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Mobility and Transport of Inorganic Species in Weathered Hydraulic Disposed Coal Fly Ash: An Insight from Geochemical Fractionation and Statistical Evaluation

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Abstract

A large volume of coal fly ash generated through combustion process has raised environmental concerns due to possible release of potentially toxic species to the surface and groundwater systems. The chemical partitioning and mobility of elements in the hydraulic disposed ash dump was investigated using modified sequential extraction scheme. The geochemical distribution of the investigated elements in 33 drilled core samples was determined by x-ray fluorescence and inductively coupled plasma mass spectrometry. The ternary plot of major elements as determined by XRF showed that hydraulic disposed ash cores are silicic, ferrosilicic and ferrocalsilicic in chemical composition. The relationship between SiO₂ and chemical index of alteration (CIA) showed low, moderate to high degree of weathering. These chemical compositions and degree of chemical weathering depend on the ash sampling point and ash interaction chemistry. The Na⁺ and K⁺ soluble salts showed evidence of leaching and downward migration in the water soluble fraction indicating that the hydraulic disposed ash dump is not a sustainable salt sink. The geochemical partitioning reveals that mobility and transport of potentially toxic metal species are governed by the pore water pH, ash interaction chemistry and the

sampling point of the ash cores. The chemical interaction of drilled core ash with the ingress CO₂ and percolating rain water led to dissolution and co-precipitation of soluble major components in fly ash. This had led to incoherent patterns of elements in carbonate fraction of the ash cores.

Key words: Modified sequential extraction; Hydraulic disposed ash; Chemical index of alteration; Pore water pH; Ash interaction chemistry; Moisture content; Chemical weathering

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INTRODUCTION

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The steady increase in demand for electricity in modern society has resulted in the burning of large quantities of coal to generate electricity. World coal consumption is expected to remain on the increase by 49 % from 2006 to 2030 according to the projections made in the IEO2009 reference case (IEO, 2009). Presently, South Africa accounts for 92 % of the coal consumed in Africa and it is expected to continue to account for much of the continent's total coal consumption over the projected time (IEO, 2009).

The process of coal combustion produces a range of coal combustion by-products (CCB's). These include (a) Fly ash, (b) Bottom ash, (c) Boiler slag-molten ash and (d)

Gypsum which is formed from an oxidizing and calcium-based flue gas desulphurization process (Yazici, 2007). Some of the organic residues left include poly-chlorinated dibenzodioxins and dibenzofurans (Fytianos and Schroder, 1997). The relative amount of each residue depends on the power plant configuration, the emission control devices available and the parent coal (Page et al., 1979).

Fly ash, one of the CCB's, is the fine portion of the coal combustion ash that is entrained in the hot flue gas as it leaves the combustion chamber. It is collected by means of electrostatic precipitators or fabric filters and constitutes about 70 % of the total amount of residue generated in coal fired power plants (Fulekar and Dave, 1986).

ESKOM generates approximately 36.7 million tonnes of coal combustion by products from coal-fired power stations in South Africa annually. Of this, 1.84 million tonnes or 5 % of the ash produced is utilized in one form or another. The remaining 34.86 million tonnes of ash is disposed of by more traditional means (Petrik et al., 2003; Eskom Abridged Annual Report, 2009) such as dry dumping or by hydraulic deposition into dams. Fourie et al. (1997) observed that a marked hardening of the hydraulically deposited fly ash occurs, producing a very erosion-resistant surface. Fly ash accumulates in large volumes and becomes a significant waste disposal problem because of the inconsistent trend of its utilization (Adriano et al., 1980). The dangers of this practice on the environment include wind and water erosion and leaching of substances (e.g. salts, heavy metals) into the surface and groundwater systems. Percolating rain water as well as waste water from the ash slurry leaches toxic elements into the surface and groundwater in the vicinity of the ash dumps. Fly ash particulates when released into the atmosphere can cause irritation or inflammation to eyes, skin, throat and upper respiratory tract of humans (Haynes, 2009). Akinyemi (2011c) found that toxic elements concentrate in the insoluble fraction (residual) of core ash samples. The author concluded that dust from the weathered dry disposed ash dump would be toxic to human health (Akinyemi, 2011c).

A variety of physico-chemical forms in the fly ash can scavenge both major and trace elements as the ash ages with time. These forms include: exchangeable, bound to carbonates, bound to Fe-Mn oxides, bound to organic matter, and residual (Tessier et al., 1979). The idea of the sequential extraction scheme is the partitioning of a solid material into specific phases or fractions that are selectively extracted, i.e. liberated and released into solution (leached) along with the associated trace metals. In this procedure, appropriate reagents are used in the order of increasing strength (Tessier et al., 1979; 1992; Horowitz, 1991). The actual difficulty of the sequential extraction procedure is that the extraction from each step depends on the efficiency of previous step(s), and some factors such as leaching time, liquid-solid ratio, and strength of the chemical reagent (i.e. pH of the medium)

can influence the extracted amount of metals (Chang et al., 2009).

Despite the above highlighted drawbacks/pitfalls of chemical sequential extraction scheme. Rao et al. (2008) concluded that there are lot of advantages of chemical sequential extraction and still enormous scope for further research and developments in these areas because pollution sites are increasing throughout the world and there is urgent need of methods for faster, reliable and cost-effective pollution assessment so that suitable remedial measures can be taken up on priority basis at an appropriate time.

Sequential extraction procedures have been applied to sediments (Mester et al., 1998; Petit and Rucandio, 1999), contaminated soils (Campos et al., 1998), incinerated sludge ash (Fraser and Lum, 1983), and bottom ash and fly ash from municipal solid waste incinerators (MSWI) (Bruder-Hubscher et al., 2002; Smeda and Zyrnicki, 2002; Smichowski et al., 2008). Recently, this step-by-step sequential extraction procedure was applied to determine the distribution of various elements in a weathered dry disposed coal fly ash (Akinyemi et al., 2011b).

The wet, disposed weathered ash core was hydraulically transported and disposed in slurry form at the ash dumps at 70-80 % liquid/solid (L/S) ratio. The high saline effluents (i.e. Brine solutions) were used to hydraulically transport the ash to the ash dams. Excess water on top of the ash dams is decanted through a penstock arrangement, draining water into ash water return dams. From there, water is returned to the power station to pump more ash. Wet disposal of FA (fly ash) is a simple operation and has minimal effect on the local air quality. On the contrary, the amount of water required forming the FA slurry is considerable and recirculation of water is a costly practice. During wet ash handling, heavy metals (which are toxic in nature) leach from the matrix leading to change in the ash chemistry and ultimately pollute the environment. A major disadvantage of wet disposal is that it demands large areas of land, which are practically irretrievable for future use (Singh and Kolay, 2002). Eskom used brine to slurry the ash to the ash dumps; they also used it as repository for brine components, eventually as brine clean up mechanism, and as a method to recover water. The most recently dumped layer of ash in the study area is about 2-year-old (Ojo, 2009).

In the present study, the chemical partition, mobility and transport of elements were investigated in weathered drilled ash cores. The chemical partitioning of elements in weathered drilled cores was used to: i) understand the mineralogical association patterns of ash dump; ii) to identify and quantify the investigated elements in the physicochemical forms; and iii) to assess and reveal possible factors responsible for the mobility and transport of elements. Further, the multivariate approach (cluster and factor analysis) has been applied to understand the chemical weathering process and to assess its effect

over an extended period under a real hydraulic disposal condition.

1. MATERIALS AND METHODS

1.1 Sampling Technique and Sample Pre-treatment

Cores were drilled from weathered hydraulic disposed coal fly ash at Kragbron ash dump, Mpumalanga Province, South Africa. The details of sampling technique and sample pre-treatment are reported in our previous study (Akinyemi et al., 2011b).

1.2 XRF Analysis and pH of Interstitial Pore Water of Weathered Ash Cores

The detailed procedures used for study were reported in our previous study (Akinyemi et al., 2011a).

1.3 Moisture Content Determination

Moisture content is the quantity of water contained in a material such as soils and rocks. Physical properties such as weight, density, electrical conductivity can be influenced easily by the moisture content. Two methods are usually employed in the determination of moisture content. These are the thermo gravimetric and the loss on drying techniques. The loss on drying technique was employed in this study according to a previous study (Ojo, 2009). The moisture content of the ash samples were determined by oven drying pre-weighed samples taken at 1 m intervals down each of the ash cores for 12 hours at 105°C. The weight difference between the initial wet sample and the final dry sample was expressed as weight percent of the initial wet sample and reported as moisture content percent. The ash core samples for the rest of the determinations were air-dried and therefore moisture content was not used in weight % calculations. The other data is reported on a dry mass basis.

1.4 Cation Exchange Capacity (CEC)

The cation exchange capacity (CEC) of the core ash samples was determined by the ammonium acetate method using buffer at pH 8.2. 0.5 g of oven dried core ash samples were weighed into a 50 ml centrifuge tube and extracted using 25 ml aliquots of 1.0 M ammonium acetate. The mixture was shaken for 15 minutes and then centrifuge (at 3000 rpm) for 20 minutes. The procedure was repeated four times to give 100 ml of the supernatant. The supernatant was filtered through 0.45 µm cellulose acetate membrane. The concentration of the exchangeable cations (Ca²⁺, Mg²⁺, N⁺ and K⁺) was determined by inductively coupled plasma mass spectrometry (Agilent 7500ce). The results in ppm were then converted to meq per 100 g of sample following the method of Radojevic and Bashkin (1999).

1.5 Sequential Extraction Procedure

The modified extraction scheme adopted is a combination of the methods developed by Tessier et al. (1979) and Jegadesaan et al. (2008) with addition of the water soluble fraction. The details of selective sequential extractions procedure have been reported in our previous study (Akinyemi et al., 2011b).

1.6 Statistical Evaluation of Data

1.6.1 Data Treatment and Multivariate Statistical Methods

Multivariate statistical method was applied on the bulk chemical data (i.e. major oxides mass %) in weathered hydraulic disposed fly ash aged 35-years-old using IBM SPSS-19.0 statistical software. Varimax rotated factor analysis was performed on correlation matrix of rearranged data for hydraulic disposed weathered ash dump. The variance, cumulative and extraction sums of square loadings of the variables with Eigen values were computed. Rotation of the axis defined by factor analysis produced a new set of factors, each one involving primarily a sub-set of the original variables with a little overlap as possible, so that the original variables were divided into groups. The factor analysis of the present data set further sorted by the contribution of less significant variables (< 0.4 factor score). A varimax rotation (raw) of the different varifactors of eigen value greater than 1, were further cleaned up by this technique and in varifactors original variables participated more clearly. Liu et al. (2003) classified the factor loading as “strong”, “moderate” and “weak” corresponding to absolute loading values of > 0.75, 0.75–0.50 and 0.50–0.40, respectively.

Factor and cluster analyses were combined to assess the degree of major component matrix dissolution and determination of chemical processes. Hierarchical agglomerative clustering was performed on data normalized to zero mean and unit variance using squared Euclidean distances as the measure of similarity (Massart et al., 1988). Wards method was selected because it possesses a small space distorting effect, uses more information on cluster contents than other methods (Helena et al., 1999) and has been proven to be an extremely powerful grouping mechanism (Willet, 1987).

1.6.2 Pearson Correlation Coefficient

From an evaluation of the ICP-MS results on the SE leachates, environmental markers of the pollution trend could be identified. For each pair of variables, there is a calculated Spearman's rho and an associated p-value for testing the null hypothesis that the correlation is zero. In order to look for patterns by depth, we looked at the Spearman correlation coefficient between the recorded value and depth. A significant positive correlation would correspond to increasing response with increasing depth. A negative correlation would correspond to a decreasing response with increasing depth. The correlations were calculated for each element, age and solubility separately.

Consequently there are a large number of correlations to consider. In this study, we only looked at correlations significant at the 0.01 level.

Spearman's rho was calculated for the major and trace element concentrations in dry disposed fly ashes by age and depth using SAS 9.2 (SAS Institute Inc., Cary, NC, USA).

2. RESULTS AND DISCUSSION

2.1 XRF Results

The ternary diagram, Figure 1 (Roy & Griffin, 1982), showed that the brine impacted hydraulically disposed weathered ash core samples were sialic, ferrocalsialic and ferrosialic in composition. The ash core samples collected at the upper section (youngest section) of the ash dump are essentially Si and Al in composition (i.e. sialic). The middle and lower sections of the ash dump were ferrocalsialic and ferrosialic in chemical compositions. This indicates alteration in the lower section of the ash dump due to chemical interaction with the dolerite bedrock. This weathering could also be due longer time of interaction with the brine components in the pore water of the wet ash.

Figure 3 shows the middle and lower section had high moisture content indicating much of the brine effluent was still present in the pores of the disposed ash and this could greatly contribute to dissolution and precipitation over time leading to changing mineralogical composition with time. This trend is in accordance with the previous study carried out by Valentim and Hower (2010). The authors showed that the majority of Kentucky fly ash samples were sialic, sialic-ferrosialic or ferrosialic, depending on coal combustion temperature, the sampling point of the ash and ash interaction chemistry.

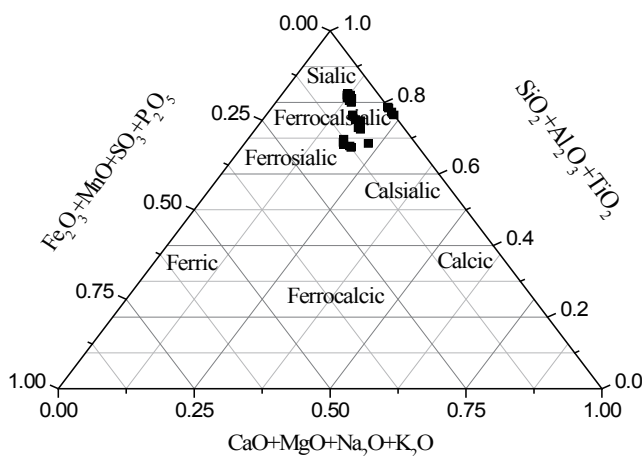


Figure 1
Ternary Oxide Plots for Classification of the 35-year-old Brine Impacted Hydraulic Disposed Ash Dump ($n = 2$)

In this study, we assumed the first factor is constant and that classification would depend on sampling point of the ash and ash interaction chemistry. The main inorganic elements found by XRF are Si and Al, suggesting an abundance of quartz and aluminosilicate, the other inorganic elements is much less abundant.

2.2 Chemical Alteration of Hydraulic Disposed Ash Dump

According to Nesbitt and Young (1982), a good measure of the degree of weathering can be obtained by calculation of the chemical index of alteration (CIA) using molecular proportions.

$$CIA = [Al_2O_3 / (Al_2O_3 + CaO + Na_2O + K_2O)] \times 100$$

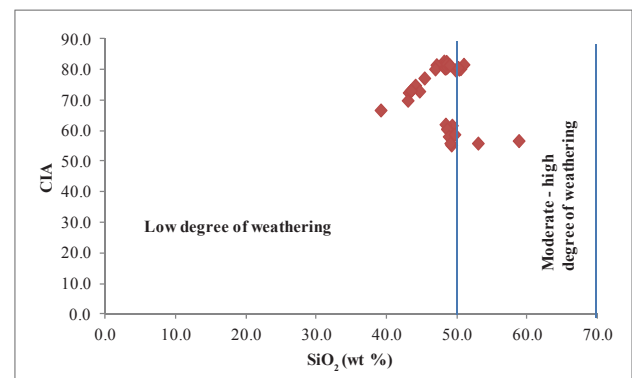


Figure 2
Relationship Between SiO_2 (wt %) and Chemical Index of Alteration (CIA) in Weathered Hydraulic Disposed Ash Dump ($n = 3$)

As a result, the chemical index of alteration (CIA) was calculated for 35-year-old ash cores. Figure 2 is a plot of CIA values against SiO_2 taken from mass % XRF data in hydraulic disposed ash dump. There is an obvious trend from relatively low values to progressively higher values in more intense chemically altered sections of the ash dump. All ash core samples from the top most part of upper (i.e. 0 - 2 m) and lower sections (i.e. 23 - 32 m) of the ash dump fall within the cluster showing moderate to high degree of chemical weathering.

