

Chemical Weathering In A Dry Ash Dump: An Insight From Physicochemical and Mineralogical Analysis Of Drilled Cores

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ABSTRACT

A typical power station in South Africa that utilizes a dry ash disposal system produces 1.765 Mt of fly ash per annum. Fly ash is conditioned for dust suppression before being conveyed to the ash dumps with high saline effluent resulting from the pre-treatment of raw water for boiler feed. In the ash dumps it is further conditioned by irrigation with the high saline effluents, therefore the ash dumps may act as salt sinks. This study is an attempt to understand the chemical weathering of the effluent conditioned fly ash in a dry disposal scenario. A combination of leaching tests was performed for fresh ash and drilled cores obtained from various sites on the dump to estimate the highly leachable species. Results from DIN-S4 tests of the fresh ash reveal that Ca, K, Na, Mg, Ba, SO₄²⁻, Se, Mo and Cr are highly leached from fresh fly ash. 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 cores obtained from areas of the dump that were older (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 drilled cores per depth profile indicated the mobility of several elements through the ash. Increased cation exchange capacity at 4-5 m depth suggests a transient mineralization zone. Darcy tests reveal that high concentrations of salts are mobilised from the initial flush of water through the ash cores during leaching. However a significant amount of the soluble salts may remain immobile as long as the ash dump does not come into contact with infiltrating water or lateral flows of groundwater. Contact of the ash with water is observed to be a crucial factor in the mobilization of constituents of the ash or of the brine used for irrigation with time. A combination of leach and hydraulic tests revealed that a dry ash dump does not act as a sustainable salt sink and evaluation of the hydrogeology of the disposal site is thus essential before dumping the ash.

KEYWORDS: Weathered fly ash, pore water, X-ray diffraction analysis, DIN-S4 test, TCLP, Cation Exchange Capacity

INTRODUCTION

South Africa is largely dependent on the combustion of coal for power generation and uses more than 100Mt of coal per annum.¹ This in turn leads to the generation of approximately 20 Mt of fly ash annually out of which only 5% of this is currently utilized, the rest being disposed of in ash dams, landfills or ponds.² 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. In the wet disposal, the ash is mixed with wastewater such as highly saline effluents generated from water treatment processes such as electro dialysis reversal (EDR), tubular reverse osmosis (TRO) and spiral reverse osmosis (SRO) to produce a slurry with controlled density that is then hydraulically transported to the ash dams. The slurry is allowed to settle and the ash-water is either drained away via a penstock to clear ash effluent dams, or percolates through the ash dam and is collected in a toe drain. In the dry disposal system, the fly ash is conditioned with waste water such as the highly saline effluents (16%) and is then conveyed to a disposal site where it is compacted and conditioned further with brine water.

The power station under 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 SRO and EDR generating large quantities of high salt loaded waste water. Fly ash from the precipitators is conditioned with the high saline waste water (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 salt sinks.

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. 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 CO₂ from the atmosphere over time. 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.

This study is an attempt to understand the chemical weathering and species mobility in the high saline effluents conditioned weathered ash. Several techniques were employed to achieve these objectives, a combination of leaching tests (DIN-S4), Darcy tests for fresh and weathered ash was employed to evaluate the highly leachable fraction. 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. Their mineralogical analysis by depth coupled to chemistry of extracted interstitial or pore water studies and fractionation by sequential extraction was applied to increase our understanding of the mobility of contaminants under disposal conditions. An XRD mineralogical profile of a wet ash dump was also included for comparison. The generated data will be applied as input for reactive transport modeling through the ash dumps in the second phase of the study.

Material and Methods

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 CO₂. 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.

Coring and drilling at the dry ash dump

A geophysics resistivity survey profile was utilized in selecting the drill site at the ash dump (Fig 1).

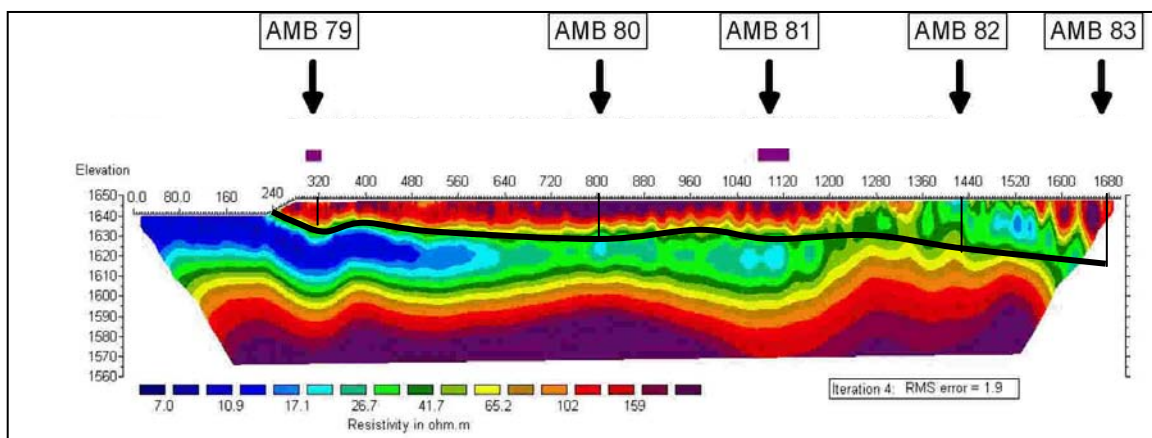


Figure 1: Approximate borehole positions in relation to the electrical resistance profile results. The black line represents the inferred ash/bedrock contact.

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.

Total Acid Digestion of Fly Ash samples

Total acid-digestion was carried out according to Jackson and Miller (1998)³ 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.

DIN-S4 Leaching Test

The water soluble fractions of the fly ashes were determined by employing the German standard leaching test DIN-S4.⁴ 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.

Toxic characteristic Leaching procedure (TCLP)

The method involves a preliminary evaluation procedure which was done to determine whether to use a sodium acetate buffer solution having a pH of 4.93±0.05 or an acetic acid solution having a pH of 2.88±0.05. This preliminary procedure was performed by placing 5.0g of the fly ash sample into a 500ml beaker. 96.5ml of de-mineralized water was added to the sample in the beaker, covered with a watch glass and stirred vigorously for 5 minutes with a magnetic stirrer. The pH was measured and was found to be higher than 5, then, as described by the method, 3.5ml 1M HCl were added and stirred briefly for 10 minutes. At the end of the preliminary test, the pH of the suspension was more than 5, and therefore acetic acid solution having pH of 2.88 was used for the leaching of the fly ash samples based on the recommendation of the leaching procedure.

For the main TCLP test, 100g of each of the fly ash samples were weighed into the extraction bottles and 2L of the acetic acid solution was added. The mixture was agitated at 30rpm for 20 h at 23±2°C. At the end of the agitation the solid was separated from the leachate by filtration using 0.45µm membrane filter. The pH was measured, EC and the TDS of the filtrates were measured. Aliquot samples from the filtrates were taken and treated accordingly and stored at 4°C for the analysis of metal concentrations.

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).⁵ 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.

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).⁶

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: $\text{Na}_2\text{CO}_3/\text{NaHCO}_3$).

Darcy Tests on the weathered ash dump Cores

The aim of a Darcy test is to obtain hydraulic conductivity of the consolidated fly ash core obtained from the drilling. The Darcy tests can be conducted under controlled laboratory conditions on the undisturbed samples. Six different types of ash core were subjected to Darcy tests. The sample preparation included the waterproofing of the sides of the core and the capping of the cores to confine flow through the ash cores. For accurate results, no leaking of water outside the core was allowed. The waterproofing and capping of the porous core to control the flow of water was a major challenge.

Salt Leach Tests on the weathered ash dump cores

The salt leach test was done using the core as for the Darcy experiments. The Electrical Conductivity (EC) of water was measured at the outflow point of the Darcy setup. After every hour a water sample was taken and the electrical conductivity of the sample was obtained. The measurements of the electrical conductivity were obtained by using a Martini (EC 59) instrument. The salt leach test provided us with information on the ease with which the salts captured in the core can leach from the intact ash core due to the movement of the passing water.

Results and discussions

Chemical and Physical Characterisation of the Fly Ash

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. Mineralogical evaluation by XRD (Figure 4) revealed that major crystalline mineral phases are quartz (SiO_2) and mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$). Low intensity lime and calcite peaks are also observed. No significant change in mineralogy is observed for the dry ash dump by depth in contrast to the wet ash dump cores in which new mineral phases were observed at 24m depth. Presence of water seems to accelerate the weathering and transformation of the ash components into new mineral phases. Chemical analysis (Table 1) shows the fly ash contains high concentrations of SiO_2 , Al_2O_3 and Fe_2O_3 as the major constituents. The fly ash seems to be enriched in Sr and Ba. The acid-digestion results (Tables 2 and 3) 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.

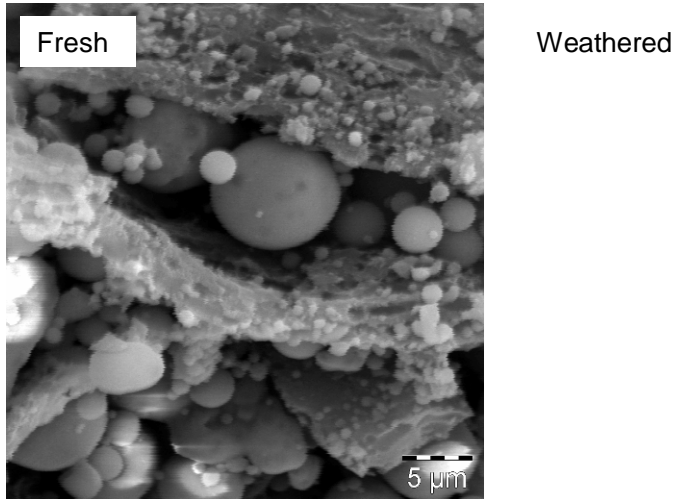


Figure 3: SEM micrograph of fresh and weathered dry ash dump coal fly ash

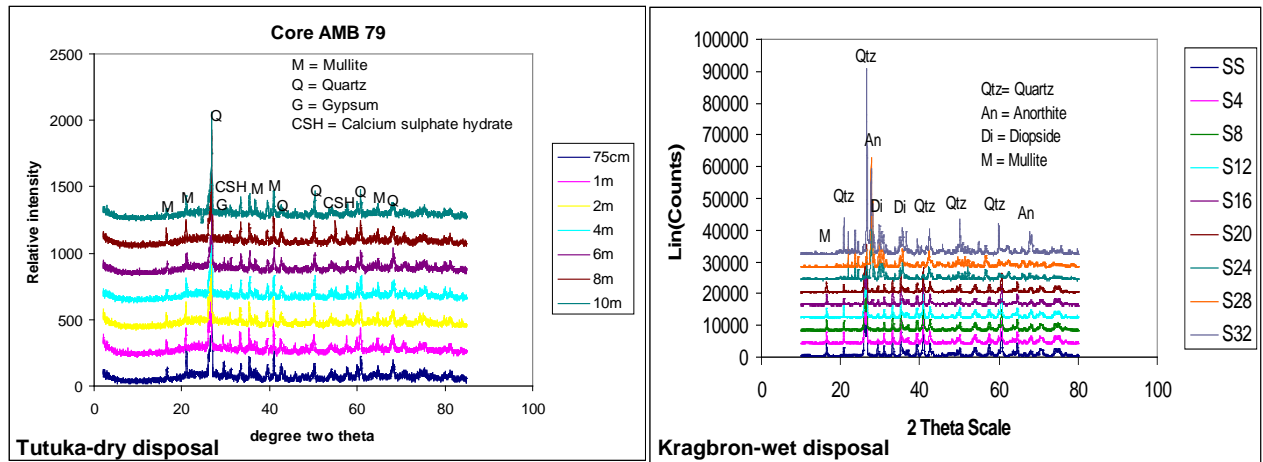


Figure 4: XRD spectra of dry ash dump samples by depth and wet ash dump.

