A Geochemical Analytical Scheme for the Appraisal of Partitioning and Mobility of Major elements in Weathered Dry Disposed Coal Fly Ash

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Abstracts

South Africa is endowed with significant deposits of coal which is utilized in electricity generation to meet the nation's energy demand. A large volume of waste solid residue from the combustion of pulverized feed coal in power stations is dry disposed in stock piles or dumps. Chemical interactions of dry disposed fly ash with ingressed CO_2 from the atmosphere and infiltrating rain water would cause dissolution of the soluble components in the fly ash matrix. Chemical partitioning and mobility of major elements in samples from cores drilled into serially stacked weathered dry disposed fly ash were investigated using a modified five steps sequential extraction scheme. A total acid digestion was carried out on the original ash core samples prior to extraction to validate the extraction procedure. The geochemical distribution of the investigated major elements in 59 drilled core samples was determined by x-ray fluorescence and inductively coupled plasma mass spectrometry. The relationship between SiO_2 and chemical index of alteration (CIA) showed 8 year and 20-year-old core samples have a moderate to high degree of weathering. Conversely, 1-year-old cores samples showed characteristics between low and moderate-high degrees of weathering. A cluster and discriminant analysis of the major elements was also able to reveal the subtle chemical alteration differences of the core samples. Functional analysis revealed the disparities in the dissolution patterns of major soluble components in the matrix of the drilled core samples. Modified sequential extractions revealed high concentration of the major species in the leachates for every mineralogical fraction; although the bulk of the major elements are locked up in the insoluble phase of the core samples (i.e. residual fraction) which would not be released under normal environmental conditions. It is noteworthy that the concentration of major elements in the labile fractions (water soluble + exchangeable + carbonate) was high and this has implications for the long-term durability of residual mineral phases. Relative enrichment and depletion trends of major elements are promoted by heterogeneity in the ash dump (i.e. moisture content), gradual reduction of pore water pH and continuous brine and water irrigation.

INTRODUCTION

The most visible effort toward environmental management of coal fly ash disposal sites is the attempt to reduce

the contamination problems caused by windblown particulates by dust suppression. Attempts are also made to prevent burning debris or visible pollution of surface waters. Dry disposed coal fly ash in landfills would naturally come into contact with ingressed CO_2 from the atmosphere and with percolating rain water. This chemical interaction would ultimately generate leachates which pose a contamination threat to groundwater systems beneath the ash disposal site. It could take a year or more for dry disposed fresh ash to absorb enough water to yield leachates, and Choi *et al.* (2002) confirms in their studies the influence of the ash leachate from the ash disposal mound on the groundwater composition. Cherkauer (1980) reported a significant modification of groundwater quality by SO_4, Ca and Mg from disposed fly ash leachates. These authors further observed that toxic metals contained in the ash were quite mobile in the groundwater. The possibility of contamination of groundwater system by leachates from fly ash deposited in landfills is expected because of the toxic metals composition of the waste. However, the release of these inorganic metals in fly ash is expected to be highly variable depending on the composition of the feed stock coal.

The inorganic metals in combustion coal by-products are found in different physicochemical forms. It has been reported that the availability and mobility of elements present in fly ashes will depend on the physicochemical forms of the elements (Pe'rez-Bendito and Rubio, 1999). These physicochemical forms include the following broad categories: water soluble; exchangeable forms; specifically adsorbed forms; carbonate fraction; secondary Fe and Mn oxides, organic matter, sulfides, and silicates. All these may occur in a variety of structural forms (Tessier *et al.*, 1979). The concept of the sequential extraction (SE) procedure is the partitioning of a solid material into a specific phase or fraction from which it can selectively be extracted, i.e. liberated and released into solution (leached) along with the associated trace metals, by using the appropriate reagents, arranged in increasing strength (Tessier *et al.*, 1979; Horowitz, 1991, and Tessier *et al.*, 1992). These methods are based on the rational use of a series of more or less selective reagents chosen to successively solubilise the different mineralogical fractions thought to be responsible for retaining the larger part of the trace elements (Gleyzes *et al.*, 2002). Sequential extraction can provide a good insight into the sequence of metal leaching behaviour through determination of metal fractionation or association with different mineral phases in the solid matrix in coal fly ash (Fernández-Turiel *et al.*, 1994; Querol *et al.*, 1996; Goodarzi and Huggins, 2001; Sočo and Kalembkiewicz, 2007). Therefore the sequential chemical extraction procedure provides useful information in environmental studies.

Several sequential chemical extraction schemes have been reported in the literature (Tessier *et al.*, 1979; Smeda and Zyrnicki, 2002; Soco and Kalembkiewicz, 2007). The procedures are usually based on the principle of successive extractions of conceptually distinct lithological or authigenic fractions representing a range of elemental forms, from the most mobile to those strongly bound to the support mineral (Fraser and Lum, 1983). The extractant converts the metal bound in the solid phase into a soluble form. The fraction or proportion of the individual element in each phase depends on the chemical reagents used as the extractants, the chemical and physical operating parameters involved, such as pH, reagent type, concentration, time of contact, particle size, stirring system temperature, etc (Smichowski *et al.*, 2005).

In all of the sequential extraction procedures reported in literature, different chemical reagents are applied in order of increasing reactivity (Tessier *et al.*, 1979; Smeda and Zyrnicki, 2002; Jegadeesan *et al.*, 2008; Smichowski *et al.*, 2008). The sequential chemical extraction procedure reported by Tessier *et al.* in 1979 and the BCR procedure elaborated in 1993 by the Standards, Measurements and Testing Programme (SM&T) are the most representative schemes. Over the last decade an increasing number of publications that have appeared on sequential extraction have some limitations and drawbacks (Kheboian and Bauer, 1987; Shan and Chen, 1993; Go´mez Ariza *et al.*, 2000; Gleyzes *et al.*, 2002). The number of fractionation steps required depends on the purpose of the study. The selectivity of the chemical reagents toward specific physicochemical forms was not taken into consideration for most of the procedures reported (Gleyzes *et al.*, 2002). 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). In spite of these shortcomings, the sequential extraction schemes remain widely used and are considered an essential tool in establishing element fractionation in soils and sediments (Gleyzes *et al.*, 2002). Rao *et al.* (2008) concluded that there are lot of advantages in chemical sequential extraction and still enormous scope for further research and developments in these areas since pollution sites are increasing throughout the world and there is an urgent need to develop methods for faster, more reliable and cost-effective pollution assessment so that suitable remedial measures can be implemented on a priority basis at an appropriate time.

Recent studies on the sequential extraction scheme are modifications stemming from a procedure developed by 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

speciation of metals in contaminated soils (Campos *et al.*, 1998; Gleyzes *et al.*, 2002). Recently the sequential extraction scheme 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 (MSWI) 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).

In the current study, a modified sequential extraction scheme was used to determine the mineralogical association of major elements in weathered drilled cores sequentially stacked together at Tutuka ash dump. The top and bottom sections of the ash dump were deposited in the same year. The dry, disposed ash dump showed extreme heterogeneity in lithology, texture, and moisture content levels. The sequentially stacked ash dumps were continuously irrigated with highly saline effluents arising from power station effluent treatment but the older section (i.e. 20-year-old) was irrigated with water for dust prevention (Akinyemi, 2011c).