On the contrary, some core samples in the bottom most part of upper section (i.e. 3-10 m) and middle section (i.e. 11-22 m) ash dump fall within moderate to high degree of weathering. Therefore, the middle section of the ash dump is the least leached. The sampling point, ash interaction chemistry with the transporting medium (i.e. brine), ingressed CO_2 from atmosphere and percolating rain water is responsible for the disparity in the degree of chemical weathering. The moderate to high degree of weathering in the top most part of upper and lower sections of the ash dump is due to over time flushing of soluble major components of the fly ash due to percolating effluents and rainwater. This would sequentially cause over time reduction in the pore water pH (Fig. 4) and

subsequently leaches inorganic species from the ash dump. Nevertheless a slight disparity in the low degree of weathering at the middle sections of the ash dump is due to differential dissolution of fly ash matrix. Conversely, an obvious disparity in the moderate to high degree of weathering at the top most part of upper section and lower section of the ash dump could be due to differential chemical interaction of fly ash with atmosphere and dolerite bedrock respectively.

2.3 Moisture Content and Cation Exchange Capacity Results

The determined moisture content and cation exchange

capacity (CEC) of hydraulic disposed ash core samples is shown in Figure 3. There is a significant increase in % moisture content for fly samples taken at 16 - 22 m depth. This could be due to downward migration of pore water as more effluents are applied on the ash dump for dust suppression. The relatively high moisture content at 16-22 m depth could be an indication of the reaction front as the pore water migrates downwards similar to plug flow in column set up. The middle section which is the reaction front these components react to form new phases that have increased surface area and CEC. These activities explained the lower surface area and CEC at the upper layer of the ash dump.

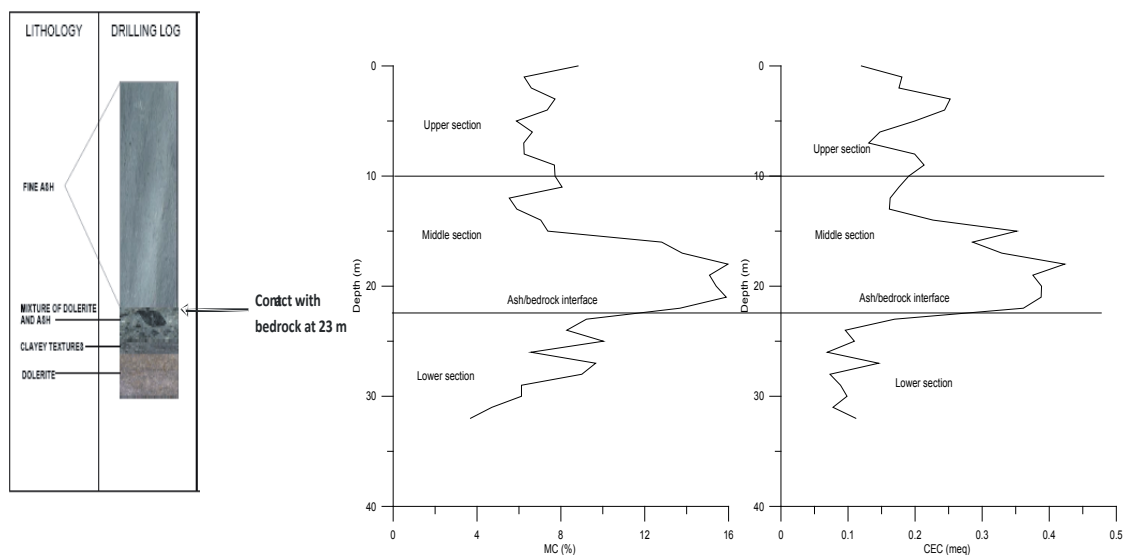


Figure 3
Relationship Between % Moisture Content and Depth of Dry Disposed Ash Dump ($n = 3$)

The uneven moisture content observed in the hydraulic disposed ash dump could be attributed to uneven ash placement conditions resulting in varying porosity due to ash packing density or varying ambient weather conditions during placement. The cation exchange capacity (CEC) and moisture content (MC %) showed relatively low values at the upper and lower sections of the ash dump. The upper layer of the ash dump is the first contact with effluents or rainwater and experiences maximum plug flow and hence retain less pore water. In the upper section of the ash dump, the main activity is dissolution of soluble mineral phases with the components being dispersed downwards due the plug flow effect.

The cation exchange capacity (CEC) shows positive correlation with the moisture content trend in the hydraulic disposed ash dump. This positive correlation could be attributed to the reactive front and possible formation of new mineral phases such as amorphous iron oxides, amorphous aluminosilicate phases that have increased surface area and consequently increased CEC.

The interaction of fly ash with the dolerite bedrock which had a lower moisture content and compaction possibly caused depletion of moisture content (MC %) and cation exchange capacity (CEC) at lower section of the ash dump.