Table 1: 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

Short term dissolution tests

DIN-S4 and TCLP leaching tests

DIN-S4 leaching test using different liquid/solid (L/S) ratios was carried out to assess the concentrations leached into solution and the water soluble fraction for dry ash dump samples. 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 similar L/S ratios (10:1 and 20:1) to assess the effect of low pH leachant on the leachability of species. The results for DIN-S4 and TCLP tests are presented in Table 2.

Table 2: DIN-S4 and TCLP tests showing the concentrations of major and minor elements (mmol/L), pH, EC (mS/cm), TDS (ppt) and alkalinity (mmol/L CaCO₃) at two liquid/solid (L/S) ratios (*n*=3)

	DIN-S4 (mmol/L)			TCLP (mmol/L)	
	L/S 10:1	L/S 20:1		L/S 10:1	L/S 20:1
Al	BDL	0.0019±6.48E-05	Al	BDL	0.016±9.54E-04
As	BDL	BDL	As	0.058±4.43E-03	0.0912±1.08E-02
Ba	0.0052±1.78E-03	0.006±1.27E-03	Ba	0.0011±2.98E-04	0.0026±2.44E-04
Cd	BDL	BDL	Cd	BDL	BDL
Co	BDL	BDL	Co	BDL	0.00016±1.54E-05
Cr	0.0069±4.97E-04	0.0042±8.20E-05	Cr	0.012±1.18E-03	0.0082±7.29E-04
Cu	BDL	BDL	Cu	0.000035±0.00E+00	0.00098±1.48E-04
Fe	BDL	0.00016±2.20E-05	Fe	0.000071±1.03E-05	0.00012±1.09E-05
Mn	BDL	BDL	Mn	BDL	0.019±1.48E-03
Mo	0.00097±7.91E-05	0.00057±2.81E-05	Mo	0.0011±8.71E-05	0.00055±5.68E-05
Ni	BDL	BDL	Ni	BDL	0.000702±4.72E-05
Pb	BDL	BDL	Pb	BDL	BDL
Se	0.000099±1.50E-06	0.000104±9.80E-06	Se	0.00046±5.89E-05	0.00032±2.17E-05
V	BDL	BDL	V	0.012±1.24E-03	0.0089±8.33E-04
Zn	BDL	BDL	Zn	0.000074±0	0.00065±9.71E-05
B	0.12±2.10E-03	0.082±4.98E-03	B	0.96±3.68E-03	0.59±3.65E-03
Ca	22.82±1.46E+00	12.46±1.57E-01	Ca	55.61±5.09E+00	33.92±2.76E+00
K	0.035±6.11E-04	0.018±2.82E-04	K	0.039±1.62E-04	0.025±6.74E-04
Mg	0.0022±1.32E-03	0.0013±1.64E-04	Mg	6.41±1.35E-01	9.53±3.91E-02
Na	0.17±2.29E-03	0.075±5.58E-04	Na	0.19±2.53E-03	0.104±2.30E-04
SO ₄	2.38±2.44E-01	1.13±5.05E-02	SO ₄	5.91±7.43E-02	3.29±6.35E-02
pH	12.7±1.21E-01	12.56±0.00E+00	pH	9.98±5.77E-03	4.84±1.00E-02
EC	7.82±1.11E-01	5.14±1.02E-01	EC	6.59±4.62E-02	4.64±3.61E-02
TDS	4.07±6.03E-02	2.67±4.93E-02	TDS	3.44±1.53E-02	2.41±1.73E-02
Alkalinity	18.96±8.65E-02	11.96±1.80E-01	Alkalinity	38.021±2.10E-01	23.12±2.09E-01

BDL-below detection limits

The pH of the leachates are highly alkaline ranging from 12.56 to 12.7 for the two L/S ratios for the DIN-S4 test. A slight increase in pH is observed on doubling the amount of fly ash in the mixture. 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.⁷ The corresponding EC values ranged from 5.14 - 7.82mS/cm for both L/S ratios indicating large quantities of

soluble species have been released from the fly ash. The fact that doubling the quantity of fly ash did not lead to doubling of alkalinity means some of the alkalinity is consumed at the high pH. This is probably through carbonation due to ingress of CO₂ at alkaline pH. The buffering effect is observed in the final pH achieved for leachates in TCLP tests. The pH ranges from 9.98 for L/S 10:1 and 4.64 for L/S ratio 20:1. At a lower L/S ratio higher alkalinity is released. At both L/S ratios 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. The concentration of these species in the leachates is observed to double as the L/S ratio is halved which has implications on the ash at disposal site that comes into contact with water. Concentrations of As, Cd, Co, Mn, Ni, Pb, and V were below detection limit in the leachates at both L/S ratios while for Cr, Al, Cu, Fe, Mo, Se and Zn concentrations were very low or near detection limit. 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. 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.

Calculated Soluble fractions

Calculated soluble fraction leached in DIN-S4 tests for fresh Ash is presented in Table 3

Table 3: % leached amounts in DIN-S4 for fresh fly ash (mmol/kg dry mass)

Species	Total acid-digestion	DIN-S4		Soluble fractions %
		L/S 10:1	L/S 20: 1	
Li	25.94	ND	ND	
P	49.18	ND	ND	
V	2.43	BDL	BDL	
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
Sr	8.49	ND	ND	
Mo	0.079	0.0097	0.011	12.28-13.92
Cd	0.002	BDL	BDL	
Ba	5.42	0.052	0.12	0.96-2.21
Hg	0.0026	ND	ND	
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
Si	12062.66	ND	ND	
SO ₄	1574.28	23.8	22.6	1.44-1.51

*soluble fraction calculated from XRF data since the ICP-AES/MS data from total acid digestion was too low compared with XRF and literature values for class F fly ash.

