

Long-term brine impacted fly ash. Part 1: chemical and mineralogical composition of the ash residues

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Received: 14 May 2012/Revised: 17 May 2013/Accepted: 17 November 2013/Published online: 17 December 2013
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Abstract The co-disposal of brine and fly ash has become a common practice in South African power utilities. This study focuses on the effects of the long-term fly ash–brine interaction on the chemical and mineralogical composition of fly ash and the quality of the brine solution after the interaction test. Long-term fly ash–brine interaction test was carried out by contacting fly ash and brine for a period of time varying from 1 week to 12 months under static and closed conditions. The results of the chemical composition of the brine decanted after the interaction test revealed that species such as B, Co, Cu, Pb, Mg, Mn, Zn, Cl and SO₄ were removed to a certain extent from brine during the fly ash–brine interaction test while Al, Si, Ca, K, Ba, Sr, Fe, As, Cr and Mo were significantly leached out of the fly ash into the brine. The X-ray fluorescence results showed that the concentrations of Na, Mg, Cl and SO₄ (as S) in the ash residues were somewhat higher than their concentrations in the fresh fly ash. Secondary mineral phases such as wairakite, charlesite, spinel and celestine which were missing in the X-ray diffraction analysis of the fresh fly ash were identified in the ash residues. This study shows that some species contained in the brine solution could be captured by the fly ash

through secondary mineralization during co-disposal in a closed static environment, while many other elements could be significantly leached into the brine.

Keywords Fly ash · Brine · Chemical and mineralogical composition · Co-disposal · Long-term interaction · Major and minor elements

Introduction

The combustion of coal for power generation is on the increase due to the increasing demand for electricity in most of the countries of the world. Huge amounts of fly ash are produced as a result of the increase in coal combustion. According to US coal combustion product (CCP) Production and Use Survey Report in 2011, US power plants produced about 60 million tons of fly ash annually, of which nearly 39 % was beneficially used (ACAA 2011). In South Africa, the main coal burning power utility produces about 40 million tons of fly ash annually (ESKOM Report 2013), 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 and Scott 2001; Kumpiene et al. 2007; Kim et al. 2003; Yunusa et al. 2006), significant amounts of fly ash are being disposed in ash dumps. Fly ash contains major and minor species such as Ca, Na, Mg, K, SO₄, Cl, As, Pb, Cu, Cr, Fe, Mo, Mn, and these species could leach out in significant quantity from fly ash when in contact with an aqueous solution (Ilic et al. 2003; Baba and Kaya 2004; Polettini and Pomi 2004). Due to the possible release of contaminants to the surrounding soils, surface and groundwater, the disposal of fly ash has environmental impacts. Apart from fly ash generated in the coal burning

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power stations in South Africa, brine (a hyper-saline wastewater), is also generated in large quantities due to water purification at these utilities. Brine contains some major and trace species such as Na, Mg, K, SO_4 , Cl, As, Pb, Cu, Se and Cr in significant quantities. The regulation guiding the disposal of brine has regulated its disposal due to its chemical composition. In 2004, South African Department of Water Affairs and Forestry (DWAF) under the National Water Act 36 of 1998 issued a regulation that the disposal of municipal and industrial wastewater to estuaries will no longer be considered (RSA DWAF 2004). This regulation may have led to the co-disposal of fly ash and brine as being practiced by some South African power stations. One of the reasons for co-disposing brine and fly ash is the hope that the interactions of the species in the waste materials may reduce the mobility of salts to the surrounding soils and groundwater. Several studies have shown that interaction of fly ash with contaminated water could lead to the removal of species from wastewater. For instance, Gitari et al. (2006) observed that some contaminants were removed from acid mine drainage (AMD) when in contact with fly ash. In the study carried out by Fatoba et al. (2011) on the effect of short term interaction of fly ash and brine on the removal of species, it was observed that fly ash could transiently remove some species from brine. However, in the study carried out by Akinyemi et al. (2012) evaluating the leachability of elements from fresh and drilled core ash from a South African ash dump, a progressive leaching pattern was observed for elements such as Na, Cl and SO_4 indicating their existence in the ash as highly soluble phases. Apart from studying the mobility of contaminants as a result of the interaction of fly ash with wastewater, the leaching of elements from fly ash when in contact with water has received the attention of several researchers (Baba and Kaya 2004; Hassett et al. 2005; Izquierdo et al. 2008, 2011). The leaching of elements from fly ash irrespective of the type of leachant depends on the liquid–solid ratio and the pH of the fly ash system (Izquierdo and Querol 2012, 2011; Dutta et al. 2009; Gitari et al. 2009). The removal of species by fly ash was also observed to be either by adsorption/desorption processes or by precipitation of transient secondary mineral phases (Izquierdo and Querol 2012, 2011; Dutta et al. 2009). Despite several studies on fly ash disposal, there was no proper record on the total volume of brine co-disposed with fly ash for a longer period of time, thereby making it difficult to estimate the amount of elements that can be removed from brine or released from the fly ash during interaction in real co-disposal scenario. The aims of this part of the study are to determine the effect of long-term fly ash–brine interaction on the quality of brine solution under static and closed conditions, and to determine the effect of the long-term

interaction on the morphological, mineralogical and chemical composition of the ash. In order to achieve the aims of this study, a long-term fly ash–brine interaction experiment was carried out in South Africa in March 2009, at different interaction times ranging from 1 week to 12 months. Thereafter, the excess brine decanted and the ash residues recovered from the fly ash–brine systems were analyzed using different analytical techniques (experimental details in “Materials and methods” section).

Materials and methods

Fly ash

The fly ashes (SFA and TFA) used in this study were produced from two different coal-fired power utilities operated in South Africa. The SFA was collected directly as dry ash from the hoppers while the TFA was collected from the conveyor belt taking the ash to the ash dump. The TFA used in this study was preconditioned with about 16 % brine solution to suppress dust before the ash was sampled. There was no access to the fresh fly ash directly from the hopper because of the regulations of the power station. The ash samples were kept in plastic containers which were tightly closed to prevent ingress of air and stored at room temperature until use.

Brine

The brine (ROB) sample used in this study was collected from the highly saline retentate stream of the reverse osmosis (RO) desalination plant at a power station in South Africa. The ROB brine was chosen for this study because of the high concentrations of the major species such as Na, Cl and SO_4 . The brine sample was collected in plastic containers and stored in a refrigerator at 4 °C until use.

Morphological, chemical and mineