generation leads to generation of large volumes of waste products such as coal combustion residues (coal fly ash) and brines (high ionic strength salts effluents). South Africa is largely dependent on the combustion of coal for power generation and uses more than 100 Mt of coal per annum (Willis, 2003). This in turn leads to the generation of approximately 27 Mt of fly ash annually out of which

only 5% is currently utilized, the rest being disposed of in ash dams, landfills or ponds (Petrik *et al.*, 2005) Due to the large quantity of ash generated and the need for its disposal due to environmental impacts, many countries have devised different methods of ash disposal. South Africa employs two different methods of disposing fly ash; dry and wet disposal.

Coal fly ash consists mainly of three main constituents, crystalline minerals (quartz, mullite, spinels), unburnt carbon matter and non-crystalline aluminosilicate glass. According to the American Society for Testing and Materials (ASTM), South Africa coal fly ash is classified as class F, i.e, the sum of $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 > 70\%$ (ASTM, 1993). Fly ash disposal on land presents an environmental problem due to the concentration of trace elements and increased mobility of these elements in weathering environments (Adriano *et al.*, 1980; Early *et al.*, 1980; Mattigod *et al.*, 1990). There is thus a potential of groundwater contamination by downward percolation of ash pore water especially if the underlying soil is permeable. Long storage of ash in ponds under wet conditions can cause leaching of toxic metals from ash that contaminates the underlying soil and ultimately the groundwater systems (Gitari *et al.*, 2006) Our previous research works on leaching properties of South African coal fly ash have revealed that contact of the ash with aqueous media leads to release of high concentrations of Ca, Na, K, Mg, Ba and SO_4 . Species such as Se, As and B Mo and Cr were observed to be highly mobile (Gitari *et al.*, 2009a)

The power station evaluated in this study produces 1.765 Mt of fly ash per annum and utilizes a dry ash disposal system. The plant is operated on a zero-effluent discharge policy (ZLED) whereby no liquid effluents are discharged into the environment. The plant treats 16.8 Ml of water per day by (a mixture of mine water and cooling water blow down) Spiral Reverse Osmosis (SRO), Vapor compression (VC) and Electro-Dialysis Reversal (EDR) generating large quantities of high salt loaded waste water (brine). This high salt loaded effluents requires disposal. Desalination technologies have increasingly been employed to increase water usage efficiency especially in water scarce regions like South Africa. However desalination technologies have been limited by the need to dispose the concentrated brines generated in the process especially in inland areas. Brine handling techniques require expensive treatment options or disposal in lined dams to minimize environmental impacts. These treatment options are capital intensive and have high operating costs.

In an attempt to reduce the cost of disposing and handling the brines, Tutuka power utility utilizes the brines in conditioning the coal fly ash (10-16 %) before being conveyed to the ash dumps. In the ash dumps it is further conditioned by irrigation with the high saline effluents. Therefore the ash dumps may act as repository

for the high salt loads in the brines (Gitari *et al.*, 2009b). The chemical and physical interactions of these highly saline effluents with fly ash are not fully understood. Fly ash is known to undergo dissolution on contact with aqueous solution including the highly saline effluents or brines (Gitari *et al.*, 2009a) Species released from ash through the interactions may lead to cleaner effluents or to significant release of pollutants over time. Moreover the interaction chemistry of the high saline effluents or brine and fly ash is bound to be influenced by ingress of CO_2 from the atmosphere over time (Muriithi *et al.*, 2011). The disposal of fly ash is of major environmental concern due to the possible release of contaminants to ground and surface water after disposal. It's therefore important to understand the mobility and release patterns of species of environmental concern once the fly ash is disposed on land and their transport through the layers of the weathered ash dump.

This study is an attempt to evaluate the chemical weathering and species mobility in the high saline effluents conditioned weathered ash. Several techniques were employed to achieve these objectives, a leaching test (DIN-S4) was employed to evaluate the highly leachable fraction in the fresh fly ash. In order to better understand the mineralogical changes under the real disposal conditions, cores were drilled at the weathered ash dump as a function of age and subjected to X-ray diffraction analysis (XRD) and scanning electron microscopy (SEM) analysis. Their mineralogical analysis by depth coupled to chemistry of extracted interstitial or pore water were applied to increase our understanding of the mobility of contaminants under disposal conditions.

1. MATERIAL AND METHODS

1.1 Fly Ash Samples

Fly ash (FA) samples were collected directly from the hoppers at the power station and immediately placed in PVC buckets which were then tightly locked to prevent ingress of CO_2 . The X-ray diffraction (XRD) analysis was done using a Philips PANalytical instrument with a PW3830 X-ray generator operated at 40 kV and 25mA. Both fresh and weathered 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 interval of 0.02° two theta from 5° to 85° and counted for 0.5 seconds per step. The chemical analysis of the bulky fly ash samples was done by X-ray fluorescence (XRF) spectrometry using a Philips 1404 Wavelength Dispersive spectrometer fitted with a Rh tube.

1.2 Geophysics Survey, Borehole Positions and Sampling

Groundwater, through the various dissolved salts it

contains, is ionically conductive and enables electric currents to flow into the ground. To identify the presence of groundwater from resistivity measurements, one can look at the absolute value of the ground resistivity, but most of the time it is the relative value of the ground resistivity which is considered for detecting groundwater.

An Abem SAS 1000 terrameter and ES 464 switching unit were used for the field surveys at Tutuka and Secunda. Four multicore cables and stainless steel pegs were used with the “roll-along” surveying method. Measurement of the resistivity of the ground is carried out by transmitting a controlled current (I) between two electrodes pushed into the ground, while measuring the potential (V) between two other electrodes. Direct current (DC) or a very low frequency alternating current is used, and the method is often called DC-resistivity. The resistance (R) is calculated using Ohm’s law. The profile was surveyed using a 10 meter electrode separation with the Schlumberger-long measuring protocol with an investigation depth of approximately 80 meters. The electrical resistivity method was applied to establish variations in ash characteristics, salt deposition and water level distribution in the subsurface. The geophysical data was used to optimize the site selection of the borehole positions (Figure 1). Sites were selected in areas with different ash age and different salt content as interpreted from the geophysics data.

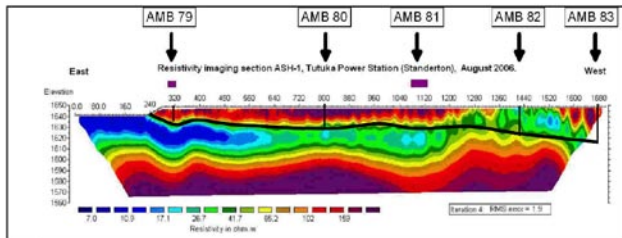


Figure 1
Approximate Borehole Positions in Relation to the Electrical Resistance Profile Results (The black line represents the inferred ash/bedrock contact)

1.3 Coring and Drilling

A combination of Air Flush Coring and direct circulation air percussion drilling were used to drill the boreholes at the dry ash dump. Air flush Coring uses a conventional drilling rig and compressor with a specialized drill bit that cores the ash without the need for water or lubrication for cooling of the drill bit (Fig 2). The advantage of using this air drilling technique is that the coring method does not use water to cool down the drill bits as in normal rock coring. The samples therefore remain chemically unchanged and physically intact. An initial starter hole was drilled using air percussion through the overburden, to the top of the ash. The Air flush coring technique was then used further down to the bottom of the ash. Standard direct circulation air percussion of 165mm diameter

was used to drill into the underlying bedrock. Casing of 140mm diameter were then installed to the bottom of the hole. The borehole depths varied from 10 to 30 meters, depending on the depth of the ash.



Figure 2
Air Flush Core Barrel and Core Inside the Barrel

1.4 Total Acid Digestion of Fly Ash Samples

Total acid-digestion was carried out according to Jackson and Miller (1998) in order to determine the total elemental composition of the fly ashes. 2mL of concentrated hydrofluoric acid (HF) and 5mL aqua regia were mixed with 0.25g of fly ash in a Parr bomb at 200°C for 2 h. The sample was allowed to cool after which the excess HF in the digestate was volatilized by the addition of 25mL of saturated H₃BO₃ solution. The digestate was filtered through a 45µm pore filter membrane and the solution was diluted to 50mL with de-mineralized water.

1.5 DIN-S4 Leaching Test

The water soluble fractions of the fly ashes were determined by employing the German standard leaching test DIN-S4 (1984). The DIN-S4 method is an agitated extraction test which involves shaking the mixture (ash/water) for a period of 24h and uses a wide range of water to solid ratios. 50g of the fly ash samples were placed in 1L polyethylene bottles and mixed with 500mL of de-mineralized water corresponding to L/S 10:1. The bottles were shaken for 24h in a horizontal shaker at room temperature. The supernatants were decanted and filtered through a 0.45µm pore membrane filter. The pH was measured and EC, TDS of the filtered leachates calculated using Hanna HI 991301 pH meter with portable pH/EC/TDS/Temperature probe. The pH meter was calibrated before using buffer solutions of pH 4.01, 7.01 and accuracy confirmed with buffer 10.01, electrical conductivity standard of 12.88 mS/cm at room temperature. All experiments were done in triplicate. Samples were prepared for both cation and anion analysis and stored at 4°C until analysis.

1.6 Pore Water Extraction for Weathered Ash

The pH of interstitial/pore water was determined using 1:1 core: water ratio by following the method of Eckert (1988). 20 grams of each of the ash core samples taken at 1 m

intervals down the profile of the ash dump were weighed and put in a beaker and an equal amount (20 ml) of ultra-water 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 triplicated.

1.7 Cation Exchange Capacity

Cation-exchange capacity (CEC) of ash is defined as the degree to which an ash can adsorb and exchange cations. Fly ash is predominantly composed of mineral phases formed initially at high temperatures. On exposure to an atmospheric environment many of these solids are metastable and will alter to form thermodynamically stable assemblages of minerals which alter its adsorption capacity. In this work CEC was applied to indirectly measure the adsorption capacity of the weathered ash cores. The method for the determination of the CEC was adapted from Chapman (1965).

1.8 Major, Trace Metal Species and Anion Analysis

Major, minor and trace elements in aqueous samples were determined using ICP-MS (Agilent 7500ce with ORS). Anions were determined by ion chromatography (Dionex ICS-1000 Ion Chromatograph, Column: Ion Pac AS14, Guard Column: AG14, Eluent: $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$).

2. RESULTS AND DISCUSSIONS

2.1 Chemical, Mineralogical and Physical Characterisation of the Fly Ash

2.1.1 Ash and Bedrock Characteristics of the Drilled Ash Cores

The graphic log and physical sample description of cores by depth is presented in Tabular form for cores AMB79, AMB81 and AMB82 (Table 1, 2 and 3). The Table 1, 2, 3 shows that at various ages and depths, differences in the ash were found varying from very hard coarse ash, to very hard fine ash, that was fractured, soft fine powdery ash and clay, mudstone or dolerite material where the bedrock was sampled. The Table also presents the mode of quenching of fly ash dust during the initial disposal of the ash. Some of the cores were in contact with water (AMB79 and AMB82) and this is bound to have an influencing effect on the pH and concentration of species in the pore water. In cases where the dump had been irrigated there were deeper layers and zones which were still unconsolidated, friable and loose indicating that no or few pozzolanic reactions had taken place over time and hard and soft layers were found directly adjacent to each other. Unconsolidated ash was prevalent in more recently placed areas of the dump. The water level in each part of the dump sampled was different, ranging from between

9 to 23 metres from the surface and in one core no water level was observed. Some portions of cores were moist and others dry. Dry zones were found in cores where the water level was non-existent or deeper lying. EC of core water sampled varied from 315 to 571 mS/m indicating differences in conductivity/resistance, in all likelihood due to the differences in brine irrigation regime practiced on different areas of the dump. There was not much homogeneity within each core nor between different cores and many fractured zones were observed; once again highlighting the heterogeneous nature of the ash.

Table 1
The Graphic Log and Physical Sample Description of Core AMB79

Well ID		AMB 79		Well Log: Lithology and Construction					
				Tutuka Ash Dump					
Drilling method:		Air Flush Core		Contract No.		20 year old ash			
Coordinate		X	E29.39340	Scale		H	23		
Surface Elevation (m)		Y	S26.77259	Diameter (mm)		V	200		
Well depth (m)		0		Commencing date		20061130			
Casing depth (m)		15		Ending date		20061130			
Layer No.	Strata	Thick (m)	Elev. (m)	Depth (m)	Column map	Lithology	Remark		
1	ASH	0.75	-0.75	0.75		Clay topsoil			
2	ASH	5.5	-6.25	6.25		solid ash			
3	ASH	0.75	-7	7		fractured porous ash			
4	ASH	1	-8	8		hard ash			
5	ASH	1	-9	9		coarse moist ash	Depth to Water level = 9.93m		
6	ASH	1	-10	10		coarse ash	EC: 335 mS/m		
7	ASH	1	-11	11		wet, moist ash			
8	DLRT	4	-15	15		dolerite, light brown and orange coloured clay			

(Irrigated and Quenched with Fresh Water)

Table 2
The Graphic Log and Physical Sample Description of Core AMB81

Well ID		AMB 81		Well Log: Lithology and Construction					
				Tutuka Ash Dump					
Drilling method:		Air Flush Core		Contract No.		8 Year old ash			
Coordinate		X	E29.40131	Scale		H	23		
Surface Elevation (m)		Y	S26.77104	Diameter (mm)		V	200		
Well depth (m)		13		Commencing date		20061130			
Casing depth (m)		0		Ending date		20061130			
Layer No.	Strata	Thick (m)	Elev. (m)	Depth (m)	Column map	Lithology	Remark		
1	ASH	0.4	-0.4	0.4		top soil			
2	ASH	1.1	-1.5	1.5		hard ash			
3	FRAC	0.05	-1.55	1.55		Fracture			
4	ASH	6.95	-8.5	8.5		hard ash			
5	ASH	0.5	-9	9		brittle ash, core loss			
6	ASH	2.5	-11.5	11.5		No Core, unconsolidated ash	No water level		
7	ASH	1.5	-13	13		layers to soft to drill			

(Irrigated and Quenched with Brine Effluents)

Table 3
The Graphic Log and Physical Sample Description of Core AMB82

Well ID		Well Log: Lithology and Construction											
AMB 82		Tutuka Ash Dump											
Drilling method:		Air Flush Core		Contract No.		4 Year old ash							
Coordinate		E29.40349		Scale		23							
Surface Elevation (m)		S26.77030		H		200							
Well depth (m)		0		Diameter (mm)		215							
Casing depth (m)		25.1		Commencing date		20061130							
Layer No.		Thick (m)		Elev. (m)		Depth (m)		Column map		Lithology		Remark	
1	ASH	0.5	-0.5	0.5							top soil		
2	ASH	2.35	-2.85	2.85							coarse ash		
3	FRAC	0.05	-2.9	2.9							2.9m fracture		
4	ASH	7.55	-10.45	10.45							coarse ash		
5	FRAC	0.05	-10.5	10.5							10.5m fracture		
6	ASH	2.35	-12.85	12.85							coarse ash		
7	FRAC	0.05	-12.9	12.9							12.9m fracture 45deg		
8	ASH	9.1	-22	22							coarse ash		
9	ASH	1	-23	23							hard fine ash	Depth to water level: 23.07 mbc	
10	ASH	1	-24	24							brittle ash	EC: 571.4 mS/m	
11	CLAY	1.1	-25.1	25.1							clay soil, weathered dolomite		

(Irrigated and Quenched with Brine Effluents)

2.1.2 Scanning Electron Microscopy (SEM), X-Ray Diffraction and X-Ray Fluorescence Analysis (XRF)

Figure 3 shows the SEM micrographs of the fresh and weathered fly ash, showing regular spherical shaped particles, although some angular particles are also observed. In contrast the weathered ash reveals more of the angular particles.

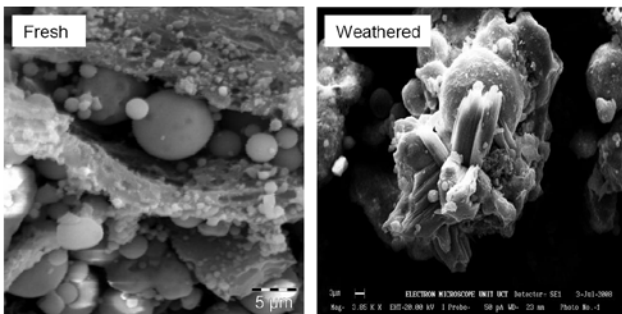


Figure 3
SEM Micrograph of Fresh and Weathered Dry Ash Dump Coal Fly Ash

Mineralogical evaluation by XRD (Fig 4) revealed that major crystalline mineral phases are quartz (SiO₂) and mullite (3Al₂O₃.2SiO₂). Low intensity lime and calcite peaks are also observed. No significant change in mineralogy is observed for the dry ash dump by depth. Presence of water seems to accelerate the weathering and transformation of the ash components into new mineral

phases. There was no difference in mineralogy between the different cores and only the XRD spectrum is shown.

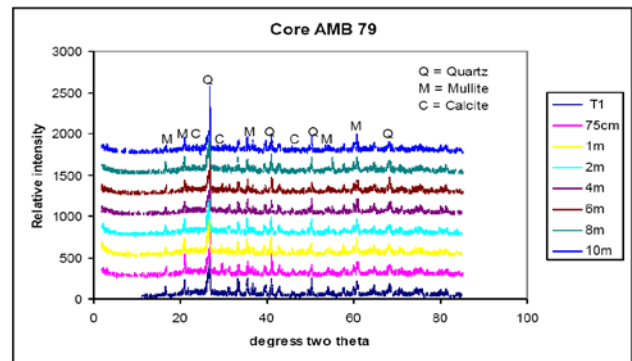


Figure 4
XRD Spectra of Dry Ash Dump Samples by Depth (AMB79: 20 Year Old)

The chemical composition of the ash and its source is a critical aspect of its environmental impact upon disposal, it determines the leachability and potential fluxes. Chemical analysis (Table 4) shows the fly ash contains high concentrations of SiO₂, Al₂O₃ and Fe₂O₃ as the major constituents. The fly ash seems to be enriched in Sr and Ba. XRF results (Table 4) indicate the main constituents are Al, Si, Ca, Na, K, Mg, Sr, Ba and SO₄. Low amounts are observed for Co, As, Cd, Cu, Se, Hg, Zn, Pb and Mo.

Table 4
XRF Analysis of Fresh Tutuka Coal Fly Ash

Major elements (% w/w)		Trace elements (ppm)	
Al ₂ O ₃	24.30±0.18	V	86.5±0.71
CaO	6.44±0.03	Cr	138.5±6.36
Cr ₂ O ₃	0.05±0	Co	24±0
Fe ₂ O ₃	4.72±0.03	Ni	96.5±0.71
K ₂ O	0.83±0	Cu	9±0
MgO	1.93±0	Zn	37±5.66
MnO	0.04±0	Ga	22±1.41
Na ₂ O	ND	Rb	29.5±2.12
NiO	0.01±0	Sr	1787±3.54
P ₂ O ₅	0.31±0	Y	79±0
SiO ₂	56.13±0.29	Zr	405±0.71
TiO ₂	1.61±0	Nb	29±0
LOI	3.52±0.08	Ba	1243±43.13
Total	99.89±0.63	La	70±22.6
		Ce	240±24.04
		Nd	63±2.83
		Pb	45±5.66
		Th	17±2.83
		U	3±1.41

2.2 Short Term Dissolution Tests

2.2.1 DIN-S4 and TCLP Leaching Tests

DIN-S4 leaching test at a liquid/solid (L/S) ratio of 10 was carried out to assess the highly leachable and water soluble fraction for the dry ash dump. This method was used to simulate the condition at the ash dump when rainwater percolates through the ash dump, and was

used as a measure of short term release of highly soluble species. The toxicity characteristic leaching procedure (TCLP) performed at a similar L/S ratio of 10 to assess the effect of low pH leachant on the leachability of species. The low pH of leachant simulates low pH rainwater contacting the ash in the surface dump. The use of batch leaching tests although not close to field conditions can be used to estimate the initial concentration of a solute in leachate. The results for DIN-S4 and TCLP tests are presented in Table 5.

