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Chemical Weathering and Mobility of Inorganic Species in Dry Disposed Ash: An Insight from Geochemical Fractionation and Physicochemical Analysis

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ABSTRACT

The burning of low-grade coal produces vast amounts of ash and other solid by-products. In South Africa, coal combustion by-products undergo disposal on land as dry heaps or slurried to dams. In this study, the geochemical partitioning, transport, and mobility of elements in dry disposed ash dumps were investigated using a modified sequential extraction scheme. The chemical and mineralogical compositions of 50 drilled core samples were investigated by X-ray fluorescence (XRF), X-ray diffraction (XRD), and inductively coupled plasma mass spectrometry. Ternary plots of major elements as determined by XRF showed that the 15-year-old and 2-week-old dry disposed ashes are sialic, and the 4-year-old ash cores are sialic and ferrocalsialic. The relationship between SiO2 and the chemical index of alteration showed a moderate to high degree of weathering. The variation in chemical compositions and degree of chemical weathering are ascribed to differences in the chemistry of feedstock coals and ash/water/CO2 interaction chemistry. Multivariate statistical analysis revealed the subtle chemical alteration differences and disparity in dissolution of major components of fly ash. The pH profile of the cores indicates that contact with atmosphere and consequent ingress of CO2, leaching by rainwater, and point of saturation have a great effect on the chemical weathering of the dry disposed fly ash. XRD analysis of two weathered drilled core samples taken from 4-m depth intervals showed the presence of calcite. The chemical interaction of fly ash with ingressed CO2 from the atmosphere will ultimately lead to a reaction with buffer components such as CaO and the subsequent conversion into calcite. The modified geochemical partitioning scheme revealed that relative enrichment and depletion in the inorganic elements at various depth sections of the ash dump are governed by chemical interaction of fly ash with ingressed CO2 from the atmosphere, porewater pH, leaching by percolating rainwater, fluctuation in water level (i.e., weathering over time), heterogeneity in fly ash, continuous irrigation of fly ash by high saline effluents, and fresh water.

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1. Introduction

Coal is currently the leading nonrenewable energy resource that provides 77% of South Africa’s primary energy needs. Eskom Holdings (Ltd.) generated 36.7 Mt of coal combustion by-products from coal-fired power stations in South Africa during 2009. Of this total, 1.84 Mt, or 5% of the ash produced, was utilized. The remaining 34.86 Mt of ash underwent disposal in dry landfills (Petrik et al., 2003; Anonymous, 2009). Fly ash accumulates in large volumes and becomes a significant disposal problem because of the inconsistent trend of its utilization (Adriano et al., 1980). These processes and applications include, but are not limited to,
addition to cement and concrete products; structural fill and cover material; roadway and pavement utilization; addition to construction materials as a light weight aggregate, infiltration barrier, and underground void filling; and soil, water, and environmental improvement (Halstead, 1986; Ahmaruzzaman, 2010).

The mobilization of toxic elements from ash dumps to potable water sources is a threat to human health. Inorganic components in by-products of coal combustion occur in different physicochemical forms. The availability and mobility of elements present in fly ashes will depend on the physicochemical forms of the elements (Pérez-Bendito and Rubio, 1999). The sequential extraction (SE) procedure partitions an element into a specific phase by using appropriate reagents arranged in increasing strength (i.e., increasing acidity) (Tessier et al., 1979; Horowitz, 1991; Tessier, 1992; Smeda and Zyrnicki, 2002; Jegadeesan et al., 2008; Smichowski et al., 2008).

The main drawback of sequential extraction schemes are lack of selectivity of reagents, re-adsorption and redistribution of metals solubilized during the extraction, sample pretreatment, and general methodology (Shan and Chen, 1993; Gleyzes et al., 2002). Despite these disadvantages, there are many advantages of chemical sequential extraction and enormous scope for further research and development, especially in the case of studying the relationship between the elemental phase locations and their bioavailability (Chlopecka and Adriano, 1996; Davidson et al., 1999; Rao et al., 2008). One of the most extensively used sequential extraction procedures in the literature was proposed by Tessier et al. (1979), in which total elements are fractionated into (a) exchangeable forms; (b) forms bound to carbonates, (c) Fe and Mn oxides, or (d) organic matter; and (e) a residual that is bound to the primary mineral structure.