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. 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 SO_4^{2-} (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.

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.

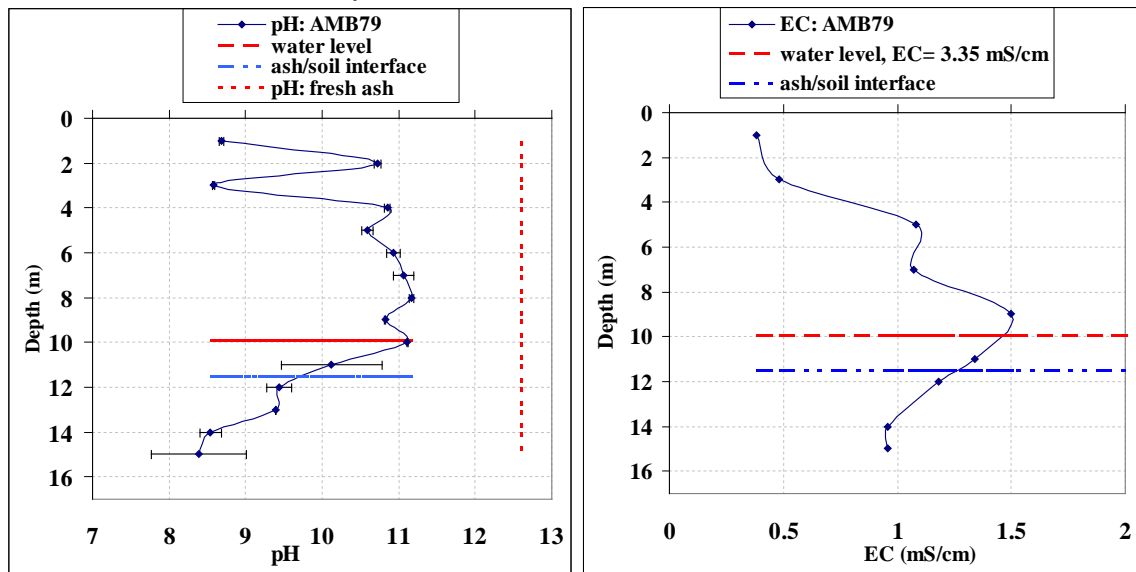


Figure 5: pH and EC of pore water versus depth (m) for AMB79 core (error bars represents 1 SD below and above the mean, n=3).

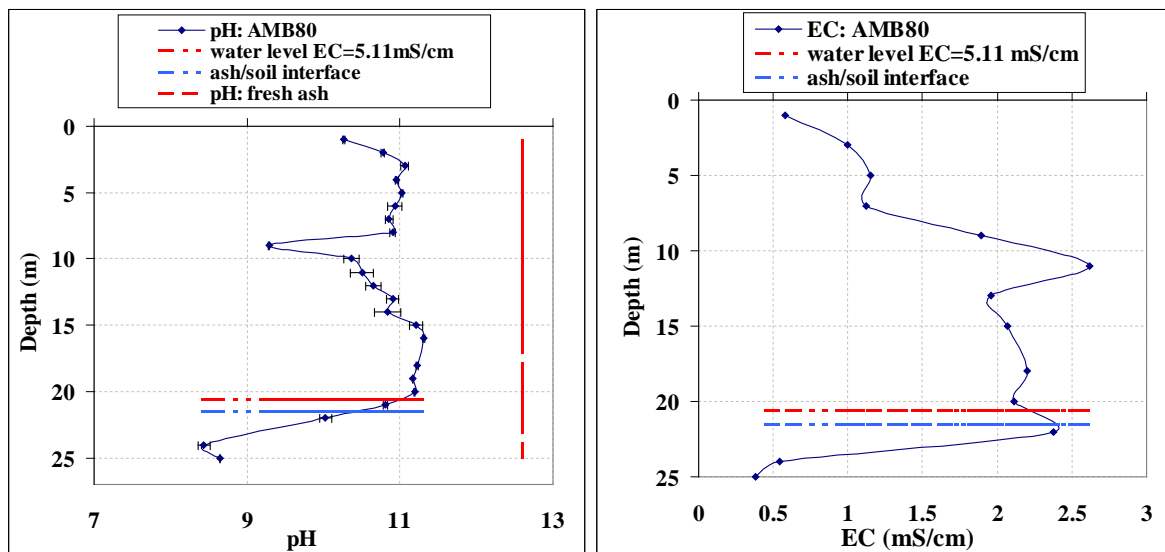


Figure 6: pH and EC of pore water versus depth (m) for AMB80 core (error bars represents 1 SD below and above the mean, n=3).

