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Geochemical Partitioning of Major Elements in Brine Impacted Coal Fly Ash Residues

O. O. Fatoba[a],*; L. F. Petrik[a]; R. O. Akinyeye[a]; W. M. Gitari[b]; E. I. Iwuoha[c]

[a] Environmental and Nano Sciences Research Group, Chemistry Department, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa.
[b] Department of Ecology and Resources Management, School of Environmental Sciences, University of Venda, Private Bag X5050, Thohoyandou, 0950, Limpopo, South Africa.
[c] SensorLab, Chemistry Department, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa.
* Corresponding author.

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Abstract

Fly ash-brine co-disposal technique has been considered as a way of disposing fly ash and brine (hyper-saline water) by some power stations in South Africa. This practice was aimed at using the fly ash to capture most of the elements in brine. However, the geochemical partitioning of the major elements in the waste materials after the fly ash-brine interaction has not been fully understood. This study focuses on understanding the geochemical partitioning of the major elements captured in the fly ash solid residues after the fly ash-brine interaction experiment. XRF and sequential extraction procedure were respectively applied to determine the chemical composition and partitioning of the major elements in fresh fly ash and the solid residues recovered after fly ash-brine interaction. The comparison of the results of the XRF analysis carried out on the fresh fly ash and the solid residues showed that the major elements such as Si, Ca, Mg and Na increased in the solid residues after the fly ash-brine interaction. This indicates that Ca, Mg and Na in the brine solution were captured by the fly ash during the interaction. However, the sequential extraction results showed that significant concentrations of Ca, Na and Mg were released into the water soluble, exchangeable and carbonate fractions. The results show that significant amounts of the elements captured in the fly ash solid residues during fly ash-brine interaction exist in the form which can be easily leached out when in contact with aqueous solution.

Key words: Brine; Fly ash; Chemical interactions; Sequential extraction; Leaching; Partitioning; Solid residues; Chemical composition; Coal combustion; Chemical distribution

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INTRODUCTION

The combustion of coal for power generation is on the increase due to the increase in demand for electricity in some countries in the world. Huge amount of fly ash is produced as a result of the increase in coal combustion. According to US Coal Combustion Product (CCP) Production & Use Survey Report in 2008, US power plants produced about 70 million tons of fly ash annually, of which nearly 45 % was beneficially used (ACAA, 2008). In South African, one of the power utilities produces about 40 million tons of fly ash annually (ESKOM, 2012), out of which less than 10 % is utilized. Despite the fact that fly ash is beneficially used for agricultural purposes, waste stabilization, additive to cement, road construction among others (Iyer & Scott 2001; Kumpiene, Lagerkvist, & Maurice, 2006; Campbell, 1999; Foner, Robl, Hower, & Graham, 1999), significant amount of fly ash is being disposed of unto the ash dump. Fly ash contains major and minor species such as Ca, Na, Mg, K, SO_4, Cl, As, Pb, Cu, Cr, Fe, Mo, Mn etc., and these species could leach out in significant quantity from fly ash when in contact with aqueous solution (Ilic, Cheesman, Sollars, & Knight, 2003; Baba & Kaya, 2004; Polettini & Pomi, 2004; Adriano, Page, Elseewi, Chang, & Straughan, 1980). Due to the possible release of contaminants to the surrounding soils, surface and groundwater, the disposal of fly ash has become a major concern to the environment. In the power stations in South Africa, brine (a hyper-saline wastewater) is also generated in large quantities. Brine contains some major and trace species such as Na, Mg, K, SO_4, Cl, As, Pb, Cu, Se, Cr, in significant quantities. The regulation guiding the disposal of brine due to its chemical composition has made its disposal also a major concern. South African power stations in a way of disposing fly ash and brine have been practicing the co-disposal of fly ash and brine. One of the reasons for co-disposing brine and fly ash is that the interactions of the species in the waste materials could lead to the formation of secondary mineral phases thereby reducing the mobility of contaminants to the surrounding soils and groundwater. Several studies have shown that the interactions of fly ash with contaminated water could lead to removal of species from wastewater. For instance, Gitari *et al.* (2006) observed that some contaminants were removed from AMD when in contact with fly ash. The study carried out by Fatoba, Petrik, Gitari, & Iwuoha, (2011) revealed that fly ash can remove some species from brine solution. The removal of species by fly ash was observed to be controlled either adsorption/desorption process or precipitation of secondary mineral phases.