2.4 Interstitial Pore Water Results

Figure 4 presents the pH ranges of the interstitial pore water of the samples taken from various section of hydraulic disposed ash dump. There is an obvious trend from relatively high values in the lower portion of the upper section and middle section to progressively lower values in the intensely chemically altered lower section of the ash dump. A review by Donahoe (2004) reports that this major decrease in pH is caused by carbonation, hydrolysis and precipitation after the depletion of portlandite ($\text{Ca}(\text{OH})_2$). This pH range in all the ash cores indicates the alkaline nature of a typical coal fly ash dump, but shows long term acidification trends over time due to weathering processes. The trend of high pH values

with corresponding increase in EC and TDS values was observed in the middle section of the ash dump. This is attributed to the downward dispersion of dissolved species from the upper layer of the ash dump to the reactive front

in the middle section of the ash dump. Lower pH values with corresponding decrease in EC and TDS values were observed in the lower section of the ash dump.

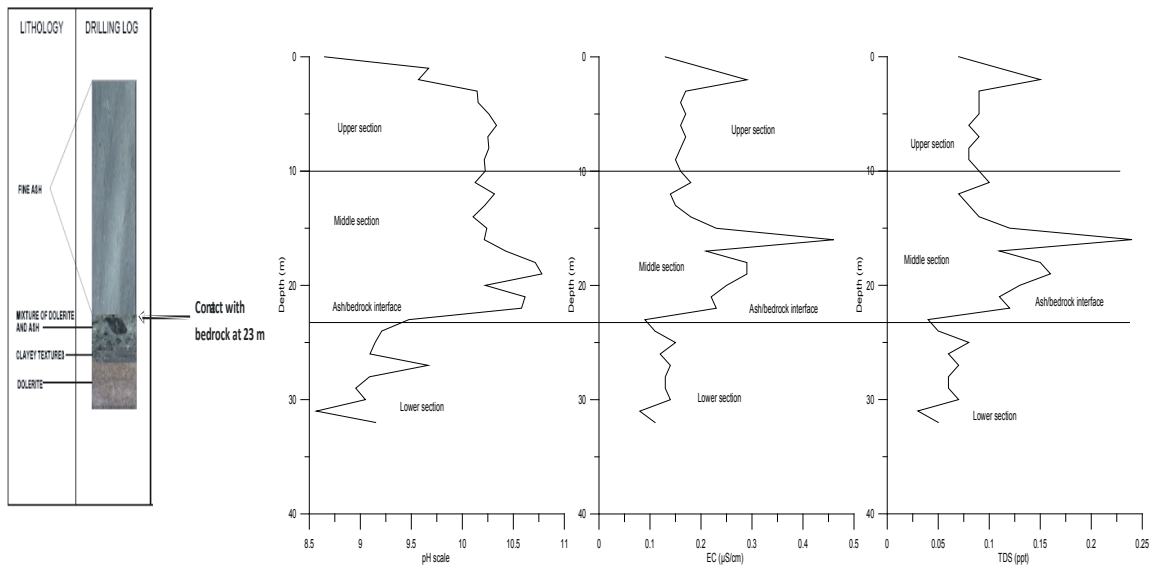


Figure 4
pH, EC and TDS of the Interstitial Pore Water of Hydraulic Disposed Ash Core Samples ($n = 3$)

This could be attributed to the interaction of the ash with the bedrock leading to possible dilution, reaction of the ash pore water components and subsequent reduction in pH, EC and TDS. The reduction of pore water pH (Fig. 4) in the upper section of the ash dump is due to chemical interaction of fly ash with ingressed CO₂ from the atmosphere and percolating rain water. The upper section of the ash dump represents the area of maximum interaction with effluents, rainwater and CO₂ and hence maximum dissolution with subsequent reduction in pH, EC and TDS. The reducing pH of the interstitial water would have a significant effect on the mobility of trace element in fly ash (Theis and Wirth, 1977; Khanra *et al.*, 1998; Jankowski *et al.*, 2006).

2.5 Statistical Analysis

2.5.1 Cluster Analysis

The relationship among the hydraulic disposed ash cores obtained through cluster analysis synthesized by the dendrogram plots (distance cluster combine) is shown in Figure 5. This gives subtle indication on the degree of chemical weathering of the hydraulic disposed ash cores. Statistical evaluation of the data based on dendrogram cluster analysis using the major elements Al₂O₃, SiO₂, CaO, MgO, MnO, Fe₂O₃, Na₂O, K₂O, TiO₂, P₂O₅, SO₃ and LOI as variables classified the hydraulic disposed weathered ash core samples into 2 groups (Fig. 5).

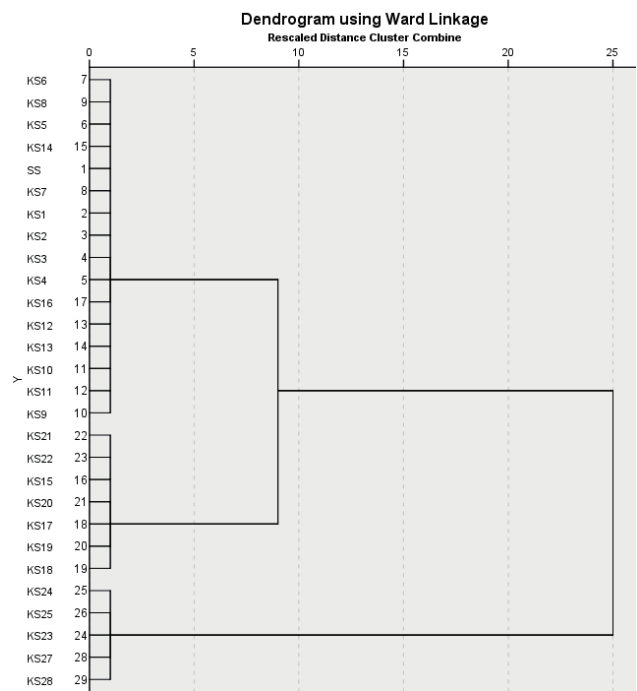


Figure 5
Dendrogram Cluster Analysis of Hydraulic Disposed Weathered Core Samples Using Major Elements Reported as Oxides (wt %) and Loss on Ignition as Variables