This study appraises the chemical partitioning and mobility of investigated major elements in weathered drilled ash cores. The chemical speciation of major elements in drilled cores at different weathering stage was used to: i) understand the mineralogical association patterns with ages in various sections of ash dumps; ii) to identify and quantify the investigated major elements in the physicochemical forms; and iii) to assess and reveal possible factors responsible for the mobility of major 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 dry disposal scenario.

1. MATERIALS AND METHODS

1.1 Sampling Technique and Sample Pre-Treatment

Three cores of different ages were drilled from 1 year (B 83), 8 year (B 81) and 20-year-old (B 79) sections of Tutuka ash dump. 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 and more 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 3 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 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 is reported in our previous study (Akinyemi *et al.*, 2011b).

1.5 Data Treatment and Multivariate Statistical Methods

Multivariate statistical method was applied on the bulk chemical data (i.e. major oxides mass %) in weathered dry disposed fly ash at different stage of weathering using IBM SPSS-19.0 statistical software. Varimax rotated factor analysis was performed on correlation matrix of rearranged data for three different weathered ash dumps. 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 newset 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).

2. RESULTS AND DISCUSSION

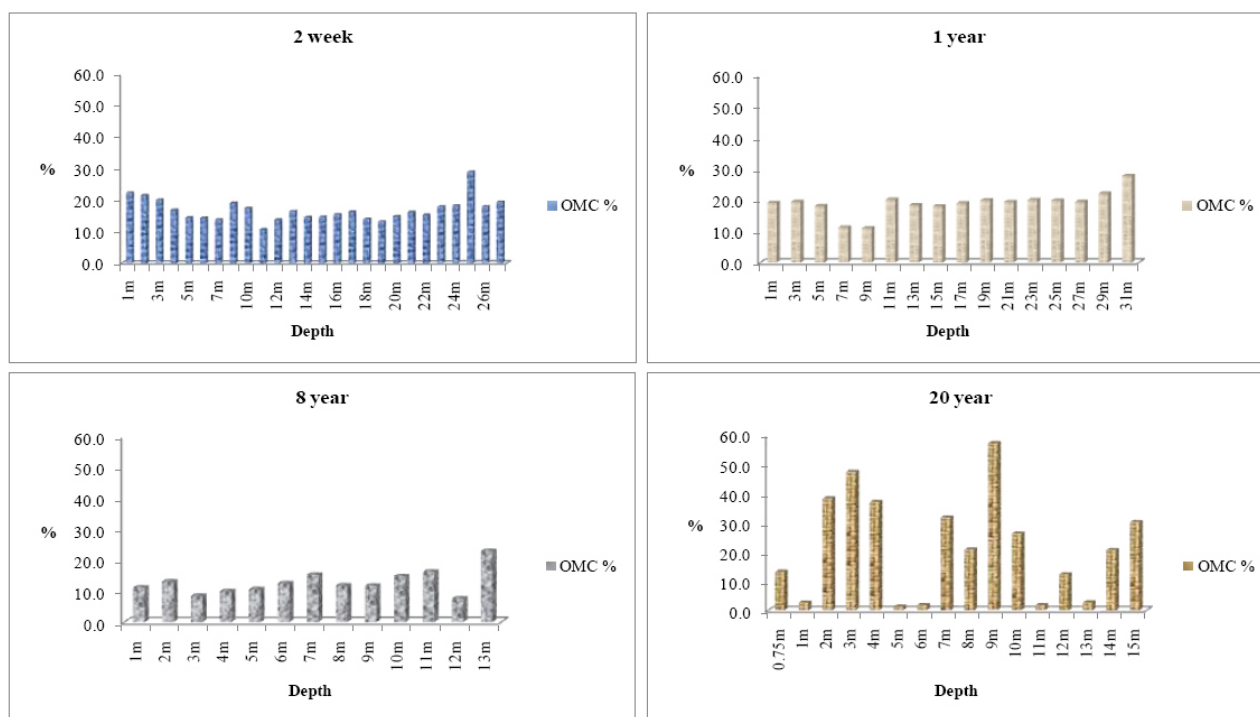### 2.1 Moisture Content, EC and pH of Interstitial Pore Water

Figure 1
Relationship Between % Moisture Content and Depth of Dry Disposed Ash Dump

The determined moisture content of dry disposed fly ashes is shown in Figure 1. There is a significant increase in % moisture content for fly samples taken at 25 m depth (2-week-old). This could be due to migration downward of moisture used for dust suppression. A slight variation in the moisture content in the 1-year-old ash dump indicate very little drying out during first year of dumping. For 8-year-old fly ash dump, the % moisture content shows a steady increase until 3–4 m depth intervals where there is a considerable decrease in the moisture content. Noticeable uneven % moisture content is observed in 8-year-old dry disposed ash dump but a significant increase in % moisture content occurs at 13 m depth. This indicates that the ash dump is slowly drying out over time but is still very damp at the bottom. There is a gradual increase in the % moisture content as a function of sample depth for 20-year-old ash dump which indicates that continuous surface irrigation with water caused high % moisture and salt saturation (highly conductive). However, the moisture content of 20-year-old ash dump decreases inhomogenously at various levels between 5 - 6 m depths (low conductive). A significant increase in moisture content is observed for the core sample in direct contact with groundwater level [i.e. 20 year (9 m)] (Figure 4). The uneven moisture content observed in 20 year, 8

year, 1 year and 2-week-old fly ash dumps could also be attributed to uneven ash placement conditions resulting in varying porosity due to ash packing density or varying ambient weather conditions during placement. Generally in the weathered dry disposed ash relatively low moisture content is observed at the top sections compared to the bottom sections of the ash dumps. Noticeable uneven % moisture content is observed in 8 year and 20-year-old dry disposed ash cores compared to 2 week and 1 year ash cores. The % moisture content showed strong a correlation with inhomogeneity in the ash dump due to textural differences (Akinyemi, 2011c) and in-homogenous brine irrigation. High % moisture content correlate with coarse textured ash cores whilst low % moisture content correlated with fine textured ash core samples.

The coarse texture and resultant high porosity and high % moisture content could lead to salt saturation and thus make the ash conductive (lowering the resistivity) of the section of dump (Akinyemi, 2011c). The continuous surface brine irrigation of dry disposed ash dump would ultimately promote mobility of the chemical species.

Table 1
EC, pH and TDS of the Unweathered and Weathered Core Ash Samples

Ash cores	pH	EC (mS/cm)	TDS (g/L)
2 week	11.0 - 12.0	0.4 - 0.6	0.1 - 0.24
1 year	8.7 - 10.6	0.2 - 0.7	0.12 - 0.42
8 year	9.0 - 10.7	0.51 - 1.03	0.03 - 0.25
20 year	7.2 - 9.9	0.04 - 0.46	0.02 - 0.27

Table 1 shows pH ranges of the interstitial pore water of the samples taken from various aged cores of the ash dump. There is an obvious trend from relatively high values in 2-week-old cores to progressively lower values in more intensely altered 20-year-old ash cores. A review by Donahoe (2004) reports that this major decrease in pH is caused by carbonation, hydrolysis and precipitation after the depletion of portlandite (Ca(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 decrease in EC values was observed in the 2-week-old ash cores. This could be due to non-dissolution or precipitation of

the soluble species in surface layers that may initially also act as pH buffering constituents in fly ash (Gitari *et al.*, 2009).

