

An Investigative Study on the Chemical, Morphological and Mineralogical Alterations of Dry Disposed Fly Ash During Sequential Chemical Extraction

S. A. Akinyemi^{1,*}; A. Akinlua¹; W. M. Gitari²; S. M. Nyale³; R. O. Akinyeye³; L. F. Petrik³

¹Fossil Fuel and Environmental Geochemistry Group, Department of Earth Sciences; University of the Western Cape, Private Bag X17, Bellville 7535, South Africa.

²Environmental Remediation and Water Pollution Chemistry Group, Department of Ecology and Resources Management, School of Environmental Studies, University of Venda. Private Bag, X5050, Thohoyandou, 0950, South Africa.

³Environmental and Nano Sciences Group, Department of Chemistry; University of the Western Cape, Private Bag X17, Bellville 7535, South Africa.

*Corresponding author.

E-mail: akinyemi70@gmail.com

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Abstract

The hazardous elements associated with various physicochemical forms in coal fly ash are of environmental concern due to their leaching potential and subsequent contamination of surface and groundwater in the vicinity of the ash dump. Selective sequential extraction was performed on dry disposed fly ash samples from a coal-fired power station in Mpumalanga province, South Africa. The alteration of the chemical, morphological and mineralogical species of weathered fly ash during the selective sequential extraction was investigated using X-ray fluorescence (XRF), Nano-scan electron microscopy (NANOSEM) and X-ray powder diffraction (XRD). Insoluble residue from the water-soluble fraction is composed of amorphous alumino-silicate. The residues from exchangeable, carbonate and Fe and Mn fractions consisted mostly of amorphous alumino-silicate spheres with a lesser quantity of iron-rich spheres. The iron-rich spheres are surrounded by amorphous alumino-silicate spheres. The leaching behavior of trace metals (such as Ce, Y, Nb, Rb, U, and Tl) in weathered dry disposed fly ash was considered to have a dependency relationship with the components of SiO₂, CaO, MgO, P₂O₅, and

amount of unburned carbon. The decrease in the quantities of calcite with successive extraction could be considered as a marker of progress of sequential extraction technique. At the same time, the increase in the quantities of quartz could be also considered as an indicator of progress of the sequential extraction scheme. Trace elements bound to exchangeable or carbonate fraction during sequential chemical extraction were found associated with calcite. The elemental concentrations, as determined by electron dispersive x-ray spectroscopy (EDS), were consistent with XRF and XRD data. Therefore, the chemical extractant used in this study proved efficient for extraction of inorganic metals associated with various physicochemical forms in weathered fly ash.

Key words: Coal fly ash; Selective sequential extraction; Major components; Trace elements; Morphology; Mineralogical composition

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INTRODUCTION

Huge volumes of solid materials like coal fly ash (CFA) are generated during the production of electrical power from coal. The properties of CFA depend on the physicochemical properties of the coal, combustion conditions and other factors (Saikia *et al.*, 2006).

Coal fly ash is the finest coal combustion residue (0.001 - 90 µm) resulting from the transformation of mineral matter present in coal (Tomeczek and Palugniok, 2002; Chen *et al.*, 2005a,b; Hower *et al.*, 2008; Silva *et al.*, 2010a,b). Accordingly, the solid combustion residue

is a complex mixture of a variety of materials. Coal fly ash consists of fine, powdery particles predominantly spherical, either solid or hollow, and mostly glassy (amorphous) (Ahmaruzzaman, 2010). Bhanarkar *et al.* (2008) recognized factors such as differences in the coal types, boiler types, combustion conditions and pollution control equipment may influence the size distribution of the particulate matter. The fine texture of CFA results in water permeability and infiltration rates of ash deposits being characteristically low (Cope, 1962; Townsend and Hodgson, 1973; Bern, 1976). Cope (1962) noted that lateral hydraulic conductivity in CFA deposits can be much greater than vertical conductivity. Many coal fly ashes are composed mostly of silt-sized spherical amorphous ferro aluminosilicate materials and are usually characterized by low permeability, low bulk density, and high specific surface area (Petrik *et al.*, 2007). As noted, CFA contains 60 - 95 % of particles in the silt plus fine sand fractions and there is a lack of any aggregate formation. Accordingly, dry CFA surfaces are susceptible to wind erosion especially if they have been disturbed (e.g. cultivated). The ultra/nano fines CFA particles can be carried from disposal sites thereby contributing to visual and dust pollution experience in adjacent townships (Junor, 1978). Indeed, wind erosion is often the most obvious pollution hazard of CFA disposal sites.

The surface area of fly ashes is dependent on particle size. The large surface areas of fly ash are attributable to carbonaceous particles of highly porous character (Schure *et al.*, 1985). The specific gravity of CFA usually ranges from 2.1 to 3.0, while its specific surface area may vary from 170 to 1000 m²/kg (Mattigod *et al.*, 1990).