Recent studies on the sequential extraction scheme are modifications from Tessier et al. (1979). The schemes were originally developed for the examination of aquatic sediments (Campos et al., 1998; Mester et al., 1998; Petit and Rucandio, 1999) but gained wide acceptance as tools for the identification of metals in contaminated soils (Campos et al., 1998; Gleyzes et al., 2002). Lately, sequential extraction has been applied to incinerated sludge ash (Kim et al., 2003; Feng et al., 2007), bottom ash and fly ash from municipal solid waste incinerators to determine the distribution of elements (Bruder-Hubscher et al., 2002; Smeda and Zyrnicki, 2002; Zielinski et al., 2007; Smichowski et al., 2008), and partitioning of elements in fly ash acid mine drainage-derived solid residues (Gitari et al., 2010).

The current study evaluates the geochemical fractionation and transport of elements in sequentially stacked ash dumps, continuously irrigated with fresh water (i.e., 15-year-old [AMB 80]) and highly saline effluents (i.e., 4-year-old [AMB 82]). The objectives of this study were to (1) elucidate mineralogical association with age in various sections of the ash dumps, (2) identify and quantify the elements in their physicochemical forms, and (3) appraise and reveal factors responsible for the transport of major elements. Additionally, multivariate statistical analysis has been applied to reveal the chemical weathering process and to consider its effect over an extended period under a real dry disposal scenario.

2. Materials and Methods

2.1. Sampling technique and sample pretreatment

Two cores of different ages were drilled from a 15-year-old (AMB 80) dry ash dump continuously irrigated with fresh water and a 4-year-old (AMB 82) landfill irrigated with highly saline effluents. The 2-week-old (T 87) ash core was obtained from the same site and not irrigated. The details of sampling and sample pretreatment techniques were reported in our previous publications (Akinyemi et al., 2011b; Gitari et al., 2011). An intact block was extracted from the core, secured in zip-lock plastic bags, and degassed for preservation before analysis. The zip-lock plastic bags were labeled accordingly and kept in plastic containers with a closed lid. The sealed, evacuated plastic containers were kept away from any source of heat, out of direct sunlight, and away from fluctuating temperatures to avoid physicochemical alteration of stored samples.

2.2. XRD and XRF analysis and pH of interstitial porewater of weathered ash cores

The detailed procedures of X-ray diffraction (XRD) and X-ray fluorescence (XRF) analysis were reported in our previous publication (Akinyemi et al., 2011c). The pH of interstitial/porewater was determined using a 1:10 core:water ratio. Ten grams of each of the ash core samples taken at 1-m intervals down the profile of the ash dump were weighed, put in a beaker, and suspended in 100 mL of ultrapure water. The mixture was then agitated thoroughly for 30 minutes, and allowed to settle for 15 minutes. The pH and electrical conductivity (EC) of the supernatant were measured using a Hanna HI 991301 pH meter with a portable pH/EC/total dissolved solids/temperature probe. Triplicate analyses were carried out in each case.

2.3. 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, and EC) can be influenced easily by moisture content. Two methods are usually used in the determination of moisture content: thermo-gravimetric and loss on drying. The loss on drying technique was used in this study following Ojo (2009). The moisture contents of the ash samples were determined by oven drying preweighed samples taken at 1-m intervals down each of the two drilled ash cores for 12 hours at 105°C. The weight difference between the initial wet sample and the final dry sample was expressed as a weight percentage (wt%) of the initial wet sample and reported as moisture content percent. The ash core samples for the rest of the determinations were air dried; therefore, moisture content was not used in weight percent calculations. The other data are reported on a dry mass basis.

2.4. Sequential extraction procedure

The five-step sequential extraction scheme applied in this study was a modified form of a method proposed by Tessier et al. (1979; steps 2, 3, 4, and 5). The fractions are as follows: (1) water soluble fraction (deionized water), (2) exchangeable fraction (CH3COONH4 at pH 7), (3) carbonate fraction (CH3COONH4 at pH 5), (4) amorphous iron and manganese fraction (NH4OH+HCl), and (5) residual fraction (HF, HClO4, HNO3, 3:3:1). The detailed procedures are as follows.

2.4.1. Steps 1–4. Common procedure

The mixtures from each step were mechanically shaken at room temperature for 1 hour. The procedure was repeated to give triplicate samples. The solution was allowed to settle for 1 hour, then centrifuged at 1610 × g for 20 minutes, and the supernatant
was filtered through a 42-μm nucleopore membrane. The remaining solid portion was decanted into a 100-mL clear plastic bottle without any weight loss. Ten milliliters of the supernatant was measured into a standard volumetric flask, diluted to 100 mL with ultrapure water, and set aside for multielement analysis with inductively coupled plasma mass spectrometry (ICP-MS). Two drops of 1% HNO₃ were used to acidify the mixture to prevent metal precipitation before ICP-MS analysis. The solid residue from each step was completely recovered and refrigerated for the next extraction step. One gram of the fly ash samples from various intervals in the ash horizon was weighed into 50-mL centrifuge tubes, and 45 mL of ultrapure water was added. Forty-two milliliters of filtered supernatant was recovered. Dry weight concentration of the analytes for this sequential extraction step was calculated using the dilution factor and original weight of the sample. This process was repeated with the solid residue from each step with buffers of varying pH.