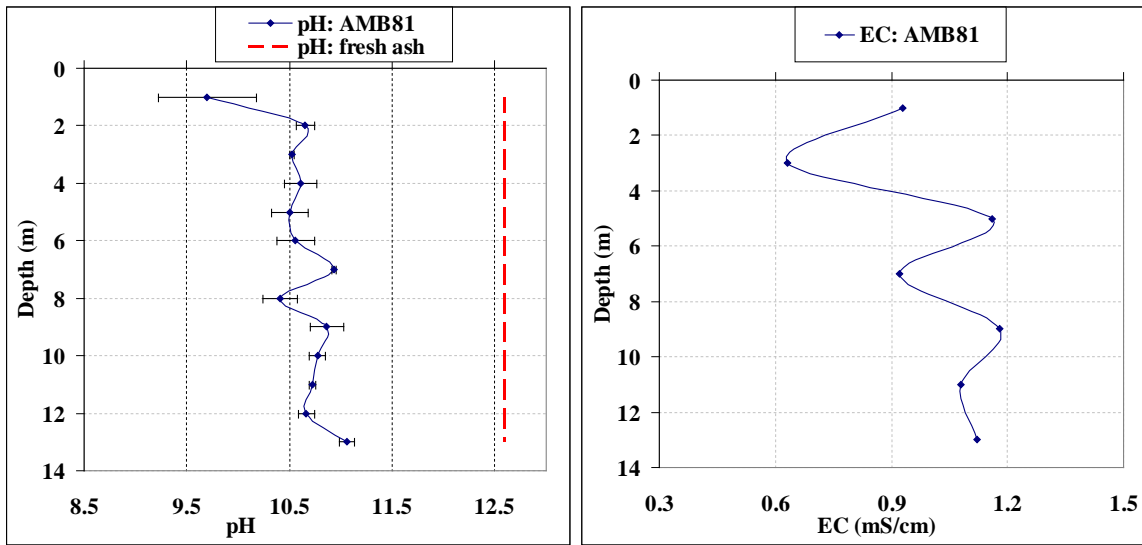


Figure 7: pH and EC of pore water versus depth (m) for AMB81 core (error bars represents 1 SD below and above the mean, n=3).

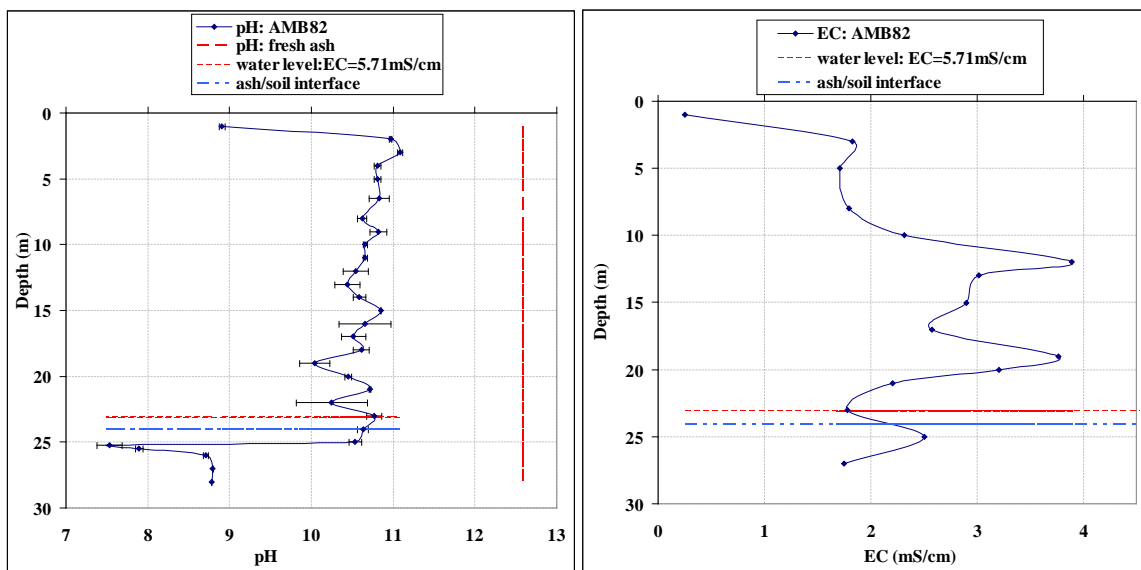


Figure 8: pH and EC of pore water versus depth (m) for AMB82 core (error bars represents 1 SD below and above the mean, n=3).

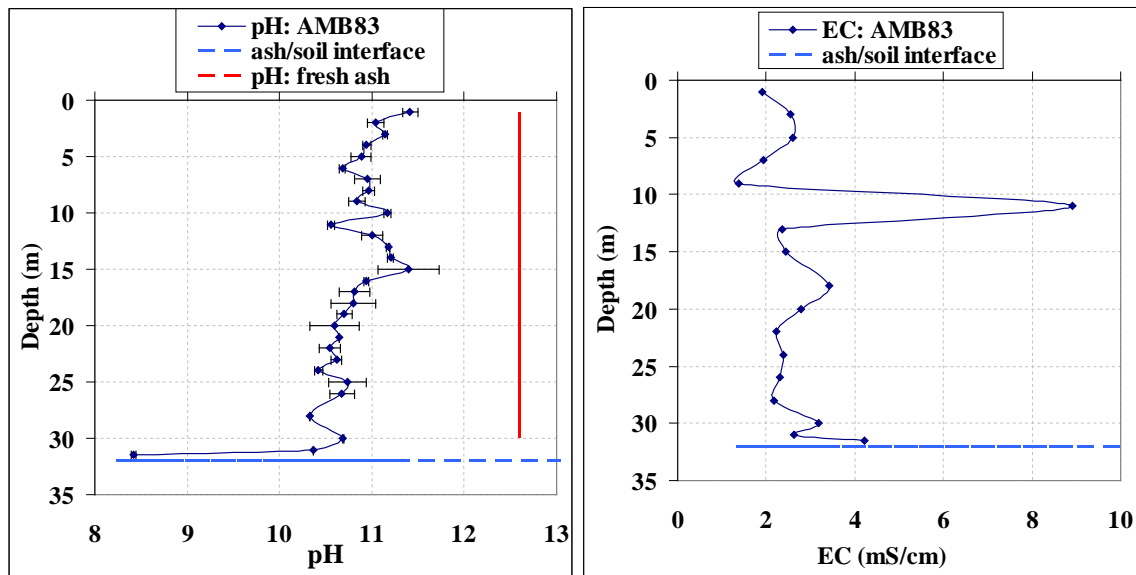


Figure 9: pH and EC of pore water versus depth (m) for AMB83 core (error bars represents 1 SD below and above the mean, n=3).

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. 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.

Chemical Characterization of the Extracted Interstitial pore water of the drilled ash dump core

The pore water chemistry data is presented for the core AMB79 (20 years old) 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.