In order to understand the availability of the species in solid residues, and the forms in which the species in the solid residue exist, sequential extraction methods have been widely used (Wong & Selvam 2006; Jegadeesan, Al-abed, & Pinto, 2008; Tessier, Cambell, & Bisson, 1979; Nurmesniemi, Pöykiö, Kuokkanen, & Rämö, 2008; Albores, Cid, Gómes, & Lópes, 2000; Pueyo *et al.,* 2003; Al-Abed, Jegadeesan, Purandare, & Allen, 2007). These methods have been applied to understand the partitioning of metals in different forms in soils and fly ash, and to estimate the bioavailability of metals and their potential mobility to the environment. Sequential extractions, according to Tessier *et al.* (1979), was said to be the appropriate extraction methods that furnish detailed information about the biological and physicochemical availability, mobility and transport of trace elements. Although sequential extraction methods were suggested to be used only for qualitative instead of quantitative analysis (Van Herck & Vandecasteele, 2001), it is been used in the recent times to determine the association of metals in their geochemical forms in fly ash (Al-Abed *et al.,* 2007). Metals in soils and sediments such as fly ash have been shown to exist in different geochemical phases (Wong & Selvam 2006; Jegadeesan *et al.,* 2008; Tessier *et al.,* 1979). These phases may act as reservoirs or sinks for major, minor and trace elements thereby inhibiting their mobility to the environment. The geochemical phases in which metals exist in soils or fly ash include; water soluble, exchangeable, carbonate, reducible, oxidizable and residual. The water soluble and exchangeable fractions are the most mobile fractions and are easily available metals, carbonate fraction are the metal release at lower pH, reducible and oxidizable fractions are released only under extreme conditions while the residual fraction are almost unavailable. Despite several studies on fly ash and its interaction with water and acid mine drainage (AMD), study on the interaction of fly ash and brine has not been widely reported except in Fatoba *et al.* (2011). Previous study by Fatoba *et al.* (2011) revealed that some of the major elements such as Ca, Na and Mg were removed from brine as a result of the interaction between fly ash and brine solution. However, the geochemical forms in which the species removed from the brine by the fly ash exist after the fly ash-brine interaction have not been fully understood. This study focuses on the application of sequential extraction procedure to understand the geochemical partitioning of the species that were captured by the fly ash during the fly ash-brine interaction.

2. MATERIALS AND METHODS

2.1 Sample Description

Fly ash samples were obtained from two power utilities in South Africa. The fresh fly ash samples, which were labelled SA and TA, were stored in closed containers at room temperature. Part of these samples was reacted with brine solution at different reaction times varying from 1 week to 12 months (details of fly ash-brine interaction experiments in Fatoba 2010). The solid residues (SR) recovered from the fly ash-brine interactions were dried and stored in closed containers at room temperature before used in this study. Samples SR1, SR2, SR3 and SR4 are the fly ash residues recovered from the SA fly ash-brine interaction at 1 week, 1 month, 6 months and 12 months respectively while TR1, TR2, TR3 and TR4 are the residues of TA fly ash-brine interaction at 1 week, 1 month, 6 months and 12 months respectively.

2.2 XRF Analysis

Chemical analysis of the fresh fly ash samples and the solid residues were performed using X-ray fluorescence (XRF) with a Philips 1404 Wavelength Dispersive Spectrometer fitted with a Rh tube. The samples were oven-dried at 105 ℃ for 12 hours to remove the water content before the XRF analysis. The XRF technique reports in % oxides for major elements and in ppm for minor elements. The elements reported as % oxides were converted to ppm using element conversion software assessed at http://www.marscigrp.org/oxtoel.html.

2.3 Sequential Chemical Extractions of the Solid Residues (SR)

The sequential extractions method used was a combination of the methods developed by Jegadesaan *et al.* (2008) and Tessier *et al.* (1979) with slight modification. After each extraction, samples were centrifuged at 3000 rpm for 20 minutes and the supernatants were filtered through a 0.45μm membrane filter. The extraction experiments were done in triplicate. Multi-elemental analysis was done using the ICP-AES (major elements) and ICP-MS (trace elements).

The extraction procedures were divided into five different fractions as described below.

Water soluble fraction (Step 1): 1 g of the ash sample was weighed into 50 mL centrifuge tubes and 45 mL of de-ionized water added. The sample was shaken on a mechanical shaker at room temperature for 1 hour. The solution was centrifuged at 3000 rpm for 20 minutes. 20 mL of the supernatant was measured into a 200 mL standard flask and the solution was made up to the mark with de-ionized water. The solution was acidified with dilute HNO_3 to prevent precipitation of species.

Exchangeable fraction (Step 2): 45 mL of 1 M ammonium acetate buffer solution (pH 7) was added to the residue recovered quantitatively from step 1. The solution was shaken on a mechanical shaker for 1 hour at room temperature. The solution was centrifuged at 3000 rpm for 20 minutes. 20 mL of the supernatant was measured into a 200 mL standard flask and the solution was made up to the mark with de-ionized water.

Carbonate fraction (Step 3): 45 mL of solution containing the mixture of 1M acetic acid (CH_3COOH) and 1M ammonium acetate buffer (pH 5) was added to the residue recovered quantitatively from Step 2. The fly ash solution was shaken on a mechanical shaker for 1 hour at room temperature. The solution was centrifuged at 3000rpm for 20 minutes. 20 mL of the supernatant was measured into a 200 mL standard flask and the solution was made up to the mark with de-ionized water.