2.4.2. Step 5. Residual fractions
The solid residue recovered above was rinsed with ultrapure water, transferred to a crucible, oven dried at 105°C, and weighed. Dried sample (0.90 g) was carefully transferred into the Teflon cup of a Parr bomb, and 14 mL of the 3:3:1 acid was added; the Parr bomb was sealed and heated to 180°C for 3 hours and then removed from the oven and allowed to cool. After cooling and the solution was diluted with 40 mL of 1% HCl and filtered through a 42-μm nucleopore membrane. Supernatant solution (10 mL) was measured into a standard volumetric flask and diluted to 100 mL with ultrapure water. The solution was set aside for multielement analysis with ICP-MS. Dry weight concentrations of the analytes for this residual fraction were calculated using the dilution factor and the weight of the solid.

2.5. Data treatment and multivariate statistical methods
Multivariate statistical method was applied on the bulk chemical data determined by XRF analysis (i.e., major oxide mass percent) in dry disposed fly ash at different stages of weathering using IBM SPSS-19.0 statistical software. Varimax rotated factor analysis was performed on a correlation matrix of rearranged data for three different weathered ash dumps. The variance, cumulative, and extraction sums of square loadings of the variables with

Table 1
The graphic log and physical sample description of 15-year-old core (AMB 80)

<table>
<thead>
<tr>
<th>Layer No.</th>
<th>Strata</th>
<th>Thick (m)</th>
<th>Elev. (m)</th>
<th>Depth (m)</th>
<th>Column map</th>
<th>Lithology</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>ASH</td>
<td>0.55</td>
<td>-0.55</td>
<td>0.55</td>
<td></td>
<td>clay topsoil</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>ASH</td>
<td>7.45</td>
<td>-8</td>
<td>8</td>
<td></td>
<td>porous ash</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>ASH</td>
<td>5</td>
<td>-13</td>
<td>13</td>
<td></td>
<td>very brittle, porous ash</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>ASH</td>
<td>8</td>
<td>-21</td>
<td>21</td>
<td></td>
<td>ash</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>ASH</td>
<td>2</td>
<td>-23</td>
<td>23</td>
<td></td>
<td>clay content, moist ash</td>
<td>Depth to water level = 20.61m</td>
</tr>
<tr>
<td>6</td>
<td>MDSN</td>
<td>2</td>
<td>-25</td>
<td>25</td>
<td></td>
<td>dry mudstone</td>
<td>EC = 511.3mS/m</td>
</tr>
</tbody>
</table>

(Irrigated and quenched with fresh water)
eigenvalues were computed. Rotation of the axis defined by factor analysis produced a new set of factors, each one involving primarily a subset of the original variables with as little overlap as possible, so that the original variables were divided into groups. The factor analysis of the present data set was further sorted by the contribution of less significant variables (<0.4 factor score). A varimax rotation (raw) of the different varifactors of an eigenvalue greater than 1 was 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).

3. Results and Discussion

3.1. Physicochemical and mineralogical analysis of drilled cores

3.1.1. Lithological characteristics of drilled cores

The graphic log and physical sample description of cores by depth is shown in Tables 1 and 2 for 4-year-old and 15-year-old drilled cores. Tables 1 and 2 show, at various ages and depths, differences in the ash, varying from very hard coarse ash to very hard fine ash that was fractured, soft fine powdery ash and clay, mudstone, or doleritic material where the bedrock was sampled. The tables also present the mode of quenching fly ash dust during the initial disposal of the ash. Some of the cores were in contact with water (AMB 80 and AMB 82) and would influence the pH and concentration of species in the porewater (Gitari et al., 2011).

In cases where the dump had been irrigated, deeper layers and zones were still unconsolidated, friable, and loose, indicating that no or few pozzolanic reactions had taken place over time. Some hard and soft layers were found directly adjacent to each other. Unconsolidated ash was prevalent in more recently placed areas of the dump.
surface, and in core AMB 82, no water table was observed (Table 2).

Some portions of cores were moist and others dry. Dry zones were found in cores where the water table was nonexistent or deeper lying. EC of core water sampled varied from 315 to 571 mS/m, in all likelihood because of the differences in brine versus freshwater irrigation regime practiced on different areas of the dump. There was not much homogeneity within each core or between different cores, and many fractured zones were observed, once again, emphasizing the heterogeneous nature of the ash.