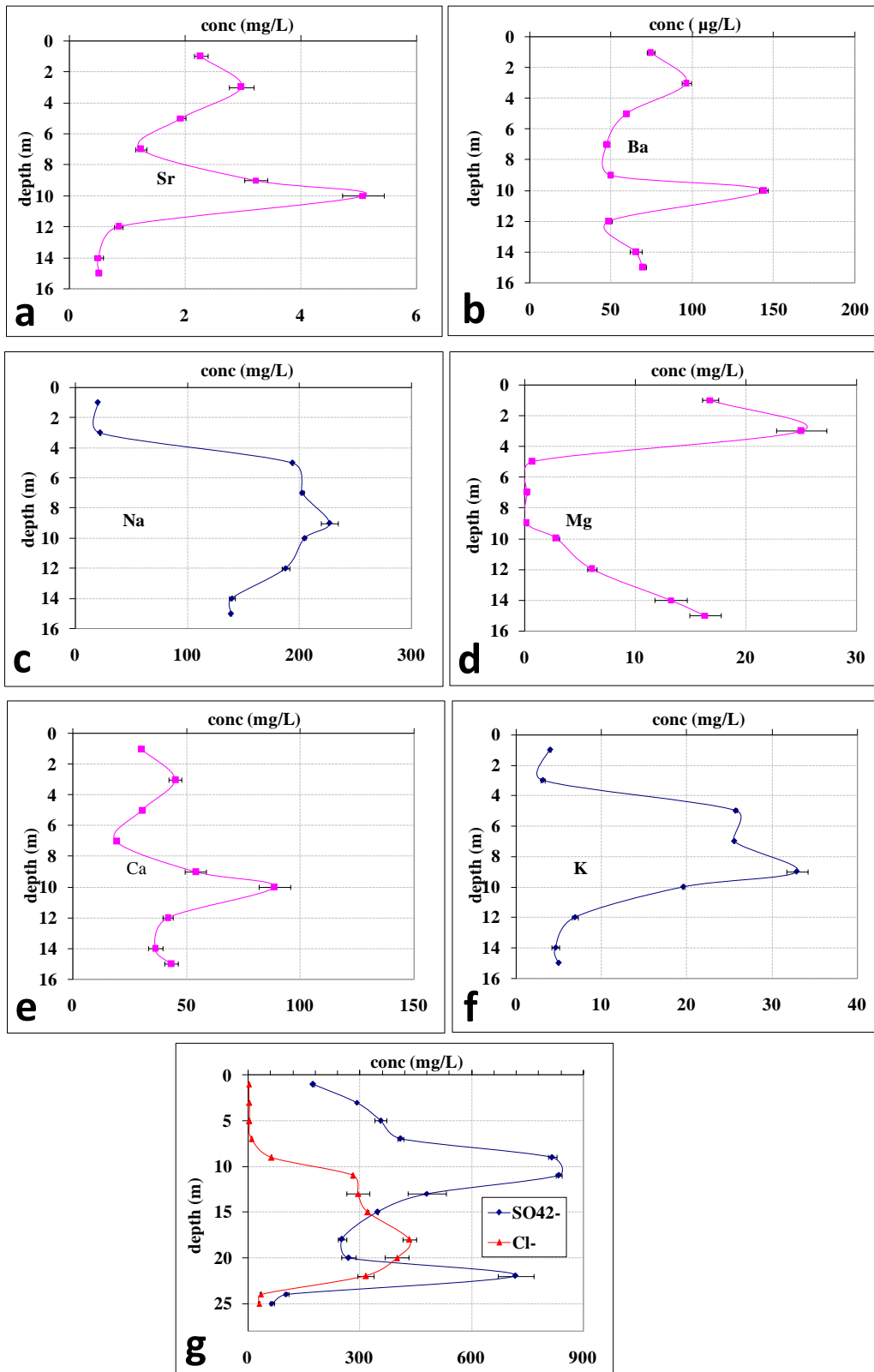


Figure 10: Concentration of alkali, alkali earth metals, sulphates and chlorides by depth for the core AMB79