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). The lower pH values with corresponding increase in EC values would lead to release of significant amount of chemical species. This is due to the dissolution of soluble components in the ash matrix and hence to leaching from the ash dump over time. The reduction in the extracted pore water pH (see Table 1) of the weathered ash dump is due to chemical interaction of fly ash with ingressed CO$_2$ from the atmosphere and percolating rain water. This observation suggests that contact with atmosphere, ingressed CO$_2$, microbial respiration (Schramke, 1992) and leaching by infiltration of rain water has a profound effect on the degree of weathering of disposed fly ash. Schramke (1992) also reported that in fly ash leachates the rate of input of CO$_2$ (g) into the leachate is expected to control the overall rate of pH equilibrium.
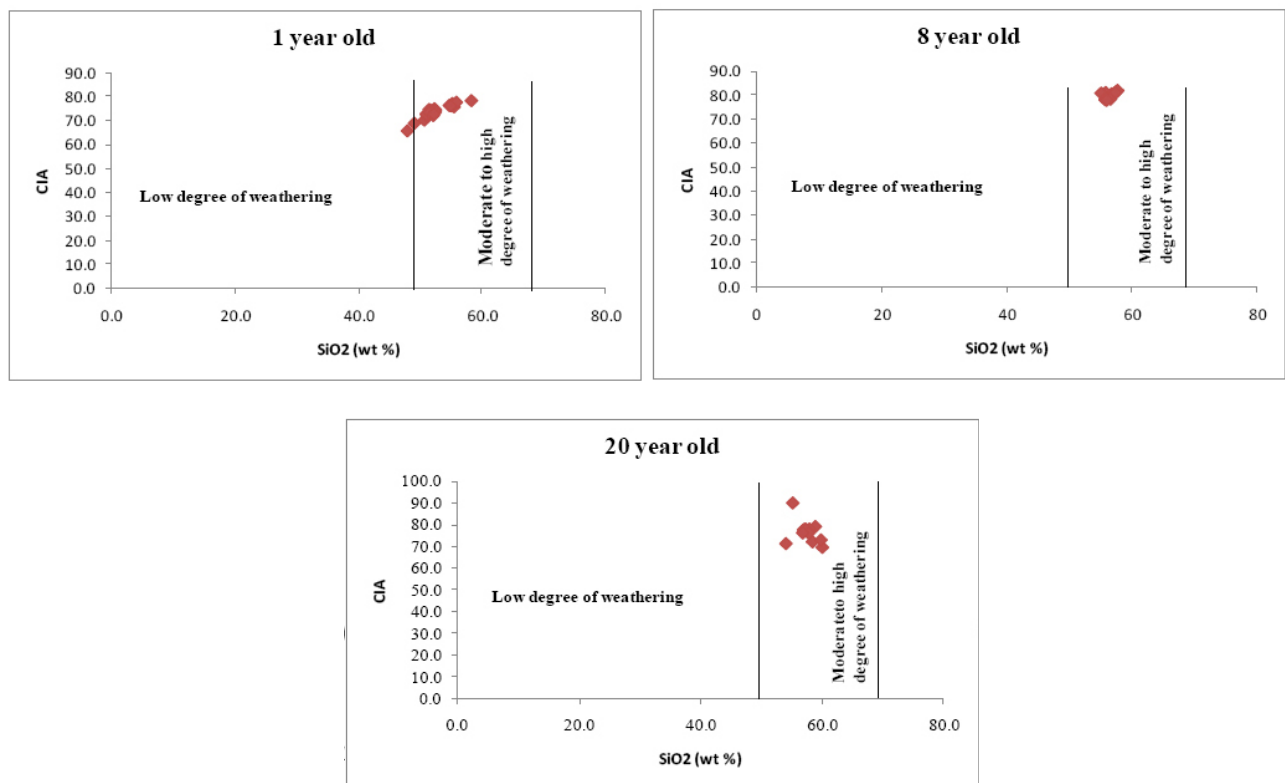

Figure 2
Relationship Between SiO$_2$ (wt %) and Chemical Index of Alteration (CIA) in Weathered Dry Disposed Fly Ashes of Different Ages

2.2 Chemical Alteration of the Dry 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.

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

As a result, the chemical index of alteration (CIA) was calculated for 2 week, 1 year, 8 year and 20-year-old cores. Figure 2 is a plot of CIA values against SiO_2 taken from mass % XRF data in three dry disposed core ashes of different ages. There is an obvious trend from relatively low values in the 1-year-old to progressively higher values in more intense chemically altered 20-year-old core ash. All the core samples from 8 year and 20-year-old ash dumps fall within the cluster showing moderate to high degree of weathering. On the contrary, some core samples in the 1-year-old ash dump fall within low degree of weathering while others fall in the moderate to high degree of weathering. Therefore, the 1-year-old ash dump is the least leached.

The inhomogeneous continuous brine irrigation which makes some section of the dump to receive much more brine than the other is responsible for the disparity in the degree of weathering in the 1-year-old cores. The moderate to high degree of weathering of 8 year and 20-year-old core samples is due to flushing of soluble major components of the fly ash over time. This in turn causes reduction in the pore water pH over time (see Table 2) and subsequently leaches inorganic species from the ash dump. Nevertheless an obvious disparity in the degree of weathering of 20-year-old core samples is due to differential dissolution of fly ash matrix. A slight but obvious disparity in the degree of weathering of 20-year-old core samples could also be due to inhomogeneous continuous water irrigation.

Table 2
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	Comp. III	Communality
MnO	0.97			0.96
Na₂O	0.91			0.85
MgO	0.91			0.85
TiO₂	-0.80	0.45		0.91
SiO₂		-0.96		0.98
P₂O₅		0.89		0.80
CaO	-0.49	0.79		0.91
LOI		0.72	0.49	0.77
SO₃		0.61		0.52
K₂O			0.93	0.88
Al₂O₃	-0.63		-0.88	0.88
Fe₂O₃	0.97		0.66	0.87
EV	4.88	3.07	2.21	
VAR(%)	40.7	25.57	18.42	
CVAR(%)	40.7	66.26	84.69	

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

2.3 Bulk Chemistry of Unweathered and Weathered Drilled Ash Cores

X-ray fluorescence analytical results of unweathered (i.e. 2-week-old) and weathered core ash samples [i.e. 1 year (B 83), 8 year (B 81) and 20-year-old (B 79)] is shown Figure 3. The chemical composition of the major elements in weathered core ash samples showed varying values compared to their composition in the unweathered core ash (2-week-old). The small degree of enrichment of Na in the weathered core samples compared to the unweathered could be attributed to the interaction of irrigated brine with the fly ashes. The conditioning of Tutuka fly ash with brine during and after disposal could be responsible for the slight enrichment of Na content.
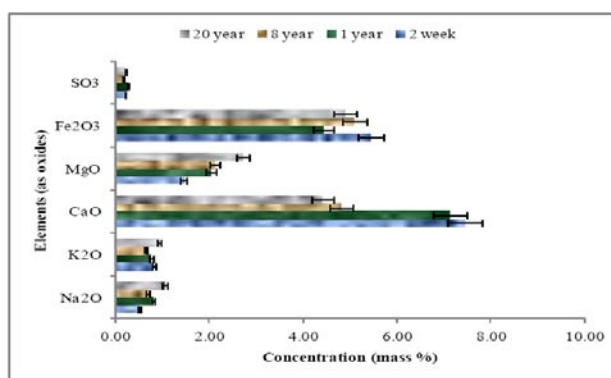

Figure 3
Total Mass % of Na, Ca, K, Mg, Fe and S (as Oxides) in Unweathered (i.e. 2-Week-Old) and Weathered Core Ash Samples (i.e. 1 Year, 8 Year and 20-Year-Old) (n=3) and (*Error Bars Shows 5 % Value*)

The mass % of the calcium as (CaO) in the weathered core ash samples showed high variability over the longer term stored ash. According to Choi *et al*. (2002), Ca is

associated with the highly soluble phase of the fly ash particles, which rapidly dissolves when in contact with infiltrating rain water. The dissolution and subsequent precipitation of calcite in the weathered core samples was responsible for CaO depletion and enrichment observed in the samples (Akinyemi *et al*., 2011). Relative depletion of K_2O is observed in 1 year and 8-year-old core ash and could be due to brine conditioning of ash dumps that promotes leaching over time. The mass % of MgO fluctuates in the weathered core ash over time. Nevertheless, Mg is relatively enriched in the weathered core ash compared to the unweathered core ash. Levels of Fe_2O_3 and SO_3 showed an inconsistent trend in the weathered core ash which could be due to variability of the feed stock coal burnt. In general, Fe_2O_3 was relatively enriched in the unweathered core ash compared to weathered core ash samples. The depletion of Fe_2O_3 in weathered core ash is attributed to chemical weathering.

2.4 Statistical Analysis

2.4.1 Cluster Analysis

The relationship among the weathered dry disposed ash dump obtained through cluster analysis synthesized by the dendogram plots (distance cluster combine) is shown in Figure 4. This gives subtle indication on the degree of chemical weathering of the dry disposed ash dumps. Statistical evaluation of the data based on dendrogram cluster analysis using the major elements Al_2O_3, SiO_2, CaO, MgO, MnO, Fe_2O_3, Na_2O, K_2O, TiO_2, P_2O_5, SO_3 and LOI as variables classified the weathered core samples into 2 groups (Fig. 4).
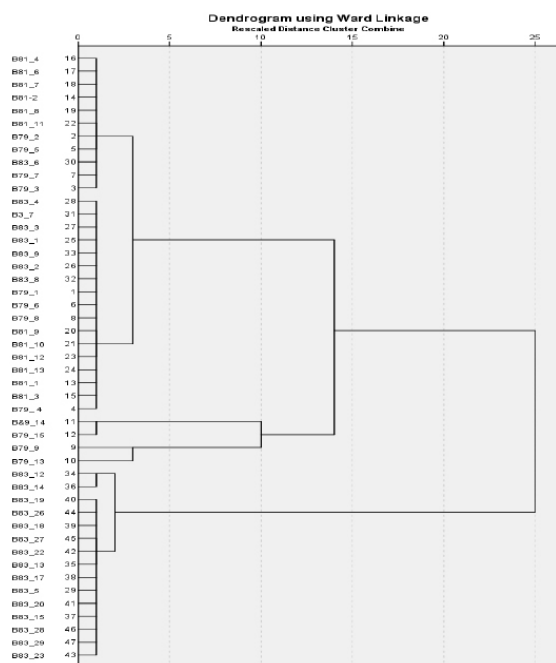

Figure 4
Dendrogram Cluster Analysis of 3 Drilled Weathered Core Samples Using Major Elements Reported as Oxides (wt %) and Loss on Ignition as Variables

Group I consisted of samples mainly from 8 year and 20-year-old ash cores except samples B83-1 m – B83 4 m, and B83-7 m – B83-9 m; group II consists of samples mainly from 1-year-old core samples. The discriminant function analysis performed by comparing structure matrix to functional group centroid, showed strong association of SiO_2, K_2O, MgO, MnO and Fe_2O_3 with group I. On the other hand, Al_2O_3, CaO, Na_2O, P_2O_5, TiO_2, SO_3 and LOI showed weak association with group II at a Function I. The groups are 100 % different from each other. The dendogram shows a sequence in the association, displaying the information as degree of chemical weathering between dry disposed ash dumps. From a look at the dendogram 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 low degree of weathering but the first group falls in the moderate to high degree of chemical weathering.

2.4.2 Functional Analysis

To comprehend the effect of ageing (weathering), which is responsible for enrichment or depletion of major elements and their movement in the 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 and moisture content) in the Tutuka ash dump. The functional analysis of the major elements reported as oxides using rotated component matrix showed 3 components (Table 2). Component I represents 33.52 % of total variance, which is found to be depleted in elements such as TiO_2, CaO, Fe_2O_3 but showed enrichment in Na_2O, MgO, and MnO; Component II represents 29.56% of total variance, which is associated with TiO_2, P_2O_5, CaO, SO_3 and LOI but are depleted in SiO_2 and Component III represents 21.62% of total variance, which is found to be enriched in K_2O, Fe_2O_3 and LOI but are depleted in Al_2O_3.

The depletion of CaO, TiO_2 and Fe_2O_3 in the component I and Al_2O_3 in the component II and III coincide with samples taken from saturated zones in the 20-year-old section of the ash dump. On the other hand, depletion of SiO_2 in the component II coincides with the middle and bottom sections of the 1-year-old 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 CO_2 from atmosphere, infiltrating rain water and fluctuating saturation level over an extended period.

2.5 Partitioning and Mobility of Major Elements in Weathered Drilled Cores

2.5.1 Aluminium and Silicon

Figure 6 shows the average amount of major elements

in the water soluble fraction of samples taken from weathered dry disposed fly ash cores. Si in the water soluble fraction of the 1-year-old ash cores correspond to 5.64 % of the total mass % (which was 57.47 %) in the ash core. In the case of 8-year and 20-year old ash cores, Si in the water soluble fraction was 1.56 % of SiO_2 of total mass % (which was 56.27 %) of the whole ash sample, and 4.33 % of total Si mass % (which was 52.71 %) of the whole ash sample in the ash cores correspondingly. The concentration of Si in the exchangeable fraction was found to be lower than what was observed in the water soluble fraction in the case of ash cores of 1 and 20-year-old section of the dump. The inconsistent concentration trend of Si in the exchangeable fraction of dry, weathered disposed ash cores was attributed to the variation in the pH of the ash pore water.

Al in the water soluble fraction generally showed low concentration in 1 year and 20-year-old cores but represents about 20 % of the total Al mass % (which was 24.28 %) of the whole ash sample. Al concentration in the exchangeable fraction was very low irrespective of the age of the ash cores. The concentration of Al in the 8-year-old ash cores represents 0.29 % of total Al mass % (which was 24.28 %) of Al_2O_3 in the ash core samples while Al concentration in the exchangeable fraction of 1 year and 20-year-old ash cores represented 0.29 % of total Al mass % (which was 24.28 %) and 5.3E-05 % of total Al mass % (which was 21.46 %) of Al_2O_3 in the weathered ash cores respectively.