3.1.2. XRD analysis of drilled cores

The results of mineralogical analysis of drilled cores are shown in Figures 1a and 1b. The main mineral phases are quartz and mullite. Other minerals in minor quantities are hematite, calcite, lime, anorthite, mica, and enstatite. Akinyemi et al. (2011c) reported that samples drilled from a 2-week-old fly ash dump show similar mineralogical composition, except for the absence of calcite and mica. The mullite present in fly ash was formed by the thermal decomposition of kaolinite (White and Case, 1990), in the parent coal. The moment the fly ash comes into contact with the

![X-ray diffraction spectra for (a) 15-year-old (AMB 80) and (b) 4-year-old (AMB 82) fly ash dumps.](image-url)
atmosphere, the ingress of CO2 will lead to reactions with buffering components such as CaO and subsequent conversion into calcite (Soong et al., 2006; Muriithi et al., 2011). This would further explain the relative decrease in porewater pH of the 15-year-old weathered section of core samples compared with the pH of 4-year-old weathered sections of ash dump (Figure 2).

### 3.1.3. Interstitial porewater pH and optimum moisture content of drilled ash cores

The interstitial porewater pH of the drilled ash cores ranged from 8.2 to 11.7 over the period investigated (Figure 2). For the purpose of comparison, the pH of the fresh ash sample collected from the same coal-fired power station was slightly greater than 12. The porewater pH of 15-year (i.e., AMB 80) and 4-year-old (i.e., AMB 82) drilled ash cores within 30 minutes of agitation ranged from 8.8 to 11.8 and 8.2 to 11.2, respectively, congruently demonstrating the alkaline nature of South African coal fly ash.

The reduction in porewater pH is ascribed to carbonation processes and the rapid dissolution and initial flushing out of the major soluble species (such as CaO) in surface layers that act as pH buffering constituents in the fly ash (Gitari et al., 2009). A number of studies have shown that pH is a result of dissolution and hydrolysis of oxide components, such as CaO (Reardon et al., 1995; Iwashita et al., 2005). For both cores, pH varies between 10 and 12, and then decreases to 8 to 10. The greatest weathering was observed at the top layer (1-m depth) and bottom layer (24.5–28-m depth) in the weathered ash cores (4 years old). The greatest weathering trend is in the top layer (0.55–3-m depth), and bottom layer (22.5–25-m depth) for the 15-year-old ash dump. This shows that infiltration of rainwater and point of saturation (i.e., point of contact of ash core with water table) has a profound effect on the decrease of the porewater pH. The optimum moisture content of the 15-year-old (i.e., AMB 80) and 4-year-old (i.e., AMB 82) drilled ash cores ranges from 0.78 to 44.06 and 0.17% to 27.53%, respectively. Variations in the optimum moisture content in the ash cores with depth are attributed to heterogeneity and differences in freshwater versus brine irrigation of the ash dumps. Increased optimum moisture content led to decrease in the ash porewater pH and, eventually, mobility of chemical species in the ash cores (Figure 2). Akinyemi et al. (2011a) showed that relative enrichment and depletion trends of major elements are promoted by heterogeneity in the ash dump (i.e., moisture content), gradual reduction of porewater pH, and continuous brine and water irrigation.

### 3.1.4. Bulk chemistry of the dry disposed ash dumps

Roy and Griffin (1982) classified fly ash on the basis of the intersection of the sum of their major oxides as sialic, SiO2 + Al2O3 + TiO2; calcic, CaO + MgO + Na2O + K2O; and ferric, Fe2O3 + MnO + P2O5 + SO3, in a ternary diagram. On the basis of the chemical composition of fly ash, seven intermediate fly ash subgroups exist, i.e., sialic, ferrosialic, calsilic, ferrocalsilic, ferric, calcic, and ferrocalcic (Vassilev and Vassileva, 2007). Figure 3 shows a ternary diagram constructed from XRF data of a 15-year-old (AMB 80) water-irrigated dry ash dump, 4-year-old (AMB 82) brine-irrigated dry ash dump, and 2-week-old (T 87) dry ash dump not irrigated with high-saline effluents.