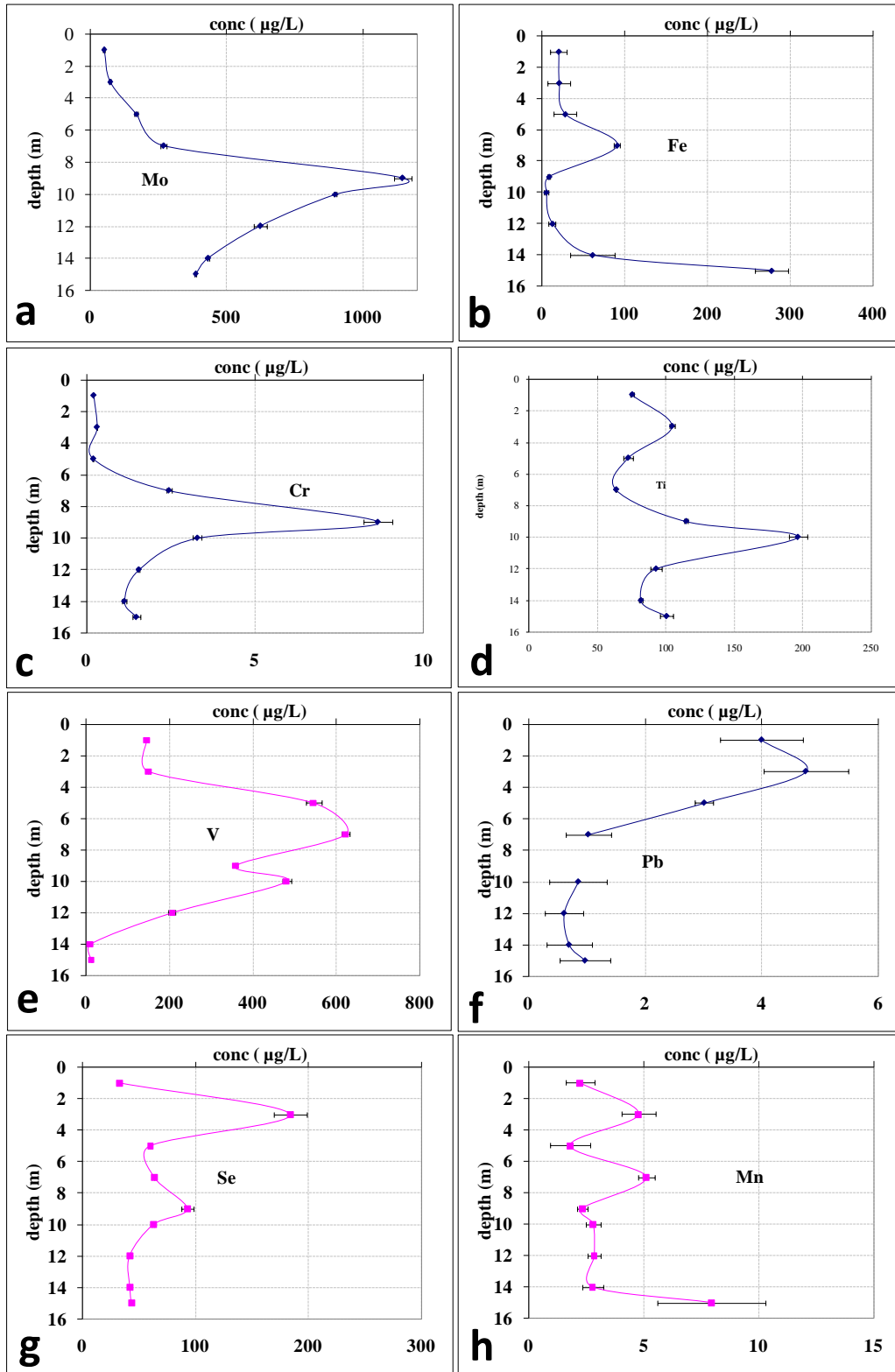


Figure 11: Concentration of oxyanions and selected heavy metals by depth in the pore waters for the core AMB79.

Al-Si Mineralization and Cation Exchange Capacity (CEC)

Figure 12 depicts the variation of the cation exchange capacity and Al, Si in the pore water by depth for the core AMB79.

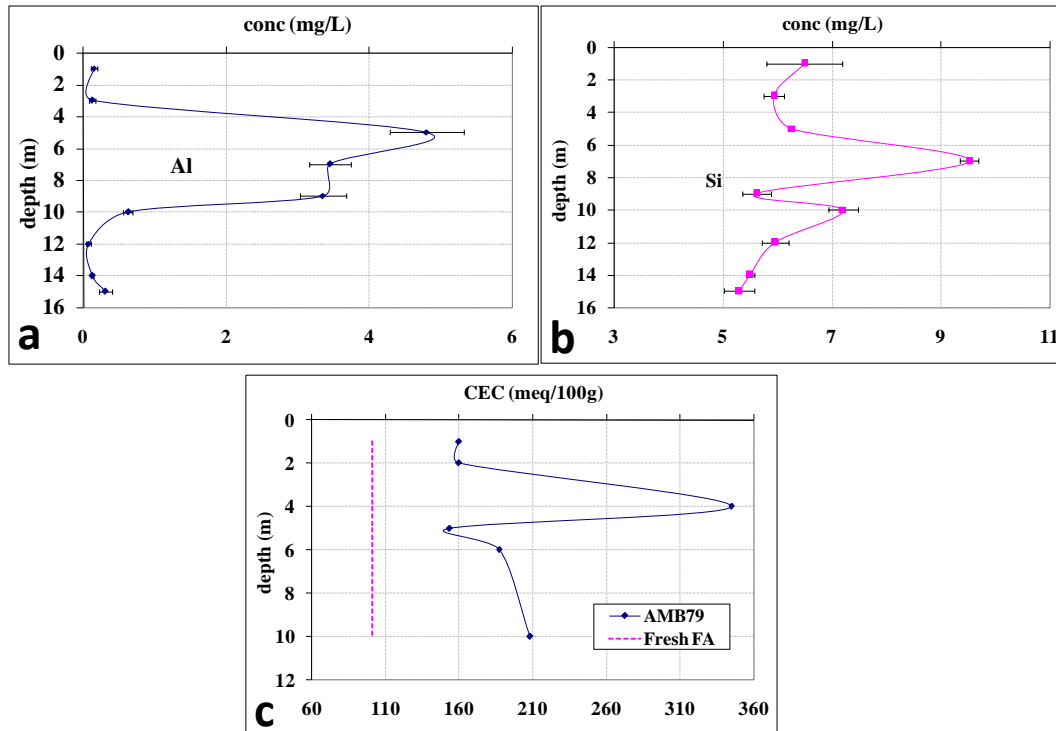


Figure 12: Concentration profile of Al, Si in the pore waters and CEC by depth for the core AMB79.

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 AMB79 water soluble fraction which suggests some kind of transient mineralization at this depth. Zevenbergen et al (1999)⁸ 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.

Ash Hydraulic Properties

Hydraulic Conductivity

Figure 13 shows the hydraulic conductivity of the cores at selected depths of the ash dump. Initial hydraulic conductivity for all the ash cores tested was high and a drop in

hydraulic conductivity is consistently observed for all the cores with the 40 hour test period. The hydraulic conductivity profile suggests a clay like swelling and reduction in flow after the initially high levels.