Table 5
DIN-S4 and TCLP Tests Showing the Concentrations of Major and Minor Elements (mg/L), pH, EC (mS/cm), TDS (ppt) and Alkalinity (mg/L CaCO₃) at Two Liquid/Solid (L/S) Ratio of 10 (n=3)

Tutuka Power Utility Coal Fly Ash			
DIN-S4 Leaching experiment		TCLP Leaching experiment	
L/S	10	L/S	10
Parameter	Mean±STDev	Parameter	Mean±STDev
Al	<0.006	Al	<0.004
As	<0.006	As	0.058±0.004
Ba	0.711±0.244	Ba	0.155±0.041
Co	<0.005	Co	<0.005
Cr	0.362±0.026	Cr	0.629±0.061
Cu	<0.002	Cu	<0.002
Fe	<0.001	Fe	0.004±0.001
Mn	<0.002	Mn	<0.002
Mo	0.093±0.008	Mo	0.107±0.008
Ni	<0.006	Ni	<0.006
Pb	<0.010	Pb	<0.010
Se	0.008±	Se	0.036±0.005
Zn	<0.002	Zn	<0.002
B	1.28±0.023	B	10.4±0.040
Ca	914.7±58.6	Ca	2229±203.8
K	1.38±0.024	K	1.54±0.006
Mg	0.053±0.032	Mg	155.9±3.28
Na	3.84±0.053	Na	4.42±0.058
SO ₄	228.7±23.5	SO ₄	568±7.13
pH	12.7±0.121	pH	9.98±0.006
EC	7.82±0.111	EC	6.59±0.046
TDS	4.07±0.060	TDS	3.44±0.015
Alkalinity	1897.5±8.66	Alkalinity	3805.6±20.97

The pH of the leachates are highly alkaline ranging from 9.98 to 12.56 for DIN-S4 and TCLP test. The dissolution and hydrolysis of the basic oxides (CaO and MgO) contribute to the increase in pH values of ash sample. Fly ash material generates an alkaline pH within a few minutes of contact with water in most cases, due to the higher quantities of soluble oxides than the soluble acid phases (Choi *et al.*, 2002) The EC values ranged from 6.59 to 7.82mS/cm for both tests indicating large quantities of soluble species have been released from the fly ash. The buffering effect is observed in the final pH achieved for leachates in TCLP tests. The final pH of 9.98 for L/S of 10 was recorded for the TCLP test. There is release of high quantities of alkali and alkaline earth metals such as Ca, Na, K and Mg. In addition B and SO₄ are also released in high quantities. A higher concentration of these species is observed for the leachates in the

TCLP tests, this is due to buffering of the pH to circum-neutral and acidic values. Concentrations of As, Cd, Co, Mn, Ni, Pb, Cr, Al, Cu, Fe, Mo, Se and Zn were largely below detection limit in the leachates. The final pH of the leachates were highly alkaline for both tests and this would appear to limit the leaching of most of the trace species. Most of these trace species would probably be released after long equilibration times when the alkalinity of the ash is significantly depleted and pH of the leachate approaches circum-neutral or acidic levels.

2.2.2 Highly Leachable Fractions

The calculated soluble fraction leached in DIN-S4 tests for fresh Ash for the L/S of 10 and 20 is presented in Table 6. This was calculated to estimate the initial amounts of major and trace species that will be initially released on fresh ash contacting water on disposal.

Table 6
Average % Leached Amounts in DIN-S4 for Fresh Fly Ash (mmol/kg dry mass)

Species	Total acid-digestion	DIN-S4		Soluble fraction %
		L/S 10:1	L/S 20:1	
Cr	3.85	0.069	0.084	1.79-2.18
Mn	6.41	BDL	BDL	
Co	0.4	BDL	BDL	
Ni	1.29	BDL	BDL	
Cu	0.62	BDL	BDL	
Zn	0.58	BDL	BDL	
As	0.19	BDL	BDL	
Se	0.024	0.00099	0.0021	4.13-8.75
Mo	0.079	0.0097	0.011	12.28-13.92
Ba	5.42	0.052	0.12	0.96-2.21
Pb	0.21	BDL	BDL	
Fe	736.26	BDL	0.0032	0-0.00043
Al	4766.31*	BDL	0.038	0-0.00080
Ca	1148.37*	228.2	249.2	19.87-21.7
Mg	368.92*	0.022	0.026	0.006-0.007
K	79.3	0.35	0.36	0.44-0.45
Na	259.24	1.7	1.5	0.58-0.66
SO ₄	1574.28	23.8	22.6	1.44-1.51

*soluble fraction calculated from XRF data , BDL-below detection limits

Calculation of the % total amounts leached in DIN-S4 revealed the easily soluble fractions within 24h of the ash/water contact. The results showed that most of the metals in fly ashes could probably be locked-up within the aluminosilicate matrix of the fly ash and would only be released through long-term weathering processes as the ash buffering capacity decreases. Species Ca, K, Na, Mg, Ba and SO₄ were observed to be the most readily soluble species: Ca (15-24.23%), K (0.23-0.45%), Na (0.58-0.82%), Mg (0.0047-0.007%), Ba (0.96-3.33%) and SO₄²⁻(0.012-1.51%). Species present as oxyanions were easily solubilized Se (2.17-8.75%), Mo (2.96-13.92%) and Cr (0.22-2.18%). Most of the heavy metals were below detection limit which is an indication that they are not readily soluble under the applied conditions and the fact that the pH remained highly alkaline in the leachates

generated.

2.3 Physicochemical Characteristics of Extracted Interstitial Pore Water

The physicochemical characteristics of the pore water in the weathered ash was evaluated to give an indication of the extent of weathering and the concentration of the species which gives an indication of the reactions likely to control release and mobility of these species in the weathered ash.

2.3.1 pH Profile of Extracted Interstitial Pore Water

The Figures 5-9 depicts the pH and EC profile of the extracted pore water for the drilled cores as a function of depth.

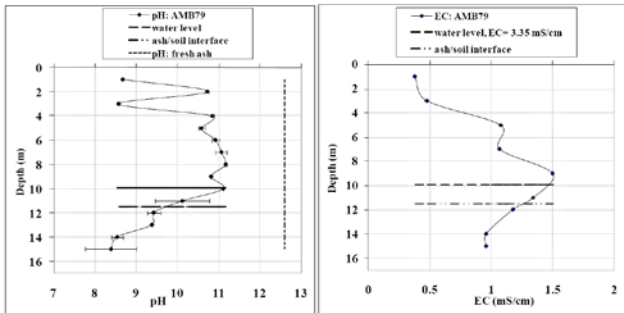


Figure 5
pH and EC of Pore Water Versus Depth (m) for AMB79 Core (Error Bars Represents 1 SD below and above the Mean, n=3)

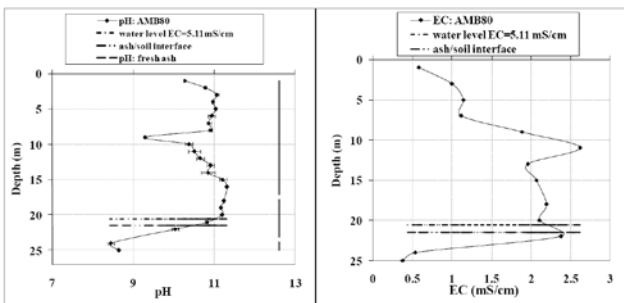


Figure 6
pH and EC of Pore Water Versus Depth (m) for AMB80 Core (Error Bars Represents 1 SD below and above the Mean, n=3)