Coal fly ash is considered to be a ferro aluminosilicate material with Al, Ca, Fe, K, Na, and Si as the predominant elements in higher concentrations relative to those found in the parent coal. Jones and Straughan (1978) reported that elements such as Al, Si, Mg, Fe, Mn, Na, and K have fly ash-to-soil concentration ratios less than 2 in the southwest region of United States. Fossil fuel wastes are also enriched with sulphur when compared with soil (Adriano *et al.*, 1980; Mattigod *et al.*, 1990). The sulphur content of the parent coal determines the pH of CFA which could range between 4.5 and 12 (Adriano *et al.*, 1980; Murarka *et al.*, 1991). Certain elements are characteristically enriched in fly ash particles, especially As, B, Mo, S, and Se (Page *et al.*, 1979; Aitken and Bell, 1985). Studies have shown that As, Cd, Cu, Mo, Pb, S, Se, Tl and Zn concentrations generally increase with decreasing particle size (Davison *et al.*, 1974; Natusch *et al.*, 1975). The suggested main mechanism for this phenomenon involves the volatilization of elements during combustion, followed by condensation on the surface of CFA ultrafine/nano particles as temperature decreases in the emission stack.

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; Gómez Ariza *et al.*, 2000; Gleyzes *et al.*, 2002). 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 number of fractionation steps required depends on the purpose of the study. 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; Quispe *et al.*, 2012). The sequential chemical extraction procedure reported by Tessier *et al.* (1979) is the most representative scheme employed. In Tessier's *et al.* procedure, they classified five chemical types of ions that bind on the surface of an inorganic matrix: exchangeable phase, carbonate phase, Fe-Mn oxides, organic matter phase, and residual (silicates) phase. The International Ash Working Group (IAWG) (1997) hypothesized that the results of sequential extraction might not necessarily reflect the associations with the claimed phases, but rather represents the different leaching conditions within a landfill over time. The exchangeable phase is immediately available under neutral conditions; the carbonates phase is potentially available under neutral conditions; the phases of Fe-Mn oxides and organic matter are potentially available under reducing conditions; the residual phase is unavailable for leaching (Wan *et al.*, 2006).

In this present study, the alteration of the chemical, morphological and mineralogical species of CFA and release of species associated with each extracted geochemical phase is explored. This is done with a view to assessing the efficiency of the extraction chemicals for each geochemical phase.

1. MATERIALS AND METHODS

Four duplicated weathered fly ash (20-year-old) samples were sequentially extracted in five geochemical fractions: water soluble fraction, exchangeable fraction, carbonate fraction, amorphous Fe-Mn oxides fraction, and residual fraction. The residues from the four fractions, named, respectively, WFR, EFR, CFR, and IFR were dried at 105 °C for 12 h and then analyzed by X-ray fluorescence (XRF), X-ray diffraction (XRD) and Scanning Electron Microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS). The extracted residue from the Fe-Mn oxides fraction were subsequently dissolved with combined acids (HClO₄: HF: HNO₃) and analysed with inductively coupled plasma mass spectrometry (ICP-MS, Agilent 7500ce).

1.1 Selective Sequential Extraction (SSE) Scheme

The five-step selective sequential extraction (SSE)

scheme applied in this study was a modified form of the method proposed by Tessier *et al.* (1979). The fractions are as follows: (i) water soluble fraction (deionised water), (ii) exchangeable fraction ($\text{CH}_3\text{COONH}_4$ at pH 7), (iii) carbonate fraction ($\text{CH}_3\text{COONH}_4$ at pH 5), (iv) amorphous Fe and Mn fraction ($\text{NH}_2\text{OH}\cdot\text{HCl}$), and (v) residual fraction (HF , HClO_4 , HNO_3 , 3:3:1). This method is not able to determine the chemical composition of each solid component separately; rather it just extracts sets of solid compounds to release mobile metals under specific environmental conditions. Detailed sampling, sample preparation, and analytical procedures were reported in our previous study (Akinyemi *et al.*, 2011a).

1.2 Bulk Chemical Composition Analysis

Takaoka *et al.* (2000) evaluated the validity of XRF analysis to the determination of elements in CFA by comparing measured values from three analysis methods: XRF, inductively coupled plasma atomic emission spectrometry (ICP-AES, Varian 710-ES) and neutron activation analysis (NAA). They concluded that XRF analysis is applicable for most elements in CFA, with very few exceptions such as arsenic, cadmium, mercury, silver etc. Therefore, XRF analysis was adopted in our study. Detailed sample preparation and analytical procedures are reported in our previous study (Akinyemi *et al.*, 2011b).

1.3 Mineralogical Composition Analysis

Mineralogical investigations of unweathered CFA (UWFA) from the same power station, weathered CFA (WFA) and residue samples from sequential extraction (i.e. WFR, EFR, CFR and IFR) were carried out by X-ray powder diffraction. The procedure for the XRD were as follows: After addition of 20 % elemental silicon (Aldrich 99.9 %) for quantitative determination of amorphous compounds, and micronizing in a McCrone micronizing mill, the sequential extraction residue samples were prepared for XRD analysis using a back loading preparation method. They were analysed with a PANalytical X'Pert Pro powder diffractometer with X'Celerator detector and variable divergence- and fixed receiving slits with Fe filtered $\text{Co-K}\alpha$ radiation. The phases were identified using X'Pert Highscore plus software. The relative phase amounts (weights %) were estimated using the Rietveld method (Autoquan Program).