Iron and manganese fraction (Step 4): 45 mL of 0.25M hydroxylamine hydrochloride (NH_2OHCl) prepared in 0.025M nitric acid (HNO_3) was added to the residue recovered from Step 3. The solution was shaken on a mechanical shaker for 1 hour at room temperature. The solution was centrifuged at 3000rpm for 20 minutes. 20 mL of the supernatant was measured into a 200 mL standard flask and the solution was made up to the mark with de-ionized water.

Residual fraction (Step 5): Solid residue from step 4 was rinsed with de-ionized water and completely transferred to a crucible and oven dried. The dried sample was transferred into Teflon tube and put into the Parr bomb. 14 mL of solution containing hydrofluoric acid (HF), nitric acid (HNO_3) and hydrochloric acid (HCl) (mixed in the ratio of 2:1:1 respectively) was added. The residue was digested in a Parr bomb at 200 °C for 3 hours. After cooling, excess HF in the digestate was volatilized by adding 25 mL of saturated H_3BO_3 solution. The solution was filtered using 0.45μm membrane filter and the filtrate was diluted and made up 100 mL.

3. RESULTS AND DISCUSSION

3.1 Total Elemental Composition of Fresh Fly Ash and Solid Residues

The XRF results (table 1) show that the total concentrations of the major elements such as Al, Si, Ca, K, Mg and Na in the fresh fly ashes (SA and TA) are very high. The concentrations of some of the major elements such as Ca, Si, Mg and Na increased after the fly ash interaction with brine solution while the concentrations of Al and K (at some stage) were lower than their concentrations in the fresh fly ashes. The increase observed in the concentrations of some of the major elements in the fly ash after the interaction with brine solution indicates that the fly ashes removed these species from the brine solution, while the decrease in concentration of some major elements in the solid residues shows that these elements were leached from the fly ash during the fly ash-brine interaction. Comparing the two fly ashes in terms of their capacity to remove major elements from the brine solution, it was observed that SA fly ash removed more major elements from the brine solution than TA fly ash. This could be attributed to the difference in the pH values of the fly ashes. For instance, when SA fly ash was in contact with aqueous solution, its final pH (12.5) was higher than that of TA fly ash (11.5) (Fatoba *et al.,* 2011). pH is a major contributor to the reactivity of fly ash components in solution.

Table 1
Major Elemental Composition (mg/kg dry weight) of Fresh Fly Ashes (SA and TA) and the Solid Residues SR1, SR2, SR3 and SR4 Recovered After SA-Brine Interaction for 1 week, 1 month, 6 months and 12 months Respectively, and TR1, TR2, TR3 and TR4 Recovered After TA-Brine Interaction for 1 week, 1 month, 6 months and 12 months Respectively (*n=3*)

Element	SA	SR1	SR2	SR3	SR4	TA	TR1	TR2	TR3	TR4
Al	21453.3	20520.2	28856.2	10046.9	9981.1	19072.6	25150.0	23244.4	9641.7	9804.4
Ca	42739.7	42306.3	44262.8	43849.3	47036.9	21575.8	23077.9	20438.2	24850.0	23985.6
K	1134.9	2184.1	4199.3	1557.9	1903.5	2363.1	2868.3	1728.2	2059.3	2192.7
Mg	5579.2	5840.3	6772.0	5688.1	6439.8	2684.9	3098.1	2674.3	3859.3	3633.8
Na	2683.0	7431.3	11950.6	7183.2	5922.6	2193.9	7450.4	4149.8	5008.6	4916.4
Si	144432.3	174971.6	224670.8	203128.9	212927.3	175155.8	219104.1	146390.7	262073.9	220133.6