The ternary diagram shows that the water-affected, dry disposed, weathered ash samples were sialic in composition (Figure 3a). Accordingly, the ash samples collected at the upper section to the bottom section of the 15-year-old (i.e., AMB 80) ash dump are essentially Si and Al in composition (i.e., sialic). The 2-week-old (T 87) dry ash dump not irrigated with high-saline effluents was also
sialic in chemical composition (Figure 3c). Conversely, the brine-affected, dry disposed ash cores are sialic and ferrocalisialic in chemical composition. The variation in chemical composition of the 4-year-old (i.e., AMB 82) ash dump could be ascribed to (1) the chemical interaction of the ash core with the hypersaline effluents (i.e., brine) used for the suppression of dust and (2) the indiscriminate dumping of Fe catalyst of the 4-year-old (i.e., AMB 82) ash dump. The second possible factor responsible for obvious variation in chemical composition of the ash dump is differences in the chemistry of feed stock coals over 15 years of coal combustion. In a similar study by Valentim and Hower (2010) on a Kentucky fly ash, the majority of the samples were sialic, sialic-ferrosialic, or ferrosialic, depending on coal combustion temperature, the sampling point of the ash, and ash interaction chemistry. In this study, we assumed the first factor is constant and that classification would depend on the sampling point of the ash, ash interaction chemistry, and chemistry of feed stock coals.

3.1.5. Statistical analysis

3.1.5.1. Cluster analysis

The association among dry disposed ash cores obtained through cluster analysis is shown in the dendrogram plot (distance cluster combination) in Figure 4. This provides insight on the degree of chemical weathering of the dry disposed ash cores. Statistical evaluation of the data based on dendrogram cluster analysis using the major elements and loss on ignition (LOI) as variables classified the dry disposed, weathered ash core samples into two groups (Figure 4). Group 1 consisted of core ash samples from both 4-year-old (AMB 82) and 15-year-old (AMB 80) ash dumps, with the exception of ash samples from the bottom section of the ash dumps.

Group 2 consists of core ash samples such as AMB80-3m, AMB80-22m, AMB80-23m, AMB80-24m, AMB80-25m, AMB82-25m, AMB82-26m, AMB82-27m, and AMB82-28m. The discriminant function analysis performed by comparing structure matrix to functional group centroid showed strong association of Al2O3, SO3, CaO, and TiO2 with the core ash samples in the group 1. On the contrary, MnO, Fe2O3, K2O, LOI, MgO, P2O5, Na2O, and SiO2 showed weak association with core ash samples in group 2 at function I. The groups are 100% different from each other.

3.1.5.2. Functional analysis

To gain deep insight on the effect of chemical weathering, which is responsible for enrichment or depletion of major elements, their transport, and mobility in the weathered, dry disposed ash dump, factor analysis with rotation was carried out to clarify the relationship between chemical weathering, major components in the ash core, pH of the ash porewater, and inhomogeneity in the ash dump (i.e., texture and moisture content).
Functional analysis of the major elements reported as oxides using rotated component matrix showed three components (Table 3). Component 1 represent 48.86% of total variance, which is found to be depleted in elements such as Al₂O₃, SiO₂, TiO₂, and SO₃, but showed enrichment in Fe₂O₃, MgO, MnO, Na₂O, and CaO content. However, component 2 represents 31.25% of total variance, which shows strong association with K₂O, P₂O₅, and SiO₂, but is depleted in Al₂O₃, CaO, TiO₂, and SO₃. Component 3 characterizes 8.48% of total variance, which is enriched in MnO and LOI, but shows relative depletion in Al₂O₃ and SO₃. As a result, relative enrichment and depletion in the major components (i.e., variables) are ascribed to chemical weathering, pH of the ash porewater, inhomogeneity in the ash dump (texture and moisture), and inhomogeneous brine and water irrigation of the ash dumps.

3.1.6. Chemical weathering in the dry disposed ash dumps

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.

\[
CIA = \left[ \frac{Al_2O_3}{(Al_2O_3 + CaO + Na_2O + K_2O)} \right] \times 100
\]  

(1)

Consequently, the CIA was calculated for 4- and 15-year-old ash cores. Figure 5 is a plot of CIA values against SiO₂ taken from mass percent XRF data in two dry disposed core ashes of different ages.

From a cursory look at the dendrogram and CIA plots, the ash cores of different ages broadly categorized into group 1 and group 2, or a moderate to high degree of weathering. Group 2 consists mainly of core samples from the bottom section of the 15-year-old ash dump. Conversely, group 1 comprises core samples from the top, middle, and bottom sections of the ash dumps (i.e., 15- and 4-year-old). The obvious differential weathering (i.e., moderate to high degree of weathering) could be attributed to chemical interaction of fly ash over time with ingressed CO₂, percolating rainwater, and subsequent reduction of ash porewater pH. Other related factors include inhomogeneous brine versus freshwater irrigation and heterogeneity in the ash dump.
3.2. 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. 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, and a negative correlation would correspond to a decreasing response with increasing depth. The correlations were calculated separately for each element, age, and solubility. Consequently, there are a large number of correlations to consider. In this study, correlations significant at the 0.01 level were presented.