1.4 Microstructural and Chemical Composition Analysis

Microstructural and chemical composition investigations of these residue samples (i.e. WFR, EFR, CFR, and IFR) were carried out by scan electron microscopy/electron dispersive x-ray spectroscopy (SEM/EDS). For SEM/EDS aluminium stubs were coated with carbon glue; when the glue was dry, but still sticky; a small amount of powder residue samples was sprinkled onto the stub. The excess residue sample powder was tapped off and the glue allowed complete drying. The residue samples

were then coated with carbon in an evaporation coater and were ready for analysis with the SEM. The SEM is an FEI Nova NanoSEM (Model: Nova NanoSEM 230.); The EDS analyses were determined at 20 Kv and 5 mm working distance. The EDS detector is an Oxford X-Max (large area silicon drift detector) using the software program INCA-(INCAmicaF+ electronics and INCA Feature particle analysis software).

2. RESULTS AND DISCUSSION

2.1 Fly Ash Chemical Composition

Tables 1 and 2 shows major and trace species in dry disposed CFA (WFA) as determined by XRF analysis respectively. The unweathered CFA (2-week-old) contained large amounts of SiO_2 (54.18 %), Al_2O_3 (25.42 %), CaO (5.29 %), MgO (1.40 %), Fe_2O_3 (4.07 %), TiO_2 (1.72 %), and Na_2O (1.82 %) while the content of other oxides was less than 1 % (Table 1). On the other hand, the weathered ash contained SiO_2 (54.39 %), Al_2O_3 (22.95 %), CaO (4.66 %), MgO (3.50 %), Fe_2O_3 (5.64 %), TiO_2 (1.35 %), and Na_2O (0.83 %) while the content of other oxides was less than 1 % (Table 1). Significant toxic species identified in both dry disposed fly ashes included As and Pb.

Table 1
Concentration of Major Elements (Dry wt %) in 2-week-old Ash, Weathered Ash and Residues from Selective Sequential Extraction (SSE) ($n=2$)

Elements	UWFA	WFA	WFR	EFR	CFR	IFR
SiO_2	54.18	54.39	51.14	53.89	54.65	54.93
Al_2O_3	25.42	22.95	24.46	25.66	25.80	25.72
Fe_2O_3	4.07	5.64	5.17	5.15	5.09	5.39
MnO	0.05	0.65	0.05	0.05	0.04	0.04
MgO	1.40	3.50	1.62	1.34	0.93	0.75
CaO	5.29	4.66	5.85	3.02	2.73	2.64
Na_2O	1.82	0.83	1.68	1.58	1.57	1.68
K_2O	0.78	0.70	0.93	0.92	0.95	0.98
TiO_2	1.72	1.35	1.70	1.75	1.77	1.84
P_2O_5	0.20	0.71	0.41	0.30	0.28	0.22
SO_3	0.05	0.72	0.02	0.01	0.01	0.01
LOI	5.03	3.85	6.90	6.27	6.16	5.42
Total	100.00	99.95	99.91	99.93	99.99	99.63

N.B. UWFA = unweathered fly ash; WFA = weathered fly ash; WFR = water soluble fraction residue; EFR = exchangeable fraction residue; CFR = carbonate fraction residue; IFR = Fe and Mn fraction residue.

2.2 Leaching of Major Components and Trace Elements in CFA During SSE

The major elements composition of the weathered CFA and the residues from selective sequential extraction (SSE), in percentage by weight, are compared in Table

1. The depletion in the amount of TiO_2 in the WFA is attributed to changes in the chemistry of feed coals over 20 years or combustion conditions. The SiO_2 and TiO_2 content was hardly degraded in the four steps (i.e. water soluble, exchangeable, carbonate, and Fe and Mn fractions) of the sequential extraction. The absolute content of SiO_2 and TiO_2 showed an increasing tendency after extraction of exchangeable phase. However, the absolute content of SiO_2 remained constant after carbonate and amorphous Fe-Mn oxides extractions. The absolute content of Al_2O_3 and SO_3 remained constant after exchangeable, carbonate, and amorphous Fe-Mn oxides extraction. At the same time, the content of CaO, MgO, P_2O_5 , and amount of unburned carbon LOI showed a decreasing tendency after exchangeable, carbonate, and amorphous Fe-Mn oxides extractions (Table 1). The degradation of Ca, Mg, P_2O_5 compounds and amount of unburned carbon (LOI) in the residues could be considered as a marker of significant progress of the selective sequential extraction. Wan *et al.* (2006) reported that the degradation of the compounds of calcium was more dependent on the condition of sequential extraction than the compounds of aluminum; in other words, the compounds of calcium could be regarded as an indicator of the progress of the selective sequential extraction. The relative increase in the absolute content of CaO and TiO_2 after water soluble extraction could be attributed to washing out of higher concentration of more soluble elements. It could also be due to hydration or carbonation of residues during washing (Table 1). The relative increase of Na_2O and K_2O after water-soluble extraction suggests that they exist in water insoluble glasses. At the same time, the relative depletion in MgO suggests it was largely exist as water-soluble sulfates.