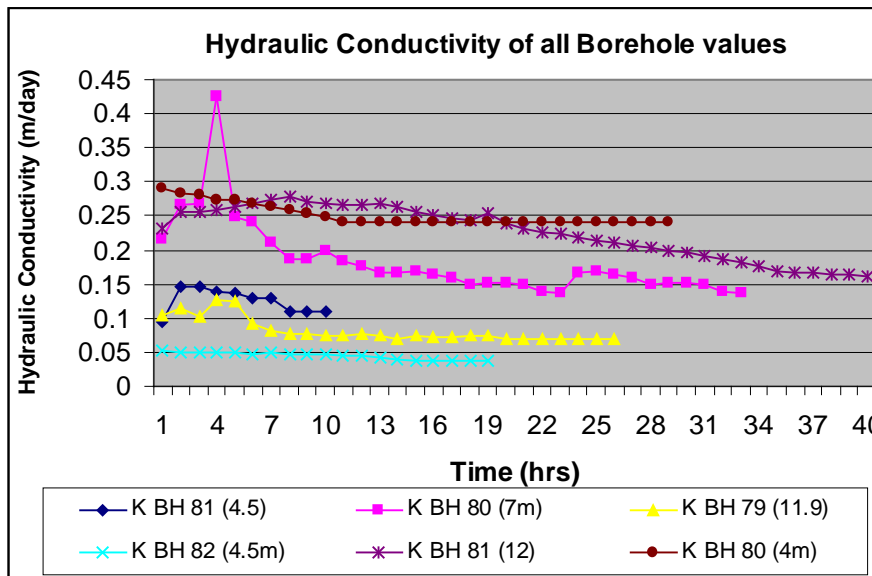


Figure 13: Hydraulic conductivity of the ash cores at selected depths.

Table 4 depicts the initial and steady state hydraulic conductivity of the various ash cores at selected depths.

Table 4: Initial and steady state hydraulic conductivity at selected depth

Core Name	Core Texture	Hydraulic K Initial peak (m/day)	Hydraulic K Steady State (m/day)
BH 81 (4.5m)	Fine-Medium	0.15	0.11
BH 80 (7m)	Very Coarse	0.425	0.15
BH 79 (11.9m)	Medium	0.13	0.07
BH 82 (4.5m)	Fine	0.06	0.04
BH 81 (12m)	Coarse	0.27	0.16
BH 80 (4m)	Fine-medium	0.29	0.24

Field infiltration methods were also utilized to determine the hydraulic conductivities of cores at different depths (double ring and mini-disk infiltrometers). Results obtained (Table 5) reveal the texture of the ash has an effect on the hydraulic conductivity of the ash at a disposal scenario.

Table 5: Summary of Hydraulic Conductivity values for the ash cores using field infiltration methods.

	Method	Number of tests	Minimum Value (m/day)	Maximum Value (m/day)
Fresh Ash	Minidisk	4	1.83	8.25
	Double Ring	4	2.95×10^{-1}	6.39×10^{-1}
Hard ash	Minidisk	8	5.44×10^{-1}	6.71×10^{-1}
	Double Ring	4	2.84×10^{-2}	9.84×10^{-2}
Reworked	Minidisk	4	1.86×10^{-1}	8.36×10^{-1}
	Double Ring	6	1.99×10^{-2}	2.95×10^{-1}
Clay top soil	Double Ring	4	4.16×10^{-2}	1.23
	Minidisk	2	6.32×10^{-2}	6.2×10^{-1}

Salt Leach tests

Figure 14 depicts the salt leaching profile as a function of time for selected ash cores measured as electrical conductivity. High initial concentrations of salts are recorded with a reduction in concentration over time. Similar trends are observed in all the cores.

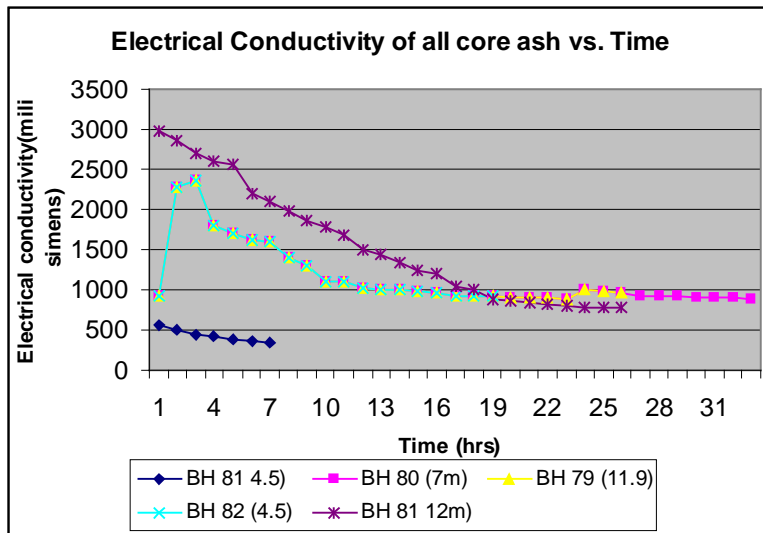


Figure 14: Salt leaching profile from various ash cores at selected depths.

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.⁹ 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 ($\text{CaSO}_4 \cdot 0.6\text{H}_2\text{O}$). 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⁻, SO₄²⁻ and NO₃⁻ were observed in the pore water of all cores. Species B, Sr, Mg, Al, Na, K, Ca, Ti, Ba, Pb, Cr, Cl⁻ and SO₄²⁻ 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 SO₄²⁻ 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.

The Darcy tests on the ash cores suggested that water flow through the ash has high initial hydraulic conductivity with a reduction in hydraulic conductivity over time hinting to clay like swelling and reduction in flow. High concentrations of salt were also mobilised from the initial flush of water through the cores. Both the hydraulic conductivity and salt concentration decreased over time to reach a steady state.

The hydraulic conductivity values obtained on the ash dump using tension infiltrometers and double-ring infiltrometers suggests that the texture of the ash plays a role in the hydraulic properties. Fine textured ash and hard pan ash had K-values in the order of 10⁻² m/day. Undisturbed ash had a K-value of about 10⁻¹ m/day. Very coarse consolidated ash, reworked ash and fresh ash have the highest K-values at a magnitude higher (between 1 and 10 m/day) compared to finer texture ash cores. The hydraulic and salt leach tests show initial high rates of flow through and salt leaching from the ash cores and a reduction to a steady state thereafter. The leaching of the salts did not approach zero during the test periods.

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