### 3.2.1. Aluminum and silicon

The porewater pH has a particularly marked effect on Si concentrations, although the mobility of Si in fly ash core cannot be predicted accurately from pH alone. As shown in Table 4, Al and Si do not show significant correlation in the sequential fractions with depth because they are poorly mobilized or previous mobilizations of soluble species, leaving insoluble species behind. This immobility could be attributed to their abundance in the Fe-Mn fraction of the drilled fly ash cores. Commonly, Si is more mobile in an alkaline medium, but as Carlisle et al. (1974) described, increasing the pH to about 9 decreases the Si concentration in solutions. In general, the solubility of Al hydroxides is low, especially in the pH range 5–8, and solubility decreases with aging (Nilsson and Bergkvist, 1983).

### 3.2.2. Sodium and potassium

Potassium shows strong positive correlation (Spearman’s rho = 0.57, p = 0.0058) with depth in the carbonate fraction of the 15-year-old ash dump (Table 4). This could result from precipitation and subsequent accumulation of soluble K$^+$ salts in the carbonate fraction at deeper levels from the formation of calcite. On the contrary, potassium shows insignificant correlation in the carbonate fraction with the depth of 4-year-old ash dump. Sodium also shows inconsequential correlation in all the sequential fractions with depth of the ash dump, possibly because of dissolution and washing away of soluble Na$^+$ and K$^+$ salts in the ash dumps.

### 3.2.3. Calcium and magnesium

Calcium shows strong negative correlation (Spearman’s rho = −0.61, p = 0.0028) in the carbonate fraction with depth in the 15-year-old ash dump from weathering over time, because most calcium is converted to calcite and will most likely associate with the carbonate fraction. Whereas Ca has a negligible correlation in other sequential fractions with the depth of the 15-year-old ash dump, Mg shows a strong negative correlation (Spearman’s rho = −0.65, p = 0.001) with depth in the Fe and Mn oxide fractions of the 4-year-old ash dump. This decreased concentration at depth could be attributed to weathering over time. Mg shows inconsequential correlation with

<table>
<thead>
<tr>
<th>Variable</th>
<th>Comp. 1</th>
<th>Comp. 2</th>
<th>Comp. 3</th>
<th>Communality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_2$O$_3$</td>
<td>0.95</td>
<td>0.96</td>
<td>0.95</td>
<td>0.96</td>
</tr>
<tr>
<td>MgO</td>
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<td>0.95</td>
<td>0.94</td>
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<td>MnO</td>
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<td>0.79</td>
<td>0.85</td>
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<td>−0.56</td>
<td>0.95</td>
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<tr>
<td>K$_2$O</td>
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<td>0.97</td>
<td>0.94</td>
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<tr>
<td>CaO</td>
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<td>−0.84</td>
<td>0.93</td>
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<tr>
<td>SiO$_2$</td>
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<td>TiO$_2$</td>
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<td>0.7</td>
<td>0.92</td>
<td>0.52</td>
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<tr>
<td>LOI</td>
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<td>0.81</td>
<td>0.81</td>
<td>0.89</td>
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<tr>
<td>SO$_3$</td>
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<td>−0.41</td>
<td>−0.66</td>
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<td>1.02</td>
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<tr>
<td>VAR%</td>
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<td>CVAR%</td>
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<td>80.11</td>
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Note: EV = eigenvalue; VAR = explained variance; CVAR = cumulative explained variance.

![Fig. 5](attachment:image.png)  
**Fig. 5.** Relationship between SiO$_2$ (wt%) and chemical index of alteration (CIA) in weathered dry disposed fly ashes of different ages: (a) 15-year-old (i.e., AMB 80); (b) 4-year-old (i.e., AMB 82).
depth in other fractions of 4- and 15-year-old ash dumps, possibly suggesting coincident dissolution and precipitation of magnesium compounds in the dry disposed ash dump.

3.2.4. Iron and manganese

The fate of Fe in chemical weathering of dry disposed ash dump seems to be dependent largely on the pH of the ash porewater system and on the stage of oxidation of the Fe compounds. Fe shows strong positive correlation (Spearman’s rho = 0.67, $p = 0.0007$) with depth in the Fe and Mn oxide fractions of the 4-year-old ash dump. This is because most of the Fe is in the form of insoluble oxides in the cores. This reducing and acid condition promotes the mobilization of Fe compounds in the ash dump. Conversely, Fe shows strong negative correlation (Spearman’s rho = −0.56, $p = 0.0068$) with depth in the exchangeable fraction of the 15-year-old ash dump. The lack of correlation of Fe in the exchangeable fraction with depth is attributed to washing away of soluble Fe and decrease in the ash porewater pH at the water table.