Group I consisted of samples mainly from upper

section of the hydraulic disposed weathered ash dump except samples KS11, KS12, KS13, and KS16; group II consists of samples mainly from middle and lower sections of the ash dump. The discriminant function analysis performed by comparing structure matrix to functional group centroid, showed weak association of Fe₂O₃, TiO₂, SO₃, LOI and P₂O₅ with group II. On the other hand, SiO₂, CaO, Fe₂O₃, MgO, MnO, Na₂O and K₂O showed strong association with group I at a Function I. The groups are 100 % different from each other. The dendrogram shows a sequence in the association, displaying the information as degree of chemical weathering between the various sections of hydraulic disposed ash dump. From a look at the dendrogram plot, the degree of the chemical weathering is broadly categorized into two major groups, i.e. low, and moderate to high degree of weathering. Therefore, the second group falls in the moderate to high degree of weathering but the first group falls in the low degree of chemical weathering. This confirms the results from the calculation of the chemical index of alteration (CIA) (Fig. 2).

Table 1
Varimax Rotated Factor Loadings Matrix and Communalities Obtained from Principal Component Analysis for the Studied Major Elements in the Weathered Ash Dump

Variables	Comp. I	Comp. II	Communality
MnO	0.97	–	0.97
Na ₂ O	0.77	-0.51	0.86
MgO	0.94	–	0.99
TiO ₂	-0.99	–	0.98
SiO ₂	–	-0.97	0.94
P ₂ O ₅	–	0.94	0.9
CaO	0.67	0.72	0.97
LOI	–	0.88	0.83
SO ₃	–	0.80	0.80
K ₂ O	0.58	-0.75	0.89
Al ₂ O ₃	-0.99	–	0.98
Fe ₂ O ₃	0.97	–	0.99
EV	7.46	3.62	
VAR (%)	52.79	39.59	
CVAR (%)	52.79	92.38	

N. B. EV=Eigen value, VAR= explained variance, CVAR=cumulative variance explained.

2.5.2 Functional Analysis

To understand the effect of chemical weathering, which is responsible for enrichment or depletion of major elements, their transport and mobility in the hydraulic disposed weathered ash dump, factor analysis with rotation has been carried out to clarify the relationship between chemical weathering, and heterogeneity in the ash dump (i.e. texture, moisture content and point of contact with dolerite bedrock) in the Kragbron ash dump. The functional analysis of the major elements reported

as oxides using rotated component matrix showed 2 components (Table 1). Component I represents 6.33 % of total variance, which is found to be depleted in elements such as TiO₂ and Al₂O₃ but showed enrichment in Na₂O, MgO, CaO, K₂O, Fe₂O₃ and MnO; Component II represents 4.75 % of total variance, which is associated with P₂O₅, CaO, SO₃ and LOI but are depleted in SiO₂, Na₂O and K₂O.

The enrichment in Na₂O, MgO, CaO, K₂O, Fe₂O₃ and MnO in the component I coincide with samples taken from lower section of the hydraulic disposed ash dump. On the other hand, depletion of SiO₂, Na₂O and K₂O in the component II coincides with the upper section of the ash dump. Accordingly, the depletion and enrichment trends of the major elements and LOI (i.e. variables) in Table 1 are attributed to flushing and/or leaching of major soluble components of fly ash. As a result, the depletion and enrichment trends are ascribed to the chemical interaction of fly ash with ingressed CO₂ from atmosphere, infiltrating rain water and fluctuating saturation level over an extended period of time.

2.6 Sequential Extraction Results

From an evaluation of the ICP-MS results on the sequential extraction leachates, environmental markers of the pollution trend could be identified. For each pair of variables, there is a calculated Spearman's *rho* and an associated *p-value* for testing the null hypothesis that the correlation is zero. In order to look for patterns by depth, we looked at the Spearman correlation coefficient between the recorded value and depth. A significant positive correlation would correspond to increasing response with increasing depth. A negative correlation would correspond to a decreasing response with increasing depth. The correlations were calculated for each element, age and solubility separately. Consequently there are a large number of correlations to consider. In this study, the correlations significant at the 0.01 level were presented.

2.6.1 Water Soluble Fraction

Table 2 and 3 show the Spearman's correlation coefficient (at 0.01 level significance) with the associated probability values of inorganic elements such as Al, Si, K⁺, Na⁺, Ca, Mg, Fe, Mn, As, Se, Mo, Cr, Pb and B by depth of hydraulic disposed ash cores aged 35-years-old. The Na⁺ (*rho* = 0.52 and *p-value* = 0.0003) and K⁺ (*rho* = 0.68 and *p-value* = <0.0001) trends in the water soluble fraction of the ash cores showed positive correlation with the depth of the ash dump. This indicates that these soluble salts are dissolved and leached out over time leading to reduction in pore water pH. These soluble salts were subsequently transported by the infiltrating rain water to the lower section of the ash dump. This suggests that hydraulic disposed ash cores are not sustainable salt sink. Sodium trend in the water soluble fraction is in accordance with sodium pattern in our previous study on the dry disposed fly ash dumps (Akinyemi *et al.*, 2011b).