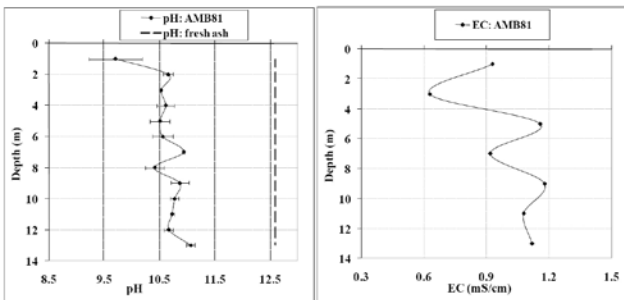


Figure 7
pH and EC of Pore Water Versus Depth (m) for AMB81 Core (Error Bars Represents 1 SD below and above the Mean, n=3)

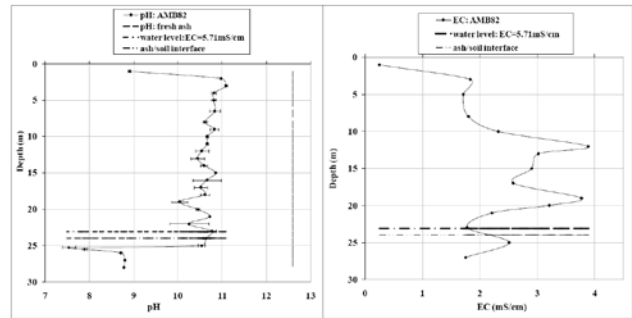


Figure 8
pH and EC of Pore Water Versus Depth (m) for AMB82 Core (Error Bars Represents 1 SD below and above the Mean, n=3)

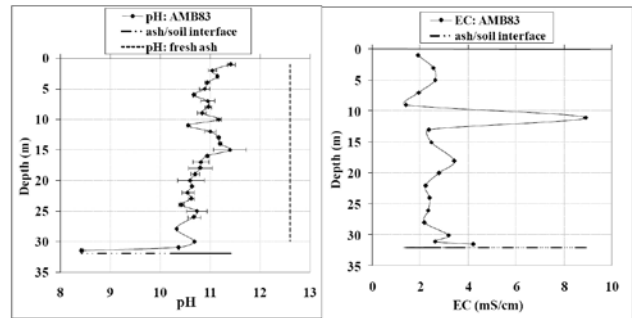


Figure 9
pH and EC of Pore Water Versus Depth (m) for AMB83 Core (Error Bars Represents 1 SD below and above the Mean, n=3)

For all the cores, lowest pH of the pore water is observed at the top layer 0.55-3m and immediately after the water level. This observation indicates greatest weathering of the fly ash has occurred at the top layer (0.55-3 m) and after the contact with water (point of saturation). For cores that did not have contact with lateral flows of water (AMB81 and AMB83) the pH of the pore water remains almost steady. The effect of the age of the ash dump can also be seen when cores AMB79 and AMD80 are compared. AMB79 shows a lower pH of the pore water than AMB80 indicating depletion of alkalinity generating components with age of ash. The pH of the pore water for the middle section before contact with water shows a similar trend for all the cores except for a few fluctuations. The pH for the pore water was maintained at 10-11.5 indicating that even without contact with water highly available alkalinity generating components are depleted probably through conversion to carbonates such as calcite.

2.3.2 Chemical Characterization of the Extracted Interstitial Pore Water of the Drilled Ash Dump Cores

This section presents and discusses the pore water chemistry by depth of selected Ash dump cores (AMB79, AMB81 and AMB82) and expounds on the mechanism that could contribute to the mobility of the various species down the depth of the core and factors that would affect

their concentration at various depths

2.3.2.1 Ash Monitoring Borehole (AMB) Ash Core 79

The pore water chemistry data is presented for the core AMB79 (20 years old), conditioned and irrigated with fresh water, as a function of depth in Figures 10-11. The availability of water soluble components in the weathered ash will depend on extent of carbonation, dissolution/flushing of the soluble salts as a function of the depth of the core. The saturation degree of the core will also influence the availability of the water soluble components. Fe, Ti, Pb, Mn, Mo, Se, Ba, Zn, As, V, Cu and Ni in the pore water were observed to be in the range (1-1500) ppb (Fig 11) while Si, Al, B, Sr, Na, Mg, Cr, Ca and K were observed to be in the range (1-250) ppm (Fig 10, 12). The observation agrees with the DIN-S4 and TCLP results where the alkali, alkaline earth elements and oxy-anions

are the most available species even in the weathered ash and are likely to leach on the ash contacting lateral flows of ground water or percolating leachates after a rainfall event.

On the species profile by depth, Ba, Sr, Ca, K and Na (Fig 10) follow a similar trend. Low concentrations are observed in the first (0-4) m depth. This is observed to increase to a maximum at a depth of (10-11) m. A peak in concentration is observed for all these species at a depth of approx. 9-9.5 m which is the point of contact of ash with water. This would represent the point of maximum saturation of the ash with water and subsequent maximum dissolution of the soluble salts. Carbonation and conversion of the alkali and alkali earth metals into carbonates would explain the low concentration observed in the top (0-4) m layer.

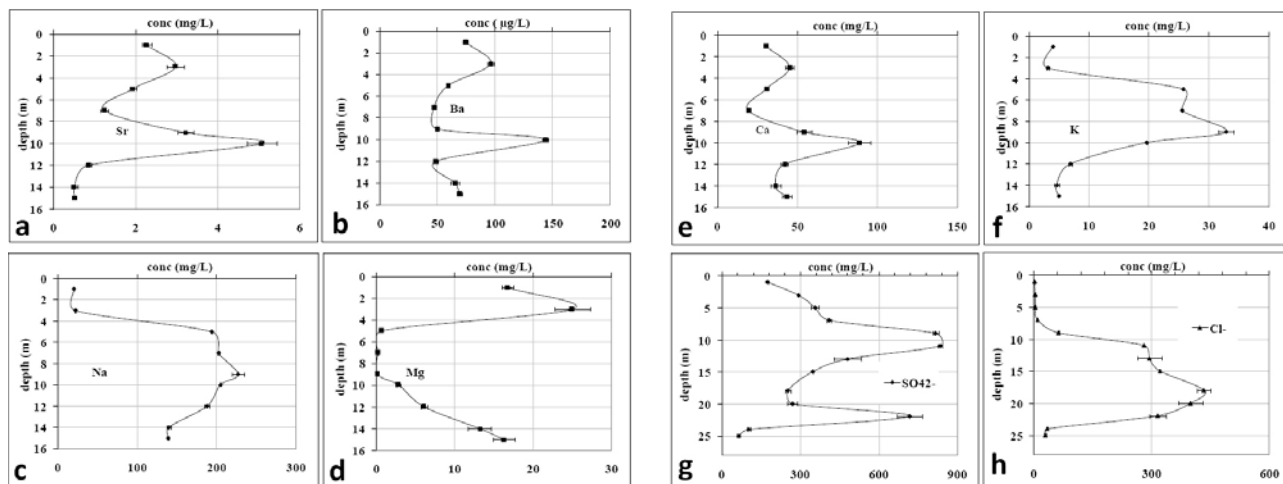


Figure 10
Concentration of Alkali, Alkali Earth Metals, Sulphates and Chlorides by Depth for the Core AMB79