Manganese shows strong positive correlation (Spearman’s rho = 0.60, $p = 0.0031$) with depth in the carbonate fraction of the 4-year-old ash dump. Manganese also shows strong positive correlation (Spearman’s rho = 0.71, $p = 0.0002$) with depth in the water soluble fraction of the 15-year-old ash dump. Correlation of Mn in the water soluble and carbonate fractions with depth is attributed to the decrease in the ash porewater pH. This phenomenon ensures the release and concentration of Mn at the deeper level of drilled cores. The released Mn oxides are reprecipitated and readily concentrated in the form of secondary Mn minerals (Kabata-Pendias, 2011). The behavior of Mn in the dry disposed ash dump is very complex and is governed by different environmental factors, of which pH conditions of ash porewater system are the most important. Lindsay (1979) established that the mobility of Mn in soils is highly dependent on the redox (Eh)–pH potential. Therefore, the most common reactions that control Mn behavior in coal fly ash dumps are oxidation–reduction and hydrolysis (Lindsay, 1979).

3.2.5. Arsenic and selenium

Arsenic and selenium show insignificant correlation in all sequential fractions with the depth of 4-year-old (AMB 82) and 15-year-old (AMB 80) ash dumps (Table 5). The inconsequential correlation of As and Se with depth is attributed to slight variations in their sorption during incorporation of calcium in calcite. Arsenic minerals and compounds in the coal fly ash dump environment are readily soluble, and arsenopyrite may be easily oxidized by both $\text{O}_2$ and $\text{Fe}^{3+}$. Nevertheless, As ion mobility could be greatly limited owing to the strong sorption by clays, iron (oxy)hydroxides, and soluble organic matter (Kabata-Pendias, 2011). Selenium is easily oxidized, and the state of its oxidation, as well as its solubility, is controlled by the pH conditions of the ash porewater system. Selenite ions resulting from oxidation processes are stable (depending on Eh) and able to migrate until they are adsorbed on mineral or organic particles in coal fly ash cores. Selenites are the preferred species of Se being adsorbed by clay minerals, particularly by montmorillonite and Fe oxides (Frost and Griffin, 1977).

3.2.6. Molybdenum and chromium

Molybdenum shows strong positive correlation (Spearman’s rho = 0.57, $p = 0.0061$) with depth in the Fe and Mn oxide fractions of the 15-year-old (i.e., AMB 80) ash dump. This trend pattern of Mo...
### Table 6a

Major element distribution in five-step sequential scheme and total metal content in samples taken at 3-m depth intervals in cores AMB 80 and AMB 82: S1 = water soluble fraction; S2 = exchangeable fraction; S3 = carbonate fraction; S4 = iron and manganese fraction; S5 = residual fraction; nd = not detected

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<tr>
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<th>1m</th>
<th>2m</th>
<th>3m</th>
<th>4m</th>
<th>5m</th>
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**Table 6b**

Trace element distribution in five-step sequential scheme and total metal content in samples taken at 3-m depth intervals in cores AMB 80 and AMB 82: S1 = water-soluble fraction; S2 = exchangeable fraction; S3 = carbonate fraction; S4 = iron and manganese fraction; S5 = residual fraction; nd = not detected.
is attributed to porewater pH reduction over time (i.e., less alkaline), which promotes mobilization of Mo compounds in the ash dump. Therefore, molybdenum mobility in the ash dump is dependent on the pH conditions of the ash porewater system. Chromium shows strong positive correlation (Spearman’s rho = 0.702, p = 0.0075) with depth in the residual fraction of the 4-year-old (i.e., AMB 82) ash dump (Table 5). The Cr trend suggests that the majority was found in the residual fraction (i.e., maybe Cr\textsuperscript{VI}) and could be mobile under specific condition (i.e., aggressive conditions, e.g., acidified rain). Soo and Kalembkiewicz (2009) reported the relative abundance of Cr in the residual fraction of coal fly ash and concluded it could migrate to the environments under aggressive conditions (e.g., acidified rain). The inconsequential correlation of Cr with depth in the Fe and Mn oxide fractions suggests that it is prevalent in this fraction and not easily mobile under this extreme condition (i.e., reducible conditions). This immobility of Cr is due to concurrent dissolution and precipitation under decreasing alkaline conditions in the ash dump.