The bulk of the total Si and Al content in the ash core samples were found in the carbonate, Fe and Mn and the residual fractions. The slow release of Si and Al in the water soluble and exchangeable fraction indicates the leaching of the soluble phases of these species from the core ash dump over time. These species will gradually and continuously leach from the ash dump even at high pH. At lower pH (pH ≤ 5), Al and Si could be released in even larger quantities due to the dissolution of the aluminosilicate phases in the fly ash dump, and the leaching of these major components of the ash matrix would in turn increase the release rate of the trace elements associated with the aluminosilicates.

2.5.2 Sodium and Potassium

The proportion of the total Na released in the water soluble fraction during the sequential extraction tests was 37.16 % of the total Na mass % (which was 1.05 %) of the total ash sample for the 20-year-old ash cores (Figure 5 & 6). Although, Na concentration in the water soluble fraction of 1 year and 8-year-old ash cores represents 24.37 % of the total Na mass % (which was only 0.68 %) of the whole ash sample and 22.49 % of mass % (which was 0.68 %) respectively.
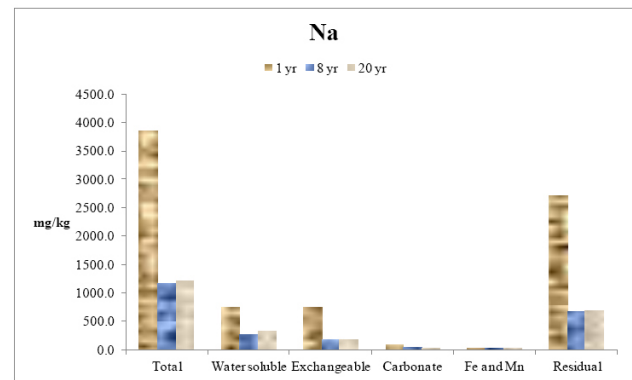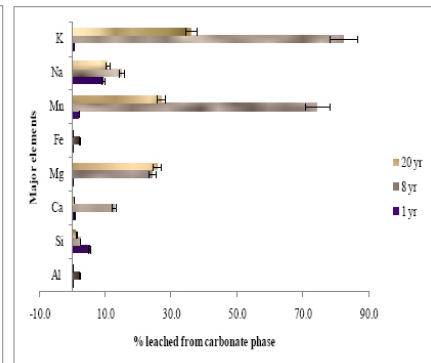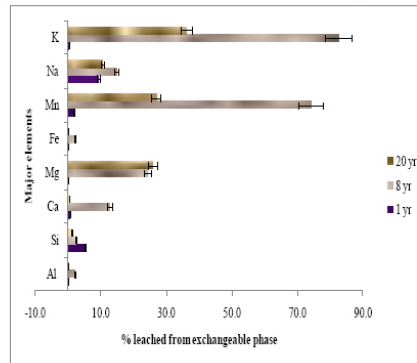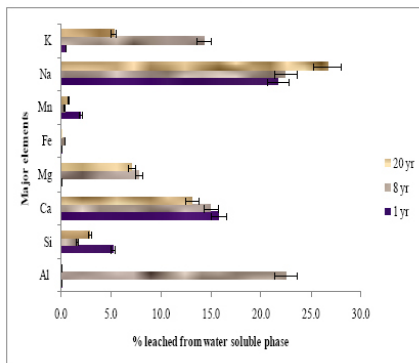

Figure 5
Geochemical Distribution of Na in the Leached Fractions of Weathered Fly Ash

The slight variation in the concentration of Na released from the core ash samples in the water soluble fraction was attributed to inhomogeneous continuous irrigation of the ash dump with highly saline effluents. There was a significant decrease in the concentration of Na in the exchangeable fraction for the three core samples with 20-year-old ash cores releasing 19.79 % of the total Na mass % (which was 1.05 %) of the total ash sample, while the 1 year and 8-year-old ash cores released concentration representing 13.03 % of total Na mass % (which was 0.80 %) and 0.68 % of total Na mass % (which was 14.82 %) of the ash samples respectively.
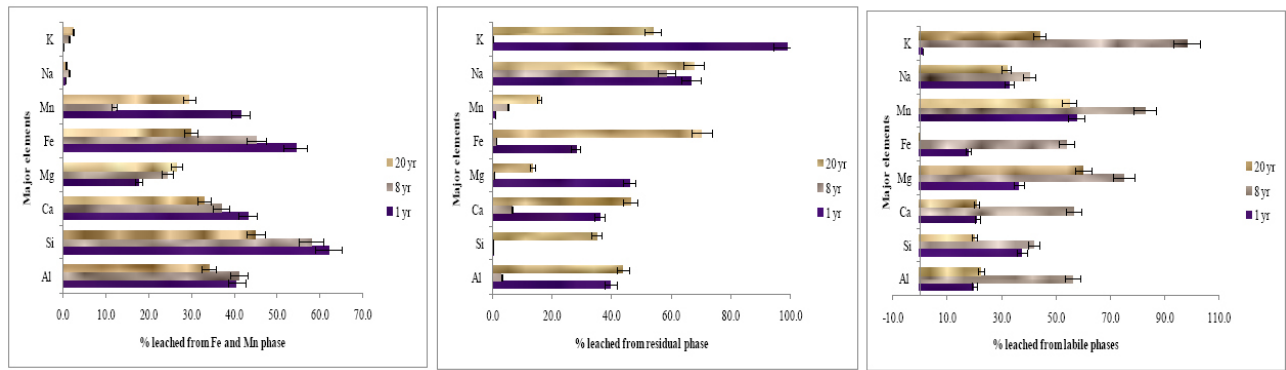
Figure 6
Distribution of Major Elements in the Mineralogical Phases of Dry, Disposed Ash Cores at Different Stages of Weathering
N.B. Labile phases =sum (water soluble + exchangeable+ carbonate)

The considerable proportion of the total Na content of ash that was released from the core ash samples in the water soluble and exchangeable fractions gave an indication that this element exists in association with highly soluble phase(s) in the ash dump (Kim *et al.*, 2003), and can easily be leached when the ash dump is in contact with water. The carbonate fraction of the sequential extraction tests contained low concentration of Na (Figures 5 & 6). On the contrary compared to the proportion of Na observed in the carbonate and Fe and Mn fractions, the % of the total Na concentration remained in the residual fraction represented the largest proportion of the total Na content. Hence, a significant proportion of the total amount of Na present in the fly ash was part of the insoluble residual ash matrix and may not be easily released from the ash dump. However, Na shows the highest % leaching when compared to other elements released in the water soluble fraction, with values in the range of 4 to 7 %. The high concentration of Na released in the labile fractions of the ash core indicated the existence of significant amounts of Na existed as highly soluble salts such as NaCl, which are soluble and mobile under natural environmental conditions. The elements that exist in the soluble labile form can be easily leached and readily reach the environment when fly ash is flushed by infiltrating rain water (Yuan, 2009). The proportional release of Na in the water soluble fraction showed that any Na that had been removed from the high saline effluents during the interactions of brine with fly ash could be rapidly leached when in contact with infiltrating water (Kirby and Rimstidt, 1993). Thus it is highly unlikely that the ash dump is a sustainable salt sink irrespective of the co-disposal method used. It is also noteworthy that nowhere in the core samples was an accumulation of Na noted and the maximum amount of Na, never exceeded 1 mass % in the ash (Figure 3).