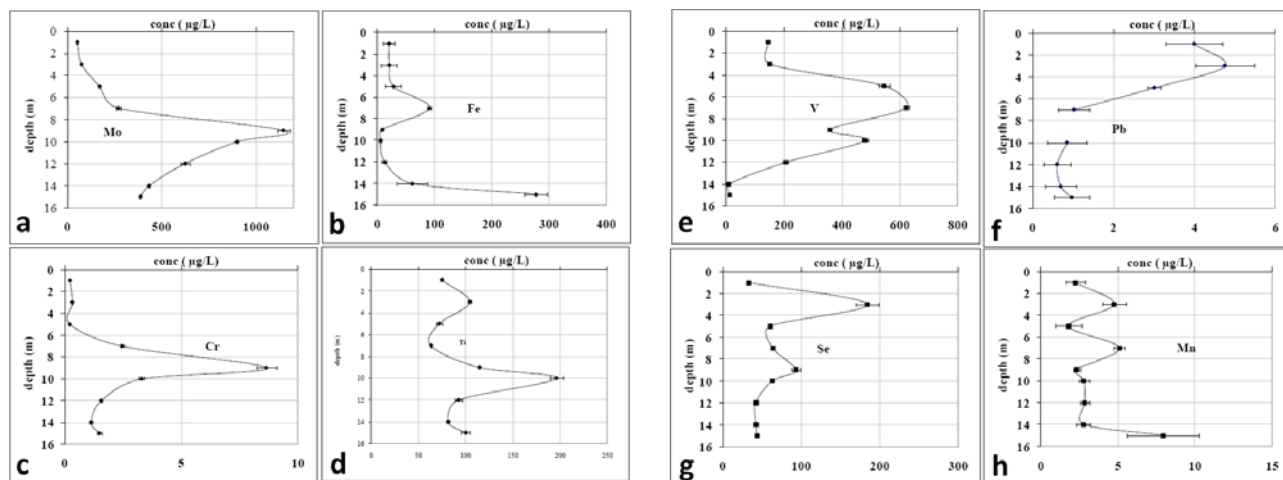


Figure 11
Concentration of Oxyanions and Selected Heavy Metals by Depth in the Pore Waters for the Core AMB79

2.3.2.2 Ash Monitoring Borehole (AMB) Ash Core 81

The pore water chemistry data is presented for the core AMB81 (8 years old), conditioned and irrigated with high saline effluents as a function of depth in Figures 12-13. The conditioning and irrigation of the ash dump with high saline waste water for dust suppression during disposal is bound to influence the reaction of the fly ash on contact with CO₂ in the atmosphere and the mineralogical transformation of the ash with time. Presence of species such as Ca, Mg in the saline effluents and generation of alkalinity once the fly ash comes into contact with the saline effluents enhances formation of CaCO₃ and MgCO₃ in the open atmosphere (Muriithi *et al.*, 2011).

The species Cl⁻, SO₄²⁻, NO₃⁻, B, Si, Al, Sr, Mg, Na, Cr, Ca and K registered high concentration for the entire depth ranging from (5-500) ppm (Fig 12). The high concentration of these species as compared to AMB79 could be due to the contribution by the high saline effluents used to irrigate this ash dump. The concentration of Se, Pb, Fe, Ni, V, As, Zn, Ba, Cu, Mo and Ti registered lower concentrations ranging from (5-600) ppb. The

relatively high pH of the pore water (Fig 7) could have contributed to the low levels of these species.

The species B, Sr, Mg, Ca, Ba, Cu and Ti exhibit a similar general trend with high concentrations in the top layer decreasing with depth. The top layer of the ash dump experiences the first contact with the high saline effluents and the contribution of species by the saline effluents will be greatest in this layer. Highly soluble salts are initially formed such as BaSO₄, SrSO₄, CaSO₄, CaCl₂, MgCl₂ that will dissolve on contact with aqueous fluids like water. The species Se, Pb, Fe, V, Si, Al, Na and K shows a general increasing trend with a peak at a depth of (5-6) m. This could be due to advection transport effect as leachates percolate through the dump especially after a rainfall event. This region of the core was characterized by hard ash (Table 3) which is cemented to form a hard pan-like layer indicating possible trapping of exchangeable species such as Na, K in Al-Si and Fe-oxyhydroxide amorphous mineral phases (Fig 16C). This core didn't experience lateral flows of groundwater (Fig 7).

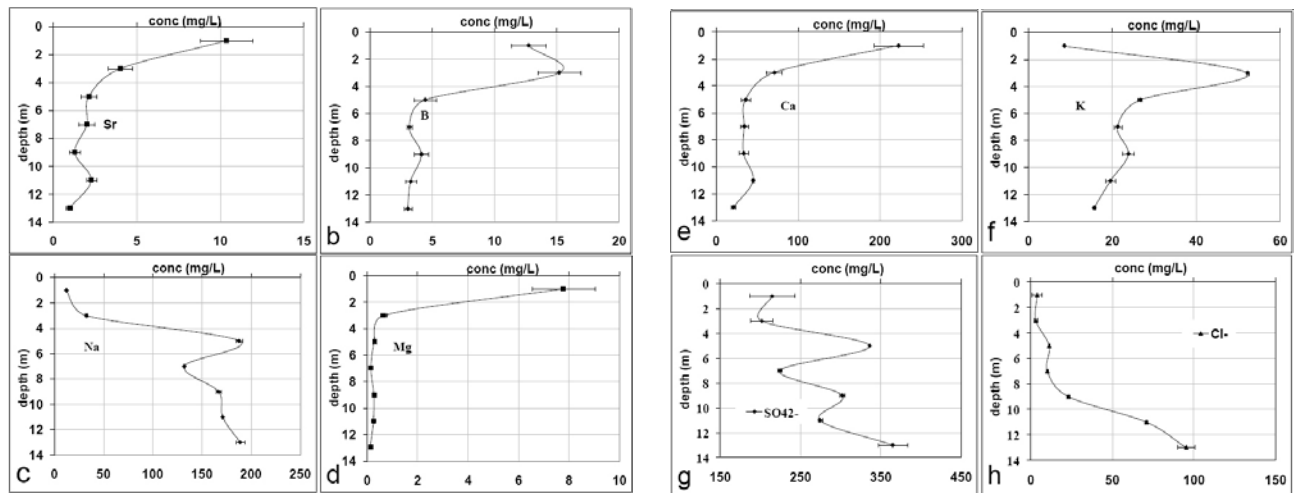


Figure 12
Concentration of Alkali, Alkali Earth Metals, Sulphates and Chlorides by Depth for the Core AMB81