The absolute content of Na_2O and K_2O remained constant after exchangeable and carbonate extractions. The absolute content of Na_2O and K_2O depicted similar trend after water-soluble and amorphous Fe-Mn oxides extractions. The depletion in the amount of Fe_2O_3 in UWFA

may perhaps be due to the presence of FeO in glass phase and not just magnetite and hematite phases. Concurrently, the enrichment of Fe_2O_3 in WFA is possibly due to conversion of FeO to Fe_2O_3 through weathering. The absolute content of Fe_2O_3 remained constant after water-soluble and exchangeable extraction. Conversely, the absolute content of Fe_2O_3 showed degradation after carbonate extraction, but it increased after amorphous Fe-Mn oxides extraction. The relative enrichment of Fe_2O_3 after Fe-Mn oxide extraction is attributed to oxidation of FeO to Fe_2O_3 during extraction. Changes or lack of changes in the masses of iron and other multivalent elements between extraction residues may be readily masked by oxidation and ignoring Fe (II). Therefore, resorption and redistribution of metals may perhaps be responsible for the inconsistent pattern (i.e. oxidation of FeO) of Fe_2O_3 in the residues of selective sequential extraction. The absolute content of MnO remained constant after water soluble and exchangeable extractions. On the other hand, the absolute amount of MnO relatively decreased after carbonate and amorphous Fe-Mn oxide extractions. The depletion of MnO after carbonate and amorphous Fe-Mn oxides extraction suggests that it is potential available under low pH conditions.

Trace element composition of weathered fly ash and residues from selective sequential extraction in ppm are compared in Table 2. The absolute content of Ce showed a decrease after exchangeable, carbonate, and amorphous Fe-Mn oxide extractions, suggesting that it can be release under pH range (i.e. pH 3 - 7) and reducing conditions. The amount of U showed an increase after exchangeable, carbonate, and amorphous Fe-Mn oxides extractions indicating that it is less available. The absolute amount of Pb showed increasing tendency after exchangeable and carbonate extractions. Conversely, Pb depletion in the water soluble and amorphous Fe-Mn oxides extraction suggests it can be release under neutral pH (i.e. pH 7) and reducing conditions.

Table 2
The Contents of Trace Elements (ppm) in Unweathered Fly Ash, Weathered Ash and Residues from Selective Sequential Extraction (SSE) (n=2)

Elements	LLD	UWFA	WFA	WFR	EFR	CFR	IFR
As	1.51	47.92	21.92	66.35	49.88	42.94	49.00
Ba	64.27	790.87	154.75	1183.65	1003.67	922.05	926.37
Ce	8.48	99.93	225.99	128.51	109.03	108.55	103.72
Co	6.39	44.92	36.65	62.47	41.40	47.38	40.33
Nb	3.62	72.98	36.78	81.92	73.45	70.00	70.09
Ni	5.27	22.80	94.35	22.13	27.29	26.74	28.08
Pb	3.96	60.84	81.45	46.99	50.59	50.30	47.44
Rb	1.51	47.84	33.92	46.96	55.48	57.94	59.31
Sr	1.22	1254.73	1653.86	1532.79	1279.46	1251.96	1265.72
V	20.83	133.54	337.24	82.34	115.63	130.74	97.87
Y	1.24	109.99	117.26	113.93	109.21	105.99	106.09
Zr	1.92	556.64	853.98	618.66	607.03	612.59	620.48
U	5.01	48.63	nd	11.79	61.75	73.27	73.46
Th	1.80	506.26	nd	634.35	516.33	504.39	506.72

N.B. LLD = low level detection; UWFA = unweathered fly ash; WFA = weathered fly ash; WFR = water soluble fraction residue; EFR = exchangeable fraction residue; CFR = carbonate fraction residue; IFR = Fe and Mn fraction residue.

The increase of Ni, Pb, Sr, V, Y, and Zr in WFA as compared to UWFA is attributed to increasing trends down the depth or increasing trends up the depth in the 20-year-old ash core. The trace metals distribution patterns in the 20-year-old core are controlled by point of contact with saturation zone, infiltration rain water, and heterogeneity in the ash dump (Akinyemi *et al.*, 2011a, 2011b). The absolute amount of Zr was depleted after exchangeable and amorphous Fe-Mn oxides phase extraction indicating its release under pH range (i. e. pH 3 - 7) and reducing conditions. However, the absolute content of Zr shows slight enrichment after water soluble and amorphous Fe-Mn oxide extractions indicate that it would not be release (i.e. less available) under neutral pH (i. e. pH 7) and reducing conditions. The absolute content of As showed depletion after exchangeable, carbonate and amorphous Fe-Mn oxides extractions indicate that it would be release under pH range (i. e. pH 3 - 7) and reducing conditions in CFA.