3.2 Partitioning of Major Elements in Fresh Fly Ash and the Solid Residues

3.2.1 Calcium and Magnesium

The concentration of Ca in all the extraction fractions was significantly high with exchangeable fraction having the highest concentration in fresh fly ashes (SA and TA) (tables 2 and 3). The Ca concentration in the water soluble fractions for SA was 14903.5 mg/kg while the concentration of Ca in the exchangeable fraction was 15714.3 mg/kg (table 2). TA was found to have 2200.5 mg/kg Ca in the water soluble fraction while its concentration in the exchangeable fraction was 11587 mg/kg (table 3). This implies that the bulk of the Ca in the fresh fly ashes exist in the water soluble and exchangeable fractions as the calculated extraction yield shows that about 60-70 % of Ca (figure 1) was released into these fractions. Similar trend was observed for the concentration of Ca in the solid residues with the exchangeable fraction having the highest concentration. In SR1, SR2, SR3 and SR4, the concentration of Ca in the water soluble fraction was in the range of 2218.8 and 5341.1 mg/kg while the concentration of Ca in the exchangeable fraction was found to be in the range of 25280.1 and 26636.1 mg/kg (table 2). In the water soluble fraction, the concentration of Ca in TR1, TR2, TR3 and TR4 was between 1362.6 and 1883.6 mg/kg while Ca concentration in the exchangeable fraction was found in the range of 12494 and 14822.9 mg/kg (table 3). The calculated extraction yield (%) shows that the exchangeable fractions account for almost 60 % of the total Ca in the residue samples (figures 1 and 2). The results show that Ca in the brine impacted ash residues is mainly associated with the exchangeable fractions. The predominance of Ca in the exchangeable fraction rather than in the water soluble fraction could be attributed to the leaching of easily soluble fraction of Ca during the fly ash-brine interaction experiments. The higher concentration of Ca in the exchangeable fraction when compared to all other fraction indicates that the Ca-rich mineral phases that may have formed in the solid residues during the fly ash-brine interaction are transient and sorbed-exchangeable phases which could easily be released when the residues are in contact with neutral-pH solution (Tack & Verloo, 1999). The geochemical phase(s) that exist in the exchangeable fractions have also been observed to be mobile phases (Pueyo *et al.,* 2003). Apart from the exchangeable fraction, the concentration of Ca in the carbonate fraction was significantly high, which indicates that significant amount of Ca exists as carbonate or locked in the fly ash matrix, which can only be released under extreme conditions such as having contact with solution of very low pH. The extraction yield for Ca in the iron and manganese and residual fractions were low indicating that small amount of Ca in the solid residues exist in the forms which are not available for leaching.

The release of Mg during the sequential extractions was observed to be higher in the exchangeable and carbonate fractions. Mg concentration was found to be at the peak in carbonate fractions with 2376.6 mg/kg, 2234.7 mg/kg, 2606.5 mg/kg, 2771.8 mg/kg and 2997.7 mg/kg for SA, SR1, SR2, SR3 and SR4 respectively (table 2) while the concentration of Mg in the carbonate fraction of TA, TR1, TR2, TR3 and TR4 was found to be 958.5 mg/kg, 1212.3 mg/kg, 1199.9 mg/kg, 1525.4 mg/kg and 1477.4 mg/kg respectively (tables 3). The extraction yields of Mg in the carbonate fraction was found to be 42.6 %, 38.3 %, 38.5 %, 48.7 % and 46.5 % for SA, SR1, SR2, SR3 and SR4 respectively, while in the TA, TR1, TR2, TR3 and TR4 the extraction yields were 35.7 %, 39.1 %, 44.9 %, 39.5 % and 40.7 % respectively (figures 1 and 2). These results show that Mg is fractionated predominantly in the carbonate fraction, which indicate that the geochemical forms/phases in which Mg exists in the solid residues are not easily soluble. The concentration of Mg in the water soluble fraction was very low when compared with its concentration in other fractions (step 2-5). This was expected because at high pH (>10), Mg in solution precipitates to form an insoluble $Mg(OH)_2$ (Gitari, Fatoba, Petrik, & Vadapalli, 2009) which could only be dissolved at a lower pH. Comparing the concentration of Mg released from the fresh fly ash (SA and TA) with the concentration of Mg released from the solid residues at each extraction step, the concentration of Mg in the solid residues was found to be slightly higher than in the fresh fly ashes in most cases. The higher concentration of Mg in the solid residues indicates that the Mg captured in the solid residues during the fly ash-brine interaction was gradually released. The increase is in agreement with the study of Pueyo *et al.* (2003) where they observed higher concentration of Mg when sequential extractions was carried out on non-contaminated reference soil and contaminated soils.

Table 2
Concentration (mg/kg dry weight) of Major Elements Released at Different Extraction Fractions; SA = Fresh Fly Ash; SR1, SR2, SR3 and SR4 = Solid Residues Recovered After SA-Brine Interaction for 1 week, 1 month, 6 months and 12 months Respectively (*n=3*)

Extraction fraction	Sample description	A1	Si	Ca	K	Mg	Na
Water soluble	SA	367.6±9	759.3±193.8	14903.5±150	14.8±3.6	20.2±1.4	86.3±5
	SR1	454.1±4.1	306.5±8.6	5341.1±47.8	127.8±2.6	49.1±1.7	2445±169
	SR2	655.7±5.8	472.9±147.5	2307.7±10.5	209.1±5.1	15.2±2.2	2075.7±7.7
	SR3	22.6±2.6	119±5.5	2218.8±32.1	106.3±29.3	12.4±0.7	2507.3±19.9
	SR4	58.3±70	2542.8±3456	2259.2±363.4	270.7±65.7	22.1±11.8	2259±171.5