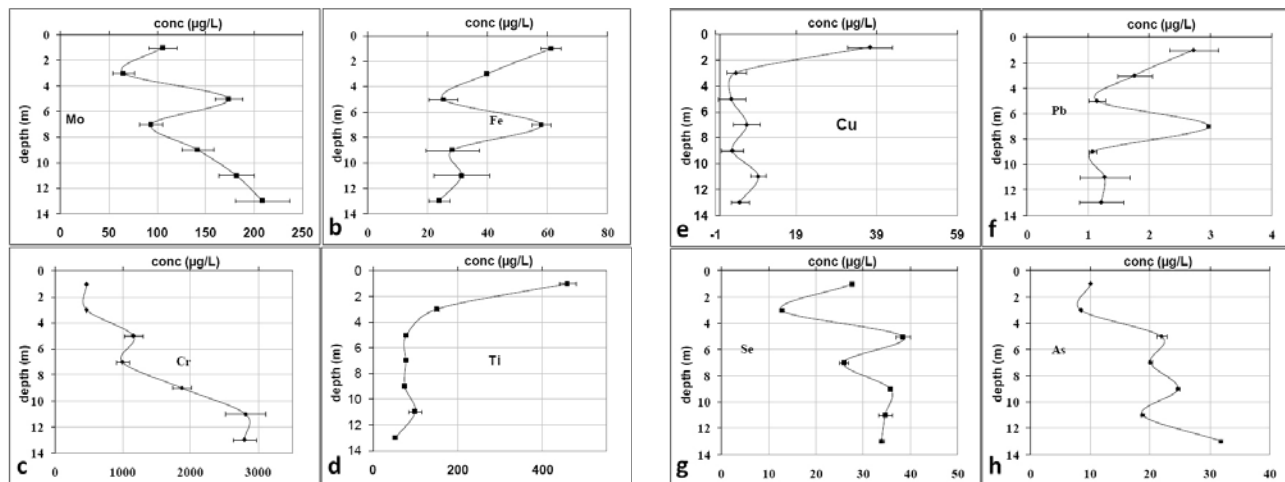


Figure 13
Concentration of Oxyanions and Selected Heavy Metals by Depth in the Pore Waters for the Core AMB81

2.3.2.3 Ash Monitoring Borehole (AMB) Ash Core 82

The pore water chemistry data is presented for the core AMB82 (4 years old), conditioned and irrigated with high saline effluents as a function of depth in Figures 14-15. The conditioning and irrigation of the ash dump with high saline waste water for dust suppression during disposal is bound to influence the reaction of the fly ash on contact with CO₂ in the atmosphere and the mineralogical transformation of the ash with time.

The species V, Mo, Si, B, Cr, Al, Sr, K, Mg, Na, Ca, SO₄²⁻ and Cl⁻ registered high concentration for the entire depth ranging from (1-1000) ppm. The high concentration of these species in the pore water as compared to AMB79 indicates the effect of irrigation with high saline effluents. The species As, Cd, Zn, Ba, Cu, Fe, Ni, Mn and Ti exhibited low concentrations ranging from (0.5-500) ppb. Majority of the species show low concentration in the top layer (0-4) m depth except for As, Zn, Ba

and Cu. This is the point of first contact with leachates and is bound to experience the greatest dissolution/flushing of ash components by percolating leachates. The concentration of leachable components is also bound to be influenced by the physical state of the disposed ash. A phenomena is observed whereby all species register low concentration at or near point of ash contacting water (Fig 8, Fig 14-15). This could signify that most of the soluble constituents have been washed away by the lateral flows of groundwater. High concentration of selected species (Mo, Cd, As, Cr, Ba, Se, Ni, Na, SO₄²⁻, Cl⁻, Ti and V) was observed in the range (5-20) m depth. This seems to be confirmed by the high EC observed over this depth range. This also coincides with the region where the ash was broken/fractured (Table 4) confirming the physical state of the ash in the dump will influence availability and mobility of species.

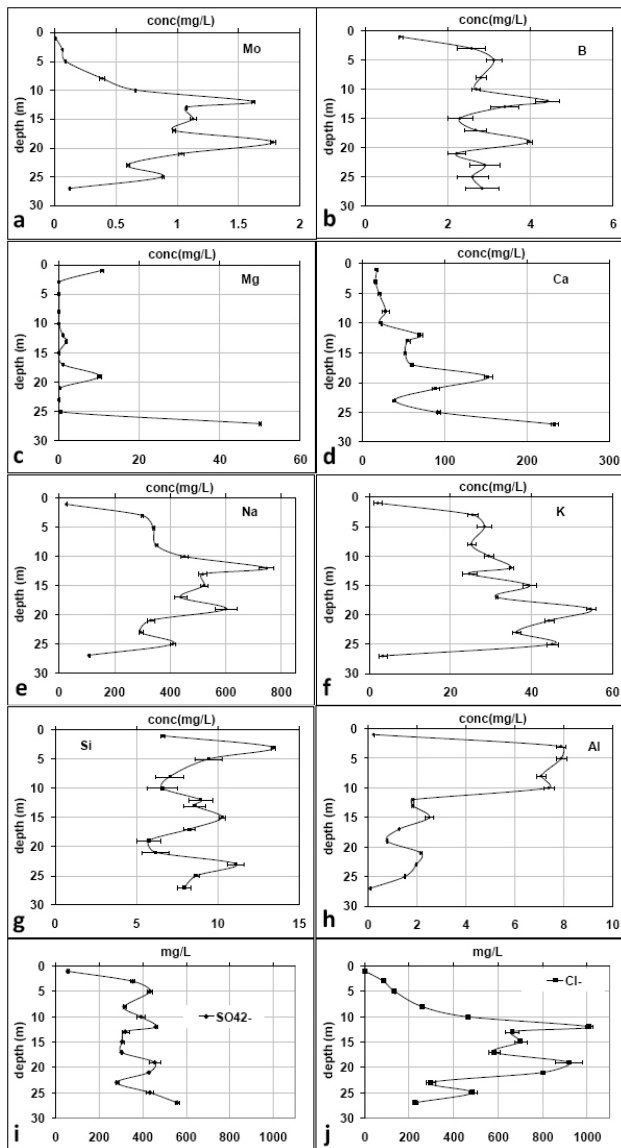


Figure 14
Concentration of Alkali, Alkali Earth Metals, Aluminum, Silicon, Sulphates and Chlorides by Depth for the Core AMB82

2.4 Al-Si Mineralization and Cation Exchange Capacity (CEC)

Figure 16 depicts the variation of the cation exchange capacity and Al, Si in the pore water by depth for the core AMB79.