K concentration in water soluble fraction represents 14.33 % of the total K mass % (which was 0.64 %) of the total ash samples in the 8-year-old ash dump. Although, K concentration in water soluble fraction corresponds to 5.22 % of the total K mass % (which was 0.64 %) and 0.42 % of the K mass % (which was 0.75 %) of the total ash samples in the 20 year and 1-year-old ash dump respectively. K concentration in the exchangeable fraction represents 82.49 % of the total K mass % (which was 0.64 %) of the total ash samples in the 8-year-old ash dump. K concentration corresponds to 36.05 % of the total K mass % (which was 0.93 %) and 0.42 % of the K mass % (which was 0.75 %) of the total ash samples in the 20 year and 1-year-old ash dump respectively. A noticeable high concentration of K in the water soluble and exchangeable fractions of 8-year-old ash dump is due to inhomogeneous continuous brine irrigation (Akinyemi *et al.*, 2011b). A significant concentration of K released in the labile fraction of core samples (Figure 6) suggests considerable amount of K exist as soluble salts. A considerable high concentration of K was found in the residual fractions (i.e. insoluble phase) of 1 year and 20-year-old ash dump.

2.5.3 Calcium and Magnesium
Ca concentration in the water soluble fraction represents 15.71 % of the total Ca mass % (which was 7.14 %) of the total ash samples in the 1-year-old ash dump. Whereas, Ca concentration in the water soluble fraction corresponds to 14.99 % of total Ca mass % (which was 4.81 %) and 13.11 % of total Ca mass % (which was 4.41 %) of the total ash samples in the 8 year and 20-year-old ash dump respectively. Ca concentration in the exchangeable fraction corresponds to 12.64 % of the total Ca mass % (which was 4.41 %) of the total ash samples in the 20-year-old ash dump. Although, Ca concentration in the exchangeable fraction represents 0.65 % of total Ca mass % (which was 7.14 %) and 0.39 % of total Ca mass % (which was 4.81 %) of the total ash samples in the 1 year and 8-year-old ash dump respectively.

A noticeable low concentration of Ca in the exchangeable fraction of relatively young cores (i.e. 1 and

8-year-old) is due to rapid dissolution of aluminosilicate minerals as a result of over time reduction of pore water pH. In contrast, relatively high concentration of Ca in the 20-year-old ash dump is due to precipitation of calcite due to chemical weathering over an extended period (Akinyemi *et al.*, 2011a). Mg concentration trend showed close similarity with Ca in the water soluble and exchangeable fractions of the 3 drilled cores (Figure 6). A considerable concentration of Ca and Mg releases in the labile fraction of 8 year and 20-year-old cores is attributed to heterogeneity in the ash dump (i.e. ash texture and moisture content). The bulk of Ca and Mg in the core samples were found in the Fe and Mn and the residual fractions (i.e. non leachable) of the 3 drilled cores (Figure 6).

2.5.4 Iron and Manganese

Fe concentration in the water soluble fraction corresponds to 0.35 % of total Fe mass % (which was 5.09 %) of the total ash samples in the 8-year-old ash dump. Nevertheless, concentration of Fe in the water soluble fraction represents 0.002 % of the total Fe mass % (which was 4.44 %) and 0.001 % of the total Fe mass % (which was 4.89 %) of the total ash samples in the 1 year and 20-year-old ash dump respectively. Fe in the exchangeable fraction represents 2.05% of mass % (i.e. 5.09 %) of the total ash samples in the 8-year-old ash dump. However, Fe concentration in the exchangeable fraction stand at 0.002% of the total Fe mass % (which was 4.44 %) and 5.24E-06 % of the total Fe mass % (which was 4.89 %) of the total ash samples in the 1 year and 20-year-old ash dump correspondingly.

Mn concentration in the water soluble fraction characterizes 1.93 % of the total Mn mass % (which was 0.05 %) of the total ash samples in the 1-year-old ash dump. Nonetheless, Mn concentration in the water soluble fraction corresponds to 0.66 % of the total Mn mass % (which was 2.71 %) and 0.31 % of the total Mn mass % (which was 0.04 %) of the total ash samples in the 20 year and 8-year-old ash dump respectively. Mn concentration in the exchangeable fraction corresponds to 74.42 % of the total Mn mass % (which was 0.04 %) of the total ash samples in the 8-year-old ash dump.

Nonetheless, Mn concentration represents 26.91 % of the total Mn mass % (which was 2.71 %) and 1.93 % of the total Mn mass % (which was 0.05 %) of total ash samples in the 20 year and 1-year-old ash dump respectively. Mn showed relative enrichment in the older ash cores but Fe shows contradictory patterns in exchangeable fraction of the ash cores (Figure 6). A considerable high concentration of Fe and Mn in the labile phase of 8-year-old core samples is possibly due to heterogeneity in the ash dump (i.e. ash texture). Notwithstanding the considerable concentration in labile phase, the bulk of Fe and Mn were found in the Fe and Mn and residual fractions of the 3 drilled cores (Figure 6).

In spite of the high concentration of the major species in the leachates at every fraction, bulk of the major elements are locked up in the matrix of the core samples (as shown in the residual fraction) which cannot be released under environmental conditions.

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).

4. SUMMARY AND CONCLUSIONS

The following summary could be drawn from the results of the investigated major elements using modified sequential extraction scheme on the ash dumps of different ages:

The concentration of each of the major elements associated with the labile fractions (water soluble, exchangeable and carbonate) was high and this has implications for the long-term durability of any secondary mineral phases that may form during ash storage. This raises question about the sustainability of disposing salts on the dry disposed ash dump. This study revealed the potential for brine irrigation to negatively impact the surface and groundwater in the vicinity of the ash dump if practiced over an extended period.

Relationship between SiO$_2$ and chemical index of alteration (CIA) showed 8 year and 20-year-old core samples have moderate to high degree of weathering. Conversely, 1-year-old cores samples lie between low and moderate to high degree of weathering.

The application of multivariate data treatment method clarifies the subtle chemical alteration and dissolution of major soluble component in the fly ash matrix. Relative enrichment and depletion trends of major elements are promoted by heterogeneity in the ash dump (i.e. packing density + moisture content), with gradual reduction of pore water pH under continuous inhomogeneous brine irrigation.

Modified sequential extractions revealed a large proportion of each of the major elements in the leachates for every fraction; although the bulk of the major elements were associated with the insoluble phase of the core

samples (i.e. residual fraction) which may not easily be released under normal environmental conditions.

It is noteworthy that the concentration of major elements in the labile fractions (water soluble, exchangeable and carbonate) was high and this has implications for the long-term durability of mineral phases.