To be continued

Continued

Extraction fraction	Sample description	A1	Si	Ca	K	Mg	Na
Exchangable	SA	2.6±0.3	1010.1±44.4	15714.3±43.5	39.2±2.5	1882.6±24	BDL
	SR1	150.3±0	597.2±0.2	25285.1±19.4	105.3±1.4	2128.5±43	337.5±24.8
	SR2	9.4±2.3	560.2±19.6	25280.1±63.2	432.4±19.6	1873.8±18	739.9±8.6
	SR3	16.4±3.3	517.6±10	25432.3±374	284.6±59	1637.1±30.3	637.2±24.5
	SR4	22.6±7.5	479.5±7.3	26636.1±185	190.2±15.6	1655±13.5	395.9±6.4
Carbonate	SA	192.1±17.3	761.4±13	3018.4±29.1	28.7±1	2376.6±17	17.9±7.8
	SR1	396.9±10.4	1659.6±21	5883.8±144.8	21.2±8	2234.7±48	136.4±3.7
	SR2	2112.1±8.1	4654.9±16.4	10252.4±69.5	30.9±6	2606.5±13	73.7±8.2
	SR3	1748.5±58.4	3469.9±25.1	13343.2±219	BDL	2771.8±25	408.4±1.9
	SR4	2213.3±72.7	4256.1±71	14499.7±293	44.1±7	2997.7±72.5	302.9±11.5
Iron and Manganese	SA	330.7±5.4	198.5±7.5	1942.7±10.5	13.1±1	1009.8±7	85.4±14.7
	SR1	293±5.9	194.4±14	2034.5±47.9	14.9±6	1156.1±41	188.1±3.9
	SR2	348.7±6.9	450.8±6.3	2060.9±29.6	17.6±2.3	1411.5±18	91.7±7.3
	SR3	2377±167	3048.5±3.6	1637.9±37.3	9.8±0	1133.2±5.9	409.3±6.9
	SR4	2612.9±67.4	4228.5±72.8	1885.5±53	55.3±9.1	1593.1±22.5	327.2±3.8
Residual	SA	20560.2±72	141703±1326	7160.8±27.6	1039±87.9	290±8.5	2493.4±28
	SR1	19226±410	172214±3876	3762±136	1915±59	272±8.2	4324±31
	SR2	25730.2±198	218532±1481	4361.7±33	3509.3±148	865±22.7	8969.8±81
	SR3	5882.5±130	195974±2932	1217.1±17.6	1157.2±48.4	133.6±4.5	3221.1±41.6
	SR4	5074±69.2	201420±2842	1756.5±74.4	1343.3±60.3	171.9±2.2	2637.6±83.4

Table 3
Concentration (mg/kg dry weight) of Major Elements Released at Different Extraction Fractions; TA = Fresh Fly Ash; TR1,TR2, TR3 and TR4 = Solid Residues Recovered After TA-Brine Interaction for 1 week, 1 month, 6 months and 12 months Respectively (*n=3*)

Extraction fraction	Sample description	A1	Si	Ca	K	Mg	Na
Water soluble	TA	371.8±12.8	544.6±164.2	2200.5±13.6	81.7±3.5	28±1.5	495.6±17.8
	TR1	162.9±15	1553.4±1147	1362.6±33	122.9±13	26.1±1.3	2413.8±38
	TR2	232.9±2.8	3539.1±1150	1883.6±9	114.3±14.5	32±4.5	2492.3±24
	TR3	6.4±0.8	106.9±5.5	1864.1±11.9	104.9±3.6	23.7±0.4	2527.1±70
	TR4	10.4±1.8	751.4±296.5	1386.8±30.6	200±1.2	11.9±0.2	2478.4±32.4
Exchangable	TA	2.1±0.3	457.3±63	11587±82.7	142.9±16.2	872±4.2	161±8.2
	TR1	BDL	468±69	12611.7±381	139.5±21.6	792.5±14.4	346.1±62
	TR2	1.3±0.5	605.3±195	12494±23.1	171±19.5	669.2±5.5	426.5±7.4
	TR3	6.5±2.6	436±7.9	14822.9±187	119±12.3	890.1±6.8	505.5±6.3
	TR4	12.7±7.2	473.1±73.5	14709.4±156	115.9±14	761.9±7	339±3.7
Carbonate	TA	995.4±15.1	1881.8±39	3741.5±18.7	16.6±3.3	958.5±3.7	BDL
	TR1	1060.2±1.3	2014.2±32	3869.1±20.3	17.1±11	1212.3±14	50±13
	TR2	1172.8±42	2018.1±298	2606.8±20.3	36.6±38.8	1199.9±17	55.7±18.5
	TR3	1252.5±23.2	2145.3±8.6	4267.8±38.5	19.7±11.8	1525.4±2.9	350.6±3.7
	TR4	1318.3±12	2480.8±22.3	4763.8±44.7	47.5±4	1477.4±9	315.1±9
Iron and Manganese	TA	314.4±12.2	223.7±15	2032.4±24.3	14.9±5.5	672.6±7.2	81.3±4.3
	TR1	365.9±18	220.5±8.6	2070.5±32	10.8±1.4	785.3±3.3	116.6±5
	TR2	281.6±7.3	201.5±8.7	1407.2±7.2	11.6±7.7	547.7±4.8	100.1±11
	TR3	2400.5±43.6	4863.3±162.5	1830.5±121.7	40.4±18.7	1269.4±45.7	363.8±20.1
	TR4	2234.8±37	4202.1±36.7	1451.8±33.1	62.5±30.3	1243.3±3.6	342.8±14.4
Residual	TA	17389±187	172048±2384	2014.5±64	2107±185	153.8±5.5	1456±25.3
	TR1	23561±583	214848±4063	3164±71	2578±143	282±3.1	4524±18
	TR2	21555.8±58	140027±2736	2046.7±21.8	1394.7±30	225.5±5.4	1075.2±12
	TR3	5976±171.9	254629±4245	2064.7±74.8	1775.4±40	150.7±4	1261.7±18.1
	TR4	6228.3±47.1	212226±1481	1673.9±66	1766.8±70.7	139.2±0.5	1441.1±28.6