The concentrations of Fe ($\rho = 0.46$ and $p\text{-value} = 0.007$) and Mn ($\rho = 0.61$ and $p\text{-value} = 0.0002$) (see Table 2) in the water soluble fraction of hydraulic disposed ash cores show positive correlation with the depth of the ash dump. The concentration of Si ($\rho = 0.77$ and $p\text{-value}$

$= <0.0001$) in the water soluble fraction of ash cores showed positive correlation with depth of the ash dump. This suggests Si, Fe and Mn are leached out from the ash core samples (Fig. 4).

Table 2
Relationship of Major Element in Different Solubility Medium with Depth of Hydraulic Disposed Weathered Ash Cores

Spearman's correlation (Only correlations that are significantly different from 0 at the 0.01 level)												
Obs	Age	Solubility	Variable	Al	Si	K	Ca	Mg	Mn	Fe	Na	Ti
1	35	Water soluble	Depth	-	0.77	0.68	-0.52	-	0.61	0.4601	0.59	-
2	35	Exchangeable	Depth	-	-	-	-	-	0.54	-	-	-0.67
3	35	Fe and Mn oxides	Depth	-0.46	-	-0.63	-	-0.50	0.79	-	-0.49	-0.82
4	35	Residual	Depth	0.72	-	-	-	0.51	0.77	0.69	0.74	-0.79
Probability (p-values)												
Obs	Age	Solubility	Variable	PAI	PSi	PK	PCa	PMg	PMn	PFe	PNa	PTi
1	35	Water soluble	Depth	-	<.0001	<.0001	0.0021	-	0.0002	0.0071	0.0003	-
2	35	Exchangeable	Depth	-	-	-	-	-	0.001	-	-	<.0001
3	35	Fe and Mn oxides	Depth	0.007	-	<.0001	-	0.003	<.0001	-	0.004	<.0001
4	35	Residual	Depth	<.0001	-	-	-	0.002	<.0001	<.0001	<.0001	<.0001

* PAI = P-value associated with Spearman's rho correlation for aluminium.

Table 3
Relationship of Trace Element in Different Solubility Medium with Depth of Hydraulic Disposed Weathered Ash Cores

Spearman's correlation (Only correlations that are significantly different from 0 at the 0.01 level)										
Obs	Age	Solubility	Variable	As	Se	Mo	Cr	Pb	B	
1	35	Water soluble	Depth	-0.85	-0.87	-0.76	-	-	-0.72	
2	35	Exchangeable	Depth	-0.84	-0.89	-0.78	-0.77	-0.47	-0.61999	
3	35	Fe and Mn oxides	Depth	-0.91	-	-	-0.70	-0.58	-0.87	
4	35	Residual	Depth	-0.76	-0.74	-0.56	-	-0.89	-0.62	
Probability (p-values)										
Obs	Age	Solubility	Variable	PAs	PSe	PMo	PCr	PPb	PB2	small p
1	35	Water soluble	Depth	<.0001	<.0001	<.0001	-	-	<.0001	3.38E-11
2	35	Exchangeable	Depth	<.0001	<.0001	<.0001	<.0001	0.0057	0.0001	7.77E-12
3	35	Fe and Mn oxides	Depth	<.0001	-	-	<.0001	0.0004	<.0001	1.62E-13
4	35	Residual	Depth	<.0001	<.0001	0.0006	-	<.0001	0.0001	5.49E-12

* PAs = P-value associated with Spearman's rho correlation for arsenic.

In the water soluble fraction, the concentrations of As ($\rho = 0.85$ and $p\text{-value} = <0.0001$), Se ($\rho = 0.87$ and $p\text{-value} = <0.0001$), Mo ($\rho = 0.76$ and $p\text{-value} = <0.0001$) and B ($\rho = 0.72$ and $p\text{-value} = <0.0001$) (Table 3) showed negative correlation with the depth of the ash dump. These trends suggest decrease in the concentration of these toxic species with ageing of the ash cores. This is due to over time leaching of toxic species caused by gradual reduction in pore water pH.

2.6.2 Exchangeable Fraction

In the exchangeable fraction, the concentration of Mn showed positive correlation ($\rho = 0.54$ and $p\text{-value} = <0.001$) with the depth of the ash dump. This suggests possible dissolution of manganese mineral in hydraulic ash cores due to chemical weathering and subsequent transportation by infiltrating rain water. The concentration of Ti in the exchangeable fraction showed negative correlation ($\rho = -0.67$ and $p\text{-value} = <0.0001$) suggesting decrease in solubility of Ti containing minerals

with the ageing/weathering of the hydraulic disposed ash core samples or probably due to enrichment in the residue as the dissolution of soluble components occurs in the weathered ash over time.

In the exchangeable fraction, the concentrations of As ($\rho = -0.84$ and $p\text{-value} = <0.0001$), Se ($\rho = -0.89$ and $p\text{-value} = <0.0001$), Mo ($\rho = -0.78$ and $p\text{-value} = <0.0001$), Cr ($\rho = -0.77$ and $p\text{-value} = <0.0001$), Pb ($\rho = -0.47$ and $p\text{-value} = 0.0057$) and B ($\rho = -0.62$ and $p\text{-value} = 0.0001$) (Table 3) showed negative correlation with the depth of the ash dump. These trends suggest leaching of toxic species in the exchangeable fraction of ash cores due to reduction of ash pH.