ACKNOWLEDGEMENTS

REFERENCES

[1] Akinyemi, S. A., Akinlua, A., Gitari, W. M., & Petrik, L. F. (2011a). Mineralogy and Mobility Patterns of Chemical Species in Weathered Coal Fly Ash. *Energy Sources, Part A, 33*, 768–784. doi: 10.1080/15567030903261881

[2] Akinyemi, S. A., Akinlua, A., Gitari, W. M., Akinyeye, R. O., & Petrik, L. F. (2011b). The Leachability of Major Elements at Different Stages of Weathering in Dry Disposed Coal Fly Ash. *Coal Combustion and Gasification Products, 3*, 28-40. doi: 10.4177/CCGP-D-11-00005.1

[3] Akinyemi, S. A. (2011c). Geochemical and Mineralogical Evaluation of Toxic Contaminants Mobility in Weathered Coal Fly Ash: as a Case Study, Tutuka dump site, South Africa. Unpublished PhD thesis, University of the Western Cape, South Africa.

[4] Al-Abed, S. R., Jegadeesan, G., Purandare, J., & Allen, D. (2007). Arsenic Release from Iron Rich Mineral Processing Waste: Influence of pH and Redox Potential. *Chemosphere, 66*, 775-782.

[5] Campos, E., Barahona E., Lachica, M., & Migorance, M. D. (1998). A Study of the Analytical Parameters Important for the Sequential Extraction Procedure Using Microwave Heating for Pb, Zn and Cu in Calcareous Soils. *Analytica Chimica Acta, 369*, 235-243.

[6] Chang, C., Wang, C., Mui, D. T., & Chiang, H. (2009). Application of Methods (Sequential Extraction Procedures and High-Pressure Digestion Method) to Fly Ash Particles to Determine the Element Constituents: A Case Study for BCR 176. *Journal of Hazardous Materials, 163*, 578-587.

[7] Cherkauer, D. S. (1980). The Effect of Fly Ash Disposal on a Shallow Ground-Water System. *Ground Water, 18*, 544-550.

[8] Choi, S. K., Lee, S., Song, Y. K., & Moon, H. S. (2002). Leaching Characteristics of Selected Korean Fly Ashes and Its Implications for the Groundwater Composition near the Ash Disposal Mound. *Fuel, 81*, 1083-1090.

[9] Comans, R. N. J. Meima, J. A., & Geelhoed, P. A. (2000). Reduction of Contaminant Leaching from MSWI Bottom Ash by Addition of Sorbing Components. *Waste Management, 20*, 125-133.

[10] Donahoe, R. J. (2004). Secondary Mineral Formation in Coal Combustion Byproduct Disposal Facilities: Implications for Trace Element Sequestration. In: Gieré R, Stille P Editors. Energy, Waste and the Environmental: a Geochemical Perspective, Geological Society, London. *Special Publications, 236*, 641–658.

[11] Fernández-Turiel, J. L., Cabañas, M., Querol, X., & López-Soler, A. (1994). Mobility of Heavy Metals from Coal Fly Ash. *Environ. Geol., 23*, 264-270.

[12] Fraser, J. L., & Lum, K. R. (1983). Availability of Elements of Environmental Importance in Incinerated Sludge Ash. *Environ. Sci. Technol., 17*, 52-54.

[13] Galbreath, K. C., & Zygarlicke, C. J. (2004). Formation and Chemical Speciation of Arsenic-Chromium-, and Nickel-Bearing Coal Combustion PM 2.5. *Fuel Proc. Technol., 85*, 701-726.

[14] Garavaglia, R., & Caramuscio, P. (1994). Coal Fly-Ash Leaching Behaviour and Solubility Controlling Solids. In: Goumans, J. J. M., van der Sloot, H. A., and Aalbers, Th. G. Editors, Environmental Aspects of Construction with Waste Materials, Amsterdam: Elsevier Science.

[15] Gitari, W. M., Petrik, L. F., Key, D. L., & Okujeni, C. (2010). Partitioning of Major and Trace Inorganic Contaminants in Fly Ash Acid Mine Drainage Derived Solid Residues. *Int. J. Environ. Sci. Tech., 7*(3), 519-534.

[16] Gitari, M. W., Fatoba, O. O., Nyamihingura, A., Petrik, L. F., Vadapalli, V. R. K., Nel, J., October, A., Dlamini, L., Gericke, G., Mahlaba, J. S. (2009). Chemical Weathering In a Dry Ash Dump: An Insight from Physicochemical and Mineralogical Analysis of Drilled Cores. World of Coal Ash (WOCA) Conference in Lexington, KY, USA.

[17] Gleyzes, C., Tellier, S., & Astruc, M. (2002). Fractionation Studies of Trace Elements in Contaminated Soils and Sediments: A Review of Sequential Extraction Procedures. *Trends in Analytical Chemistry, 21*, 451-467.

[18] Grisafe, D. A., Angino, E. E., & Smith, S. M. (1988). Leaching Characteristics of a High Calcium Fly Ash as a Function of pH: A Potential Source of Selenium Toxicity. *Applied Geochem., 3*, 601-508.

[19] Goodarzi, F., & Huggins, F. E. (2001). Monitoring the Species of Arsenic, Chromium and Nickel in Milled Coal, Bottom Ash and Fly Ash from a Pulverized Coal-Red Power Plant in Western Canada. *J. Environ. Monit., 3*, 1-6.

[20] Go´mez Ariza, J. L., Gira´ldez, I., Sa´nchez-Rodas, D., & E. Morales, E. (2000). Selectivity Assessment of a Sequential Extraction Procedure for Metal Mobility Characterization Using Model Phases. *Talanta, 52*, 545–554.

[21] Helena, B. A., Vega, M., Barrado, E., Pardo, R., & Fernandez, L. (1999). A Case of Hydrochemical Characterization of an Alluvial Aquifer Influenced by Human Activities. *Water Air Soil Pollut., 112*, 365–387.

[22] Horowitz, A. J. (1991). A Primer on Sediment-Trace

Element Chemistry. Chelsea: Lewis Publication Incorporation.

[23] Iwashita, A., Sakaguchi, Y., Nakajima, T., Takanashi, H., Ohki, A., & Kambara, S. (2005). Leaching Characteristics of Boron and Selenium for Various Coal Fly Ashes. *Fuel, 84*, 479-485.

[24] Jegadesaan, G., Al-Abed, S. R., & Pinto, P. (2008). Influence of Trace Metal Distribution on Its Leachability from Coal Fly Ash. *Fuel, 87*, 1887-1893.

[25] Jankowski, J., Ward, C. R., French, D., & Groves, S. (2006). Mobility of Trace Elements from Selected Australian F l y Ashes and Its Potential Impact on Aquatic Ecosystems. *Fuel, 85*, 243–256. doi:10.1016/j.fuel.2005.05.028

[26] Kalembkiewicz, J., Sitarz-Palczak, E., & Zapala, L. (2008). A Study of the Chemical Forms or Species of Manganese Found in Coal Fly Ash and Soil. *J. Microchem., 90*, 37-43.

[27] Khanra, S., Mallick, D., Dutta, S. N., & Chaudhuri, S. K. (1998). Studies on the Phase Mineralogy and Leaching Characteristics of Coal Fly Ash Water, Air, and Soil. *Pollution, 107*, 251–275.