3.2.2 Sodium and Potassium

The concentration of Na was predominant in the water soluble and residual fractions of the fresh fly ashes (SA and TA) and the solid residues (tables 2 and 3). The concentration of Na in water soluble fraction (tables 2 and 3) and its extraction yield (figures 1 and 2) was found to be 86.2 mg/kg (3.2%), 2445 mg/kg (32.9 %), 2075 mg/kg (17.4 %), 2507.3 mg/kg (34.9 %) and 2259 mg/kg (38.1 %) for SA, SR1, SR2, SR3 and SR4 respectively, while the concentration and extraction yield of Na in the residual fraction for SA, SR1, SR2, SR3 and SR4 were 2493.4 mg/kg (92.9 %), 4324 mg/kg (58.2 %), 8969 mg/kg (75.1 %), 3221.1 mg/kg (44.8 %) and 2637.6 mg/kg (44.5 %) respectively (tables 2 and 3; figures 1 and 2). Almost the same trend of release of Na was observed in TA and its solid residues (TA, TR1, TR2, TR3 and TR4) in the water soluble and residual fractions. High concentration of K was also observed in the water soluble and the residual fractions of the sequential extractions (tables 2 and 3). These results indicate that significant amount of Na and K exist in the fresh fly ashes and the solid residues as easily soluble salts (Kirby & Rimstidt, 1994) while the bulk of these elements exist in the less soluble glass matrix of the fly ashes (residual fraction) (Warren & Dudas 1984; Gitari *et al.,* 2009). Comparing the concentrations of Na and K released from the fresh fly ashes (SA and TA) with the concentrations released from solid residues, it was observed that concentrations of Na and K released from the solid residues were higher than what was released from the SA and TA in most cases (tables 2 and 3). The observed trend shows that Na and K captured in the solid residues (as shown in the XRF results presented in table 1) during the fly ash-brine interaction exist in soluble geochemical forms or phases, which dissolve easily when in contact with aqueous solution (Kirby & Rimstidt, 1994). Although, with the sequential extraction techniques, it is difficult to conclude which mineral phase controls the solubility of an element in the solid residues, one can assume the probable formation of mineral phases due to the high concentration of the solutes in the systems and high pH of the systems, which favours the precipitation and co-precipitation of solid phases (Georgakopoulos *et al.,* 2002). Van Herck & Vandecasteele (2001) suggested the possible formation of chloride and sulphate salts of Na and K in a system that contains significant amounts of these species. These salts are easily soluble when in contact with aqueous solution (Kirby & Rimstidt, 1994; Mattigod, Rai, Eary, & Ainsworth, 1990). Therefore, the high concentrations of Na and K in the water soluble fraction could be from the dissolution of easily soluble salts of Na and K while the high concentration in the residual fraction could be attributed to the dissolution of silicate minerals that contain these elements.