The absolute content of Ba, Sr, Y, Ni, Co, V, and Nb were depleted after exchangeable, carbonate, and amorphous Fe-Mn oxide extraction, suggesting their release under pH range (i.e. pH 3-7) and reducing conditions. The absolute content of Rb show relative depletion in WFA due to weathering for 20 years. The absolute content of Rb shows depletion after water soluble extraction indicating association with water-soluble sulfates. On the contrary, it shows relative enrichment after exchangeable, carbonate, and amorphous Fe-Mn oxides extractions. This is an indication of association with water-insoluble glasses. Thus, it is less available under pH range (i. e. pH 3 - 7) and reducing conditions. Trace elements (such as As, Pb, Ba, Ce, Co, Nb, Sr, V, and Th) bound in the exchangeable or carbonate geochemical

phase were found associated with calcite (CaCO_3) by physical and chemical adsorption. The trace elements such as Co, Pb, Ce, and V were depleted after amorphous Fe-Mn oxide extraction, indicating their potential release under reducing conditions. Trace metals associated with amorphous Fe-Mn oxides were difficult to leach under neutral (i. e. pH 7) condition and would be potentially available under reducing conditions. Wan *et al.* (2006) found high concentrations of these trace metals in Fe-Mn oxides.

2.3 Alteration of Mineralogical and Morphological Properties of Weathered Ash During SSE

The result of qualitative and quantitative XRD analysis on unweathered fly ash (2-week-old), weathered fly ash (20-year-old) is shown in Figure 1 (a and b). The characteristic mineral phases such as calcite, plagioclase, hematite, and magnetite were obvious in both fly ashes but greater quantities were observed in the weathered ash for some phases.

The absolute content of calcite showed increase tendency in the weathered fly ash (WFA) due to long-term chemical interaction of disposed fly ash with ingressed CO_2 and infiltrating rain water. The amorphous phase decreased in quantity in the weathered fly ash (Figure 1 and Table 3). The amount of quartz phase showed slight enrichment in the WFA due to removal of other soluble major component (see Table 3). As a result, the quartz crystalline mineral phase is to some extent showed resistance to chemical weathering. The obvious absence of characteristic anhydrous aluminosilicate phase [i.e. sillimanite (Al_2SiO_5)] in the WFA is attributed to differences in the chemistry of feed stock coals over 20 years.

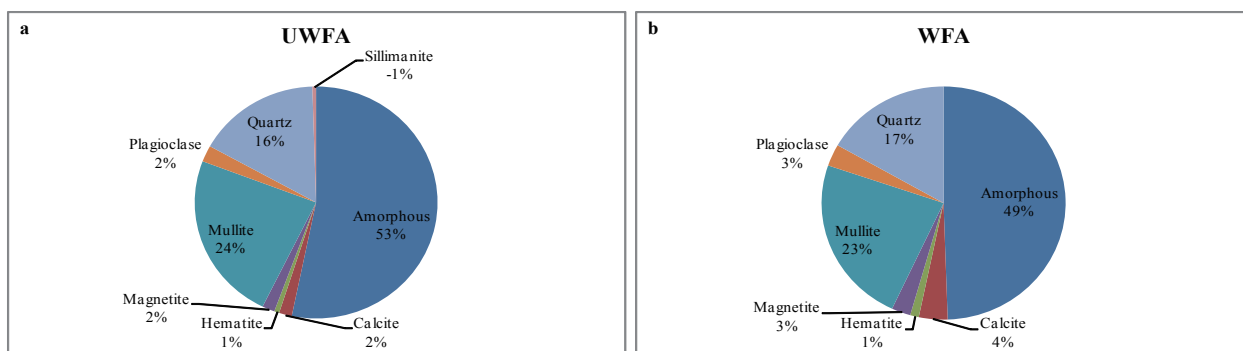


Figure 1
Phase Identification and Quantification for Unweathered Fly Ash (UWFA) and Weathered Fly Ash (WFA)

All other typical mineral phases, which were qualitatively and quantitatively identified, also survived the chemical weathering process. By linking the XRD diffraction data with the variation in the absolute content ratios of the major species (see Table 1), the sequential release of species as the various geochemical phases were destroyed can be identified. The anhydrous aluminosilicate mineral (i.e. sillimanite) appeared in the residue from

the water-soluble fraction. However, it was absent in the residue from the exchangeable, carbonate, and Fe and Mn fractions. This disappearance was consistent with the increase in residue SiO_2 and Al_2O_3 (see Table 1).