[28] Kheboian, C., & Bauer, C. F. (1987). Accuracy of Selective Extraction Procedures for Metal Speciation in Model Aquatic Sediments. *Analytical Chemistry, 59*, 1417-1425.

[29] Kim, A. G., Kazonich, G., & Dahlberg, M. (2003). Relative Solubility of Cations in Class F Fly Ash. *Environmental Science Technology, 37*, 4507–4518.

[30] Kirby, C. S., & Rimstidt, J. D. (1994). Interaction of Municipal Solid Waste Ash with Water. *Environmental Science and Technology, 28*(3), 443-451.

[31] Kukier, U., Ishak, C. F., Summer M. E., & Miller, W. P. (2003). Composition and Element Solubility of Magnetic and Non-Magnetic Fly Ash Fractions. *Environ. Pollut., 122*, 255-266.

[32] Liu, C. W., Lin, K. H., Y. M., & Kuo, Y. M. (2003). Application of Factor Analysis in the Assessment of Ground Water Quality in the Blackfoot Disease Area in Taiwan. *Sci. Total Environ., 313*, 77–89.

[33] Massart, D. L., Vandeginste, B. G. M., Deming, S. N., Michotte, Y., & Kaufman, L. (1988). *Chemometrics, A Textbook*. Amsterdam: Elsevier.

[34] Mester, Z., Cremisini, C., Ghiara, C., & Morabito, R. (1998). Comparison of Two Sequential Extraction Procedures for Metal Fractionation in Sediment Samples. *Anal. Chim. Acta., 359*, 133-142.

[35] Nesbitt, H. W., & Young, G. M. (1982). Early Proterozoic Climates and Plate Motions Inferred from Major Element Chemistry of Lutites. *Nature, 299*, 715-717.

[36] Ojo, O. I. (2009). Mineralogy and Chemical Mobility in Some Weathered Ash Dump Sites, South Africa, Unpublished M.Sc Thesis, Earth Sciences Department, University of the Western Cape, South Africa.

[37] Pe´rez-Bendito, D., Rubio, S., et al. (1999). Environmental Analytical Chemistry. Comprehensive Analytical Chemistry Series (vol. 32, pp. 709). Amsterdam: Elsevier.

[38] Petit, M. D., & Rucandio, M. I. (1999). Sequential Extractions for Determination of Cadmium Distribution in Coal Fly Ash, Soil and Sediment Samples. *Anal. Chim. Acta., 401*, 283-291.

[39] Querol, X., Juan, R., Lopez-Soler, A., Fernandez-Turiel, J. L., & Ruiz, C. R. (1996). Mobility of Trace Elements from Coal and Combustion Wastes, *Fuel, 75*, 821-838.

[40] Rao, C. R. M., Sahuquillo, A., & Lopez Sanchez, J. F. (2008). A Review of the Different Methods Applied in Environmental Geochemistry for Single and Sequential Extraction of Trace Elements in Soils and Related Materials, *Water Air Soil Pollut., 189*, 291–333.

[41] Schramke, J. A. (1992). Neutralization Of Alkaline Coal Fly Ash Leachates by CO_2 (g). *Applied Geochemistry, 7*, 481–492.

[42] Shan, X.Q., & Chen, B. (1993). Evaluation of Sequential Extraction for Speciation of Trace Metals in Model Soil Containing Natural Minerals and Humic Acid. *Anal. Chem., 65*, 802–807.

[43] Smeda, A., & Zyrnicki, W. (2002). Application of Sequential Extraction and the ICP-AES Method for Study of the Partitioning of Metals in Fly Ashes. *Microchemical, 72*, 9-16.

[44] Smichowski, P., Polla, G., Gomez, D., Fernandez Espinosa, A. J., & Lopez, A. C. (2008). A Three Step Sequential Metal Fractionation Scheme for Fly Ashes Collected in an Argentine Thermal Power Plant. *Fuel, 87*, 1249-1258.

[45] Patricia Smichowski, P., Polla, G., & Go´mez, D. (2005). Metal Fractionation of Atmospheric Aerosols via Sequential Chemical Extraction: A Review. *Anal Bioanal Chem., 381*, 302–316.

[46] Soˇco, E., & Kalembkiewicz, J. (2007). Investigations of Sequential Leaching Behavior of Cu and Zn from Coal Fly Ash and Their Mobility in Environmental Conditions. *J. Hazard. Mat., 145*, 482–487.

[47] Theis, T. L., & Wirth, J. L. (1977). Sorptive Behavior of Trace Metals on Fly Ash in Aqueous Systems. *Environmental Science & Technology, 11*, 1096-1100.

[48] Tessier, A. (1992). Sorption of Trace Elements on Natural Particles in Oxic Environments. In: Buffle, J. and Van Leeuwen, H.P., Editors (pp. 425–453). Environmental Particles, Environmental Analytical and Physical Chemistry Series, Boca Raton, F L: J. Lewis Publishers.

[49] Tessier, A., Campbell, P. G. C., & Bisson, M. (1979). Sequential Extraction Procedure for the Speciation of Particulate Traces Metals. *Analy. Chem., 51*, 844-850.

[50] Van der Hoek, E. E., Bonouvrie, P. A., & Comans, R. N. J. (1994). Sorption of As and Se in Mineral Components of Fly Ash, Relevance for Leaching Processes. *Appl. Geochem., 9*, 406-412.

[51] Van der Hoek, E. E., & Coman, R. N. J. (1999). Speciation of As and Se During Leaching of Fly Ash. *Stud. in Environ. Sci., 60*, 467-476.

[52] Wang, J., Wang, T., Burken, J. G., Chusuei, C. C., Ban, H., Ladwig, K., & Huang, C. P. (2008). Adsorption of Arsenic (V) onto Fly Ash: A Speciation-Based Approach. *Chemosphere, 72*, 381-388.

[53] Wang, T., Su, T., Wang, J., & Ladwig, K. (2007). Calcium

Effects on Arsenic (V) Adsorption onto Coal Fly Ash. Covington, Kentucky: World of Coal Ash (WOCA).

[54] Willet, P. (1987). *Similarity and Clustering in Chemical Information Systems*. Chichester: Wiley, Research Studies Press.

[55] Yinghui, L., Chuguang, Z., & Quanhai, W. (2008). Speciation of Most Volatile Toxic Trace Elements During Coal Combustion. *Dev. in Chem. Eng. and Min. Proc., 11*, 381-394.

[56] Yuan, C. G. (2009). Leaching Characteristics of Metals in Fly Ash from Coal-Fired Power Plant by Sequential Extraction Procedure. *Microchimica Acta, 165*, 91-96.

[57] Zevenbergen, C., Vander Wood, T., Bradley, J. P., Van Der Broeck, P. F. C. W. Orbons, A. J., & Van Reeuwijk, L. P. (1994). Morphological and Chemical Properties of MSWI Bottom Ash with Respect to the Glassy Constituents. *Hazardous Waste and Hazardous Materials, 11*, 371–383.

[58] Zielinski, R. A., Foster, A. L., Meeker, G. P., & Brownfield, I. K. (2007). Mode of Occurrence of Arsenic in Feed Coal and Its Derivative Fly Ash, Black Warrior Basin, Alabama. *Fuel, 86*, 560-572.