3.2.3 Aluminium and Silicon

The concentration of Al in the fresh fly ashes and the solid residues was found to be more prominent in the carbonate and residual fractions. The concentration and extraction yield of SA, SR1, SR2, SR3 and SR4 were 20560.2 mg/kg (95.8 %), 19226 mg/kg (93.7 %), 25730 mg/kg (89.2 %), 5882.5 mg/kg (58.6 %) and 5074 mg/kg (50.8 %) while the concentration and extraction yield for TA, TR1, TR2, TR3 and TR4 were 17389 mg/kg (91.2 %), 23561 mg/kg (93.7 %), 21555 mg/kg (92.7 %), 5976 mg/kg (62 %) and 6228.3 mg/kg (63.5 %) respectively (tables 2 and 3; figures 1 and 2). The prominence in the carbonate and residual fractions indicates that Al in both fresh fly ash and the solid residues exist as aluminosilicate or crystalline phases in the fly ash matrix which can only be easily dissolved or leached when in contact with solution of very low pH (Garavaglia & Caramuscio, 1994). The lower concentration of Al in the water soluble and exchangeable fractions could be attributed to the initial dissolution of soluble oxides of Al from the fly ashes during the fly ash-brine interaction (as observed in the XRF results presented in table 1). The partitioning of Si was not different from that of Al as the bulk of Si in the fly ash and the solid residues was observed in the residual fraction. The concentration and extraction yields (tables 2 and 3; figures 1 and 2) of Si in the residual fraction were found to be 141703 mg/kg (98.1 %), 172214 mg/kg (98.4 %), 218532 mg/kg (97.3 %), 195974 mg/kg (96.5 %) and 201420 mg/kg (94.6 %) for SA, SR1, SR2, SR3 and SR4 respectively, while the concentration and the extraction yields in TA, TR1, TR2, TR3 and TR4 were 172048 mg/kg (98.2 %), 214848 mg/kg (98.1 %), 140027 mg/kg (95.7 %), 254629 mg/kg (97.1 %) and 212226 mg/kg (96.4 %) respectively. The predominance of the Si in the residual fractions indicates its existence in the fly ashes and the solid residues as silicate phases such as aluminosilicates. The lower concentrations of Si observed in the water soluble, exchangeable, carbonates, iron and manganese fractions is an indication that less soluble oxides of Si remained in the solid residues due to the initial leaching of the soluble phase during the fly ash-brine interactions. The comparison of Si concentration in the residual fraction showed that more Si is present in the solid residues than in the fresh fly ashes. This could be as a result of the transformation of the glassy phases into more insoluble phases such as aluminosilicates (Kirby & Rimstidt, 1994; Dijkstra, Van der Sloot, & Comans, 2006) during the fly ash-brine interactions experiments. The sequential extraction tests revealed that Si in the solid residues exists in the geochemical forms that are not mobile under natural environmental conditions.

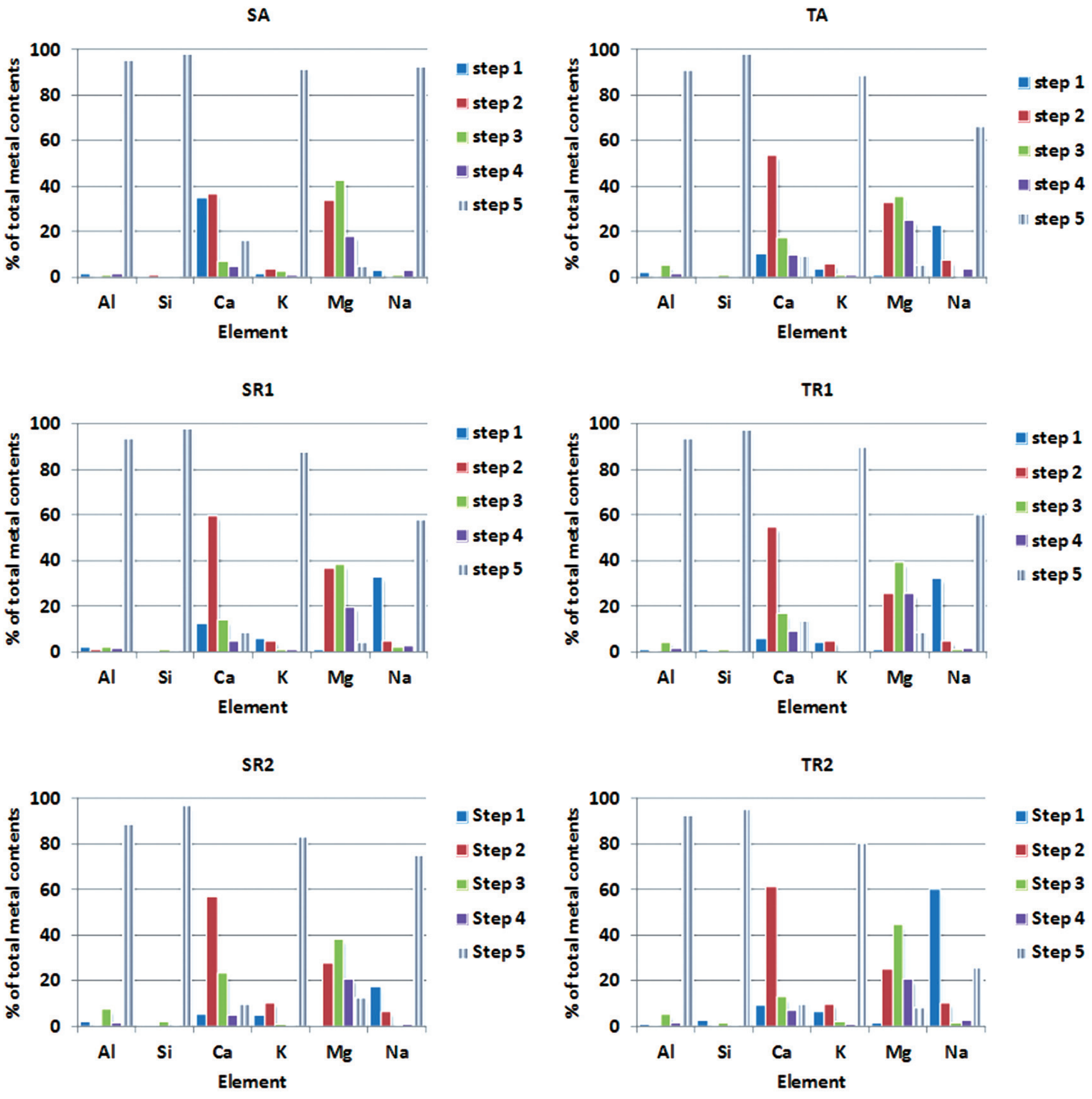
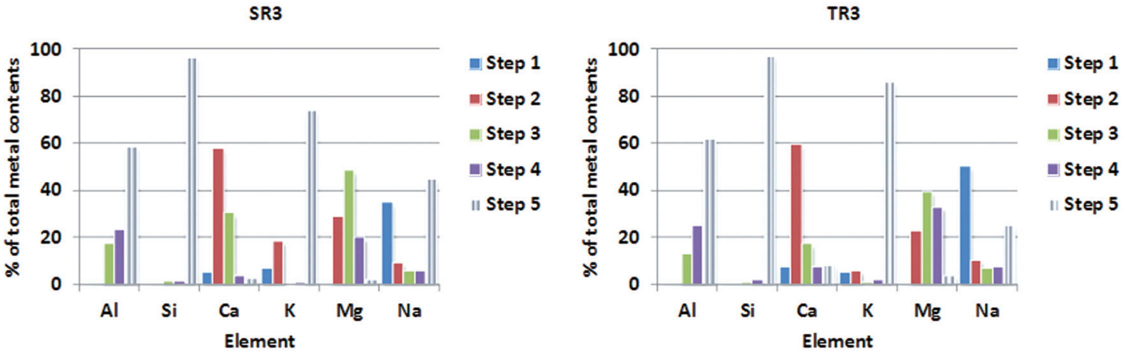