2.6.3 Fe and Mn Oxides Fraction

In the Fe and Mn oxides fraction, the concentration of Al ($\rho = -0.46$ and $p\text{-value} = 0.007$), K^+ ($\rho = -0.63$ and $p\text{-value} = <0.0001$), Mg ($\rho = -0.50$ and $p\text{-value} = 0.003$), Na^+ ($\rho = -0.49$ and $p\text{-value} = 0.004$) and Ti ($\rho = -0.82$ and $p\text{-value} = 0.0001$) (Table 2) showed negative correlation with the depth of ash dump. These trends suggest decrease in solubility of amorphous Fe and Mn oxides phase with the ageing/weathering in the hydraulic disposed ash dump. In general, the solubility of Al, Mg, Na^+ and Ti from amorphous Fe and Mn oxides decreases with the ageing/weathering. This is due to leaching over time as the ash weathers caused by reduction in the pore water pH (Fig. 4). The concentration of Mn ($\rho = 0.79$ and $p\text{-value} = <0.0001$) in the Fe and Mn oxides fraction showed positive correlation with the depth of the ash dump.

This suggests dissolution and mobility of Mn associated with the amorphous Fe and Mn oxides fraction due to reduction of pore water pH over time, moisture content (MC %), cation exchange capacity (CEC) and point of contact with dolerite bedrock.

In the Fe and Mn oxides fraction, the concentration of As ($\rho = 0.91$ and $p\text{-value} = <0.0001$), Cr ($\rho = 0.70$ and $p\text{-value} = <0.0001$), Pb ($\rho = 0.58$ and $p\text{-value} = 0.0004$), B ($\rho = 0.87$ and $p\text{-value} = <0.0001$) (Table 3) showed negative correlation with the depth of the ash dump. The obvious depletion in the concentrations of these toxic metals at the lower section of the ash dump is due to possible sorption of these toxic metals by Fe-hydroxides in the dolerite bedrock.

2.6.4 Residual Fraction

In the residual fraction, the concentrations of Al ($\rho = 0.72$ and $p\text{-value} = <0.0001$), Mg ($\rho = 0.51$ and $p\text{-value} = 0.002$), Mn ($\rho = 0.77$ and $p\text{-value} = <0.0001$), Fe ($\rho = 0.69$ and $p\text{-value} = <0.0.0001$) and Na^+ ($\rho = 0.74$ and $p\text{-value} = < 0.0001$) showed positive correlation with the depth of the ash dump. The concentration of Ti ($\rho = -0.79$ and $p\text{-value} = <0.0001$) showed negative correlation with the depth of the ash dump.

In the residual fraction, the concentrations of As ($\rho = -0.76$ and $p\text{-value} = <0.0001$), Se ($\rho = -0.74$ and $p\text{-value}$

$= <0.0001$), Mo ($\rho = -0.56$ and $p\text{-value} = <0.0001$), Pb ($\rho = -0.89$ and $p\text{-value} = <0.0001$) and B ($\rho = -0.61$ and $p\text{-value} = 0.0001$) showed negative correlation with the depth of the ash dump. These trends suggest depletion in the concentration of toxic metals in the residual fraction at the lower section of the ash dump. This is possibly due to chemical interaction of hydraulic disposed ash cores with dolerite bedrock leading to adsorption of these toxic metals.

3. FRACTIONATION SCHEME AND EFFICIENCY OF FRACTIONATION

Akinyemi *et al.* (2011b) reported that variation in the major elements concentration in each of the five fractions is due in part to the adsorption of metals by different physico-chemical forms, and the aqueous behaviour of metals. The second most important factor is the preferential weathering of ash core ash samples due to fluctuation in the pore water pH. The authors found variability (within 10 %) between sum of values obtained for different fractions (pseudo-total concentration) of Ca, Mg, Fe, Mn, and K^+ and values obtained for the same sample extracted with combined acid leach (total metal content).

SUMMARY AND CONCLUSIONS

The following summary could be drawn from the results of the investigated species using modified sequential extraction scheme on the 35-year-old hydraulically disposed ash dump: The ternary plot of major elements as determined by the XRF analysis showed that hydraulic disposed ash cores are sialic, ferrosialic and ferrocalsialic in chemical composition. These chemical compositions depend on the point of sampling and ash interaction chemistry. The relationship between SiO_2 and chemical index of alteration (CIA) showed disparity in degree of chemical weathering depending on the sampling point of ash and interaction chemistry.

The application of multivariate data treatment method reveals the subtle chemical alteration and dissolution of major soluble component in the fly ash matrix. Relative enrichment and depletion trends of major elements are controlled by ash sampling point (i.e. compaction due to overburden), ash interaction chemistry and gradual reduction of pore water pH.

The Na^+ and K^+ soluble salts showed evidence of leaching and downward migration in the water soluble fraction of the ash cores indicating that the hydraulic disposed ash dump is not a sustainable salt sink.

Modified sequential extractions reveals that mobility and transport of major and toxic elements are governed by the gradual reduction pore water pH, ash interaction chemistry with the dolerite bedrock, ingressed CO_2 from

atmosphere, the sampling point of the ash cores and infiltrating rain water.

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