Quartz increased after exchangeable, carbonate and Fe and Mn extractions (Table 3). The increase in quartz content with subsequent extraction could also be considered as a marker of significant progress of the selective sequen-

tial extraction. The increased quartz content is as a result of depletion of other major component in CFA. Calcite (Figure 2 and Table 3) showed depletion in the XRD spectra of the residue from the exchangeable, carbonate, and Fe and Mn fraction. This observed trend was consistent

with the reduction of CaO after the exchangeable, carbonate, and Fe-Mn oxide extractions (Table 1), suggesting that an amorphous calcium compound, which could not be detected by XRD analysis, was degraded after the extractions.

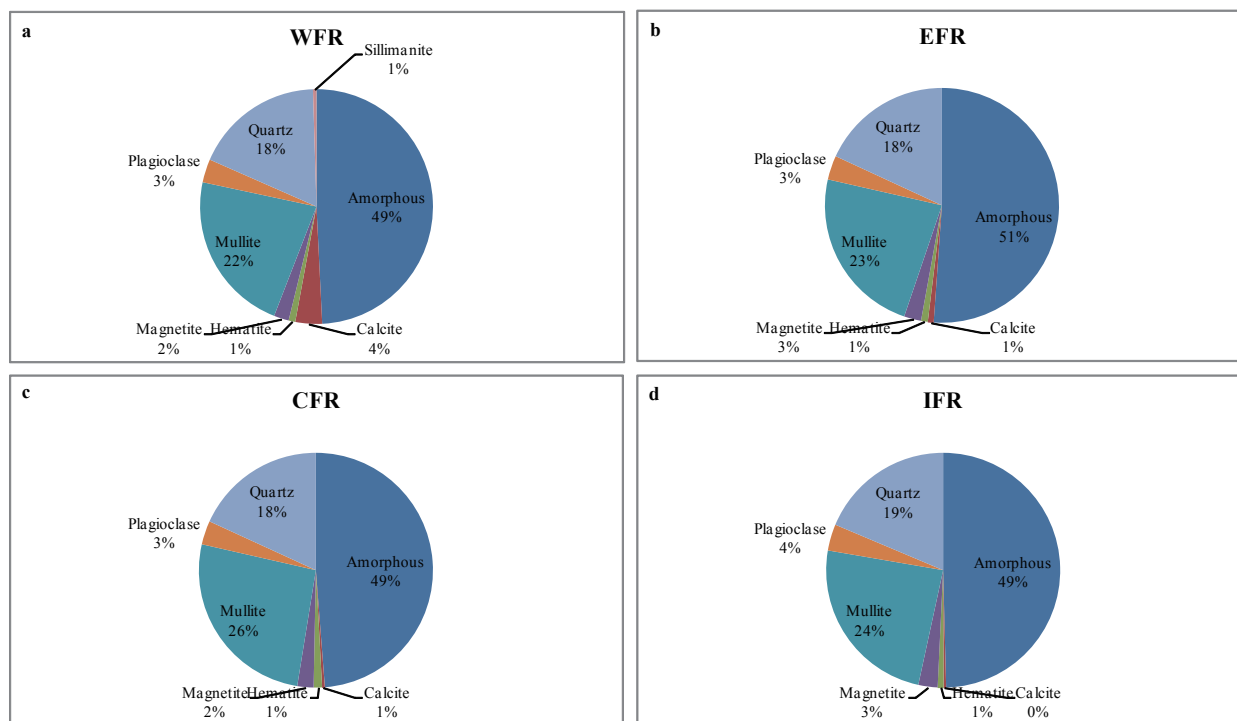


Figure 2
Phase Identification and Quantification for Residues from Selective Sequential Extraction [(a) Residue from Water Soluble Fraction, (b) Residue from Exchangeable Fraction, (c) Residue from Carbonate Fraction, (d) Residue from Fe-Mn Oxides Fraction]

As a result, it is thought that the compound of calcium in the amorphous phase would be calcium aluminosilicate or calcium trapped in the aluminosilicate matrix.

Mullite showed enrichment after water soluble, exchangeable, and carbonate extractions but depicted decreasing tendency after Fe-Mn oxide extraction (Figure 2 & Table 3). Conversely, the absolute content of CaO and MgO showed reduction after exchangeable, carbonate and Fe-Mn oxide extraction. The ratio of SiO₂ to Al₂O₃ showed reduction after water soluble extraction. On the contrary, it shows slight enrichment after exchangeable, carbonate, and Fe-Mn oxide extractions. These trends indicate dissolution of amorphous aluminosilicate during chemical interaction of CFA with water.

The amount of quartz decreased after water-soluble extraction but enriched after exchangeable, carbonate, and Fe-Mn oxide extractions. The flushing out of higher concentration of more soluble elements in the last three steps of extractions has led to enrichment in the amount of quartz (Table 1). On the other hand, the total amorphous phase showed depletion after carbonate extraction (Figure 2 and Table 3). This suggests that metals associated with

amorphous phase are likely to be released under low pH condition. The plagioclase phase shows reduction in quantities after washing the weathered ash with water. This suggests release of loosely adsorbed elements associated with amorphous aluminosilicate. Conversely, the enrichment after exchangeable, carbonates and Fe-Mn oxides extractions is attributed to washing out of higher concentration of more soluble elements. Hematite showed an increase after carbonate extraction but showed a decrease after Fe-Mn oxide extraction, suggesting that the extraction of metals associated with the amorphous Fe-Mn oxide phase led to reduction in the quantities of hematite under reducing condition.

The content of the amorphous phase in the residues showed an increase after exchangeable extraction, but remained constant after water-soluble and Fe-Mn oxide extractions. Conversely, the hematite phase remained constant after water-soluble and exchangeable extractions, suggesting it could not be released with water and under neutral (i.e. pH 7) condition.

The Fe crystalline minerals such as hematite phase show significant reduction in quantities after amorphous

Fe-Mn oxide extractions. This suggests metal associated with hematite crystalline phase could be release under reducing condition. The depletion in the amount of magnetite after water-soluble extraction may perhaps due to presence of metal chloride on the surface of magnetite. There is a significant enrichment in the quantities of magnetite phase was recorded after exchangeable, carbonate and amorphous Fe-Mn oxide extractions. This suggests that metals associated with magnetite phase could be release under neutral pH (i.e. pH 7) condition. Conversely, the increased quantities of magnetite crystalline phase after amorphous Fe-Mn oxide extraction indicate that metals

associated with magnetite crystalline phase could not be release under reducing condition.

Typical SEM micrographs of individual residues (i.e. WFR, EFR, CRF, and IF) particles are shown in Figure 3. Micron-sized inorganic particles of the residues from sequential extraction typically have spherical and rounded morphology. Particles with irregular and other shapes are also present. These fly ash particles have slight variation in proportion of Al, Si, and O (Table 4) and vary in size. Residue recovered after water soluble extraction showed a smooth appearance most likely due to combustion feature (Fig. 3).

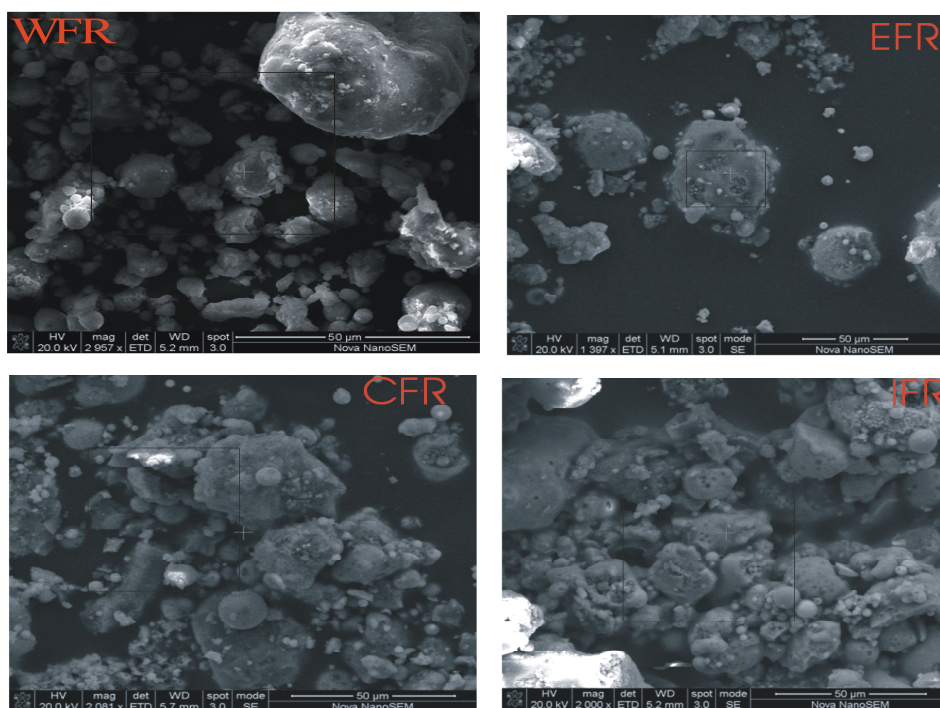


Figure 3
SEM Micrograph of Residues from Selective Sequential Extraction

The residue recovered after exchangeable extraction show muddy (i.e. malleable) and corroded appearance due to removal of inorganic metals associated with the phase. The residues recovered after carbonate and Fe-Mn oxide extractions showed typical amorphous Al-Si spheres and Fe-rich spheres with the Fe-rich spheres encapsulated by Al-Si spheres. Further, the residues exhibited muddy (i.e. malleable) appearance, etched, and corroded outer surfaces due to decomposition of compounds and removal of inorganic elements associated with carbonate and amorphous Fe-Mn oxides phases. The residue recovered after Fe and Mn extraction has cenosphere - like structures (Fig. 3) which were supposedly caused by the surface tension forces (Mollah *et al.*, 1999; Akinyemi *et al.*, 2011b). This surface tension forces is acting during decomposition and subsequent removal of inorganic elements associated with amorphous Fe-Mn oxides phase.

The extraction of inorganic metals associated with various physicochemical forms has significant impact of the morphology of the individual particles.

Energy dispersive x-ray spectroscopy (EDS) spectra were used to derive an approximate chemical composition of the analysed areas (see Figure 3 and Table 4). The content of Al-rich particles increased after water soluble and amorphous Fe-Mn oxide extractions. The decrease of Al-rich particles after exchangeable and carbonate extractions indicates that Al-rich particles could be dissolved under pH range (i.e. 5-7) condition. Conversely, Si-rich particles showed an increase after water soluble and amorphous Fe-Mn oxide extractions. The Si-rich particles decreased after exchangeable and carbonate extractions, suggesting potential dissolution under neutral pH (i.e. pH 7) condition. Calcium-rich and Ti-rich particles increased after the water-soluble extraction but

decreased after exchangeable, carbonate, and amorphous Fe-Mn oxide extractions. The Ca-rich and Ti-rich particles trends suggest possible dissolution under low pH and reducing conditions. The Fe-rich particles showed increasing tendency after water soluble and carbonate extractions. The obvious decrease of Fe-rich particles after exchangeable and amorphous Fe-Mn oxide extractions illustrate dissolution under neutral pH (i.e. pH 7) and reducing conditions. The K-rich particles increased after water soluble and amorphous Fe-Mn oxide extractions but completely depleted after exchangeable and carbonate extractions.

The reduction of K-rich particles after exchangeable and carbonate extraction indicate dissolution under both neutral (i.e. pH 7) and low pH conditions. Each particle was then classified into chemical category based on the percentages of the five most abundant elements not including C and O (Table 4). All residues contain significant amount of Si-rich particles, while Fe-rich particles are significant in the WRF, CFR, and IFR samples. Si-Al particles are the most abundant two-element category followed by Ti-Al. The Si-Al particles are present in significant amounts in all the sequential extraction residues (see Table 4). The SEM/EDS analysis indicated that Si and Al were the major constituents consistent with the elemental compositions determined by XRF (see Table 1).

The three-element categories are mostly glass phases. These glassy particles are characteristically spherical or rounded in shape (Figure 3), signifying that they were derived from solidification of once molten phases (Chen *et al.*, 2005). These glassy particles are probably formed by the reaction of Ca, Na and K, which are present in South African sub bituminous coal as carboxyl-bound molecular species, with kaolinite, and, to lesser extent, with quartz.

The sequential extraction residues exhibited abundant discrete crystals rich in Al, Ti, and Fe. For the residues from sequential extraction, Ca-Si-Al is the most dominant three-element category followed by K-Al-Si and Ti-Al-Fe (see Table 4). The XRD data indicates that over 49 % of the material in each of the samples analyzed was an amorphous phase. The Fe-rich phases identified by XRD are magnetite and hematite, consistent with previous studies of mixed Fe-oxide/Al-Si spheres (Vassileva *et al.*, 2003; Vassilev *et al.*, 2005; Kutchko and Kim, 2006). The XRD also found quartz and mullite, with plagioclase and sillimanite were present in moderately low abundance. The leaching pattern of As and Pb (Table 2) in the residues from sequential extraction are closely related with the Ca-Si-Al three element category (Table 4). This suggests that these toxic elements are likely associated with the calcium aluminosilicate (i.e. plagioclase) crystalline mineral phase in the CFA.

SUMMARY AND CONCLUSIONS

This study has revealed the alteration of microstructure, mineralogical species, and leachability of major components and trace elements in weathered, dry-disposed CFA during selective sequential extraction. Residues from exchangeable, carbonate, and Fe and Mn fractions consist mostly of amorphous Al-Si spheres with a lesser quantity of Fe-rich spheres. The Fe-rich spheres are surrounded by Al-Si spheres. Further, the residues from the exchangeable, carbonate, and amorphous Fe-Mn oxide extractions exhibited muddy (i.e. malleable) appearance and etched and corroded outer surfaces. This is attributed to decomposition of major basic oxides such as CaO and MgO and subsequent removal of associated inorganic elements. For examples Sr, Th, Y, Nb, Ce, Ba, As and Pb are concurrently removed from the solid residues after exchangeable, carbonate, and amorphous Fe-Mn oxide extractions.

The leaching behaviour of trace elements during sequential extraction was found to have dependency relationship with the components of CaO, MgO, P₂O₅, and the amount of unburned carbon in fly ash. The increase in quantities of quartz with subsequent extraction could be considered as a marker of significant progress of the selective sequential extraction. Similarly, the decrease in the calcite content with successive extraction could be considered as another marker of progress of sequential extraction technique. Trace elements bonded with exchangeable or carbonate fractions (easily available under pH sensitive fractions) were found associated with calcite (CaCO₃) and could be released under neutral (i.e. high) and low pH conditions in the ash dump. Trace elements found associated with amorphous Al-Si matrix of fly ash was not easily released. Those bound to amorphous Fe-Mn oxides are potentially released under reducing conditions. The elemental concentrations, as determined by EDS, were consistent with XRF and XRD data.

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