Figure 1
Extraction Yield (%) of Major Elements in the Fresh Fly Ashes (SA and TA) and the Solid Residues (SR1, SR2, TR1, TR2). Step 1: Water Soluble; Step 2: Exchangeable; Step 3: Carbonate; Step 4: Iron and Manganese; Step 5: Residual Fraction



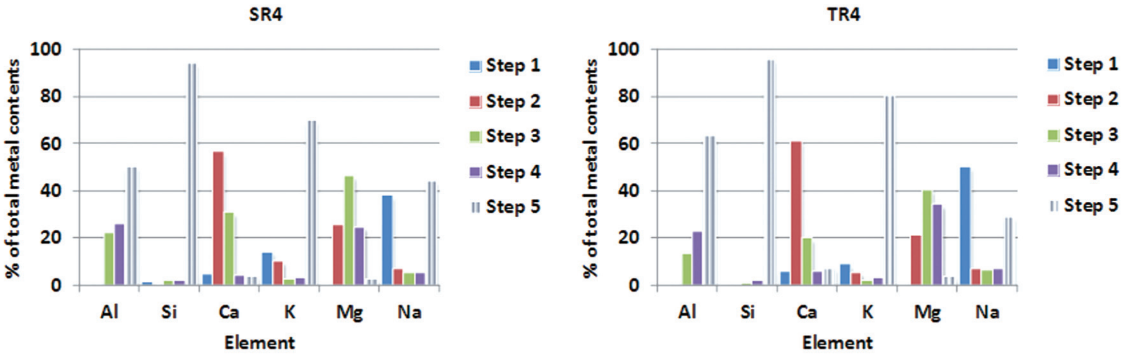


Figure 2
Extraction Yield (%) of Major Elements in the Solid Residues (SR3, SR4, TR3 and TR4). Step 1: Water Soluble; Step 2: Exchangeable; Step 3: Carbonate; Step 4: Iron and Manganese; Step 5: Residual Fraction

CONCLUSION

The increase in the concentrations of major elements such as Na, Mg, Ca and Si in the solid residues recovered after the fly ash-brine interaction experiments shows that the major elements in the brine can be removed as a result of its interaction with different South African fly ashes. Apart from the geochemical forms in which the major elements captured in the solid residues exist, this study reveals the mobility of most of the major elements in the fly ash solid residues. Significant concentrations of most of the major elements were observed in the labile fractions (water soluble, exchangeable and carbonate fractions). The implication of the observed trends, especially for Na, is that most of the major elements captured in the fly ash solid residues can be easily leached into the environment when in contact with water, and may also constitute potential environmental risk depending on their concentrations. Therefore, the co-disposal of fly ash and brine with the aim of sustainably capturing the major elements in brine solution should be discouraged unless adequate measures have been put in place to prevent the fly ash-brine solid residue from having contact with water or aqueous solution.

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