### 3.2.7. Boron and lead

Boron shows strong negative correlation (Spearman’s rho = -0.60, p = 0.0034) with depth in the Fe and Mn oxides of the 15-year-old ash dump. This trend literally suggests depletion of B at deeper levels in the ash dump. This could be attributed to its chemical states (i.e., insoluble form) under reducible conditions. This observed decreased concentration trend could also be attributed to weathering. Boron also shows negligible correlation in all other sequential fractions of 4-year-old (i.e., AMB 82) and 15-year old (i.e., AMB 80) ash dumps (Table 5). This trend suggests that B mobility in the ash dump is not dependent on the porewater pH but on its chemical states. Cox et al. (1978) found that B exists in two independent chemical states, one of which is insoluble. The absorption of B on oxides of Fe and Al and carbonates is also thought to govern its solubility in the ash dump. Pb shows strong positive correlation (Spearman’s rho = 0.72, p = 0.0002) with depth in the Fe and Mn oxide fractions of the 15-year-old ash dump. This suggests that solubility of Pb in the ash dump is strongly pH dependent. Accordingly, the increasing acidity will lead to increased solubility of Pb in the ash dump. Pb distribution within the ash dump profiles is not uniform and reveals a great association with hydroxides, especially Pb, which sorbs onto Fe and Mn hydroxides. Pb shows insignificant correlation in all other sequential fractions of 4- and 15-year-old ash dumps.

### 4. Fractionation Scheme and Efficiency of Fractionation

Akinyemi et al. (2011b) reported that variation in the major element concentrations in each of the five fractions is due in part to the adsorption of metals by different physicochemical forms and the aqueous behavior of inorganic species. The second most important factor is the preferential weathering of ash core ash samples because of fluctuation in porewater pH. Tables 6a and 6b show variability (within 10%) between sums of values obtained for different fractions (pseudo-total concentration) of major and trace element values obtained for the same sample extracted with combined acid leach (total metal content).

### 5. Summary and Conclusions

The pH profile trends of the cores indicate that contact with atmosphere and consequent ingress of CO\textsubscript{2}, leaching by rainwater, and point of saturation have a great effect on weathering of the disposed fly ash. The greatest weathering was observed to occur in the top layer (0.55–3 m depth) in the older (15-year-old) cores and the point of contact with the water table, showing that infiltration of rainwater and point of saturation have a profound effect on the decrease in porewater pH. This would probably be because of rapid dissolution and initial rapid flushing out of the soluble species that also act as pH buffering constituents. These results suggest that soluble fly ash components are highly mobile. Accordingly, any runoff or permeates from the dump will be immediately enriched in these soluble contaminants (Gitari et al., 2011).

Mineralogical analysis of two drilled core samples taken from 4-m depth intervals showed the presence of calcite. It should be noted that from the moment the fly ash comes into contact with the atmosphere, the ingress of CO\textsubscript{2} will lead to a reaction with buffering components such as CaO and the subsequent conversion into calcite. This would further explain the decrease in porewater pH of the weathered sections of core samples compared with the pH of fresh ash extracts.

The ternary plot of major elements as determined by XRF showed that 15-year-old and 2-week-old dry disposed ash cores are sialic, but 4-year-old ash cores are sialic and ferrocalisialic in chemical composition. The association between SiO\textsubscript{2} and CIA shows that the 15- and 4-year-old ash dumps experience a moderate to high degree of chemical weathering. The ash interaction chemistry with the hypersaline effluents could be responsible for the variation in chemical composition of the 4-year-old (i.e., AMB 82) ash dump. The second possible factor responsible for obvious variation in chemical composition of the ash dump is differences in the chemistry of feedstock coals over 15 years of coal combustion and generation of ash in the power utility.

The application of cluster and functional analysis on the major oxides clarifies the subtle chemical alteration and dissolution of major soluble components in the fly ash matrix. The relative enrichment and depletion trends of major elements are promoted by heterogeneity in the ash dump (i.e., packing density plus moisture content), with gradual reduction of porewater pH under continuous inhomogeneous high-saline effluents and fresh water irrigation (Akinyemi et al., 2011a).

A noteworthy decrease in concentration levels of magnesium (4-year-old ash dump) in the Fe and Mn fraction and calcium (15-year-old ash dump) in the carbonate fraction was observed at the deepest levels of the ash dump, which is in direct contact with the atmosphere, the ingress of CO\textsubscript{2} leading to a reaction with buffering components such as CaO and the subsequent conversion into calcite. This indicates the very likely continuous elution of contaminants into groundwater after permeation through the ash dumps (Gitari et al., 2011).

The sequential extraction results generally show that the relative enrichment and depletion of inorganic species at various depths are attributed to chemical interaction of fly ash with ingressed CO\textsubscript{2} from the atmosphere, porewater pH, leaching by percolating rainwater, fluctuation in the water table, heterogeneity in fly ash, inhomogeneous continuous irrigation of fly ash by high-saline effluents, and fresh water.

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References