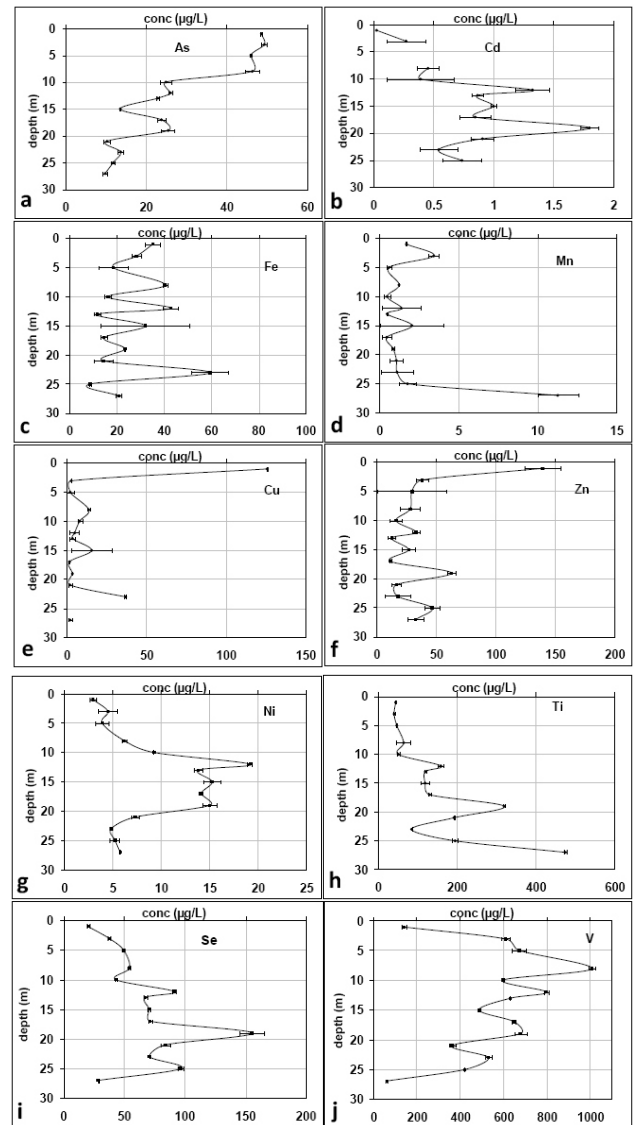


Figure 15
Concentration of Oxyanions and Selected Heavy Metals by Depth in the Pore Waters for the Core AMB82

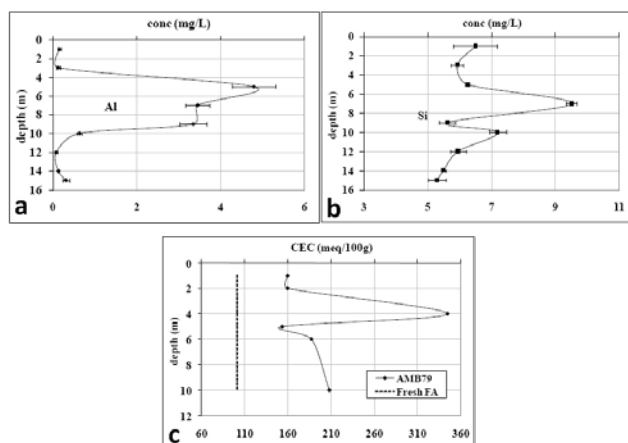


Figure 16
Concentration Profile of Al, Si in the Pore Waters and CEC by Depth for the Core AMB79

Overall there is an increased CEC for the weathered ash compared to the fresh ash indicating mineralogical changes as the ash weathers. A similar concentration profile is observed in the pore waters for Al and Si, indicating that the initially dissolved Al and Si at high alkaline pH is transforming into a kind of Al-Si rich phase that could be responsible for the high increased CEC at this depth. The increase in CEC observed at 4 m depth seems to correspond to the peaks in concentrations observed for Fe, Al, Se, Zn, Mg, Pb in core AMB79 water soluble fraction which suggests some kind of transient mineralization at this depth. Zevenbergen *et al.* (1999) observed increased cation exchange capacity of weathered ash (10 years old) as compared to fresh ash and attributed this to alteration of the aluminosilicate glass to noncrystalline clay. The clay formation was observed to fix heavy metals.

CONCLUSIONS

Chemical analysis of the weathered ash from dry ash dump revealed the major elements are Al_2O_3 , SiO_2 , Fe_2O_3 , CaO and MgO and trace elements Cr, Sr, Ba Ce and Zr. Results from DIN-S4 and TCLP tests reveals that species highly leached include Ca (15-24.23 %), K (0.23-0.45 %), Na (0.58-0.82 %), Mg (0.0047-0.007 %), Ba (0.96-3.33 %), SO_4^{2-} (0.012-1.51 %), Se (2.17-8.75 %), Mo (2.96-13.92 %) and Cr (0.22-2.18 %) per dry weight of fly ash. Leaching tests revealed that the major soluble components in solution at equilibrium are Ca, Na, SO_4^{2-} and K. XRD revealed the presence of major phases of mullite, quartz and lime.

The pH profile of the extracted interstitial water as a function of the age of the dumped ash for the dry ash dump revealed that pH of the top ash layers of various cores stabilises at $\approx 8-9$ as the fly ash ages. This indicates the chemical weathering of the ash had reached the region where dissolution of aluminosilicates controls the pH of

the pore water (Gitari *et al.*, 2006). Weathering of the cores was observed to follow a similar trend. The pH profile of the various cores indicated that contact with atmosphere and consequent ingress of CO_2 and leaching by percolation of rainwater through the dump had a great effect on the weathering of the disposed fly ash. The greatest weathering was observed to take place at the top layer (0.55-3m depth) in the older cores (15 years and older), showing that infiltration of rain water has a profound effect on the decrease of the pore water pH. This would probably be due to rapid dissolution and initial rapid flushing out of the fly ash of the soluble species that also act as pH buffering constituents. The implications of these results are that soluble fly ash components are highly mobile. Thus run off or permeates from the dump will be immediately enriched in these soluble contaminants.

XRD analysis of surface samples taken from the surface ash dump layers exposed to the atmosphere at the dry ash dump revealed the formation of either gypsum or calcium sulphate hydrate ($CaSO_4 \cdot 0.6H_2O$). It should be noted that from the moment the fly ash comes into contact with the atmosphere, ingress of CO_2 will lead to reaction with the buffering components such as CaO and subsequent conversion into carbonates. This would further explain the decrease in pore water pH of the weathered sections of core samples in comparison to the pH of fresh ash extracts.

Analysis of the extracted pore water in each of the different ash cores at a specific depth profile reveals that many elements were mobile and are moving through the ash in a progressive leaching pathway. The elements can be roughly grouped into two classes. Species such as Al, Cr, Si, B, Sr, Mg, Na, K, Ca, Cl-, SO_4^{2-} and NO_3^- were observed in the pore water of all cores. Species B, Sr, Mg, Al, Na, K, Ca, Ti, Ba, Pb, Cr, Cl- and SO_4^{2-} show a similar general trend in each of the ash cores at a specific depth profile, being highly weathered in the top layers of the cores and accumulating at about 6-10 metres down the core profile. Concentrations in pore waters at a core depth of about 6-8m ranged from 200mg/L for Na; 80 mg/L for Ca down to 30 mg/L for K. Na, Mg, K, Ca and SO_4^{2-} trends closely resemble each other indicating that these species could be present as soluble sulphate salts. These elements are highly mobile. Ba, Pb, Se, Fe, V, As, Zn, Cu, Ni and Ti were generally present in low concentrations in pore waters and Pb species present in the cores did not weather to any significant extent.

A significant decrease in levels of almost all mobile contaminant species was observed in pore waters of the cores sampled at the deepest levels of the ash dump which is in direct contact with lateral flows occurring at the contact point with the water table level present under the ash dump, indicating the very likely continuous elution of contaminants into ground water after permeation through the ash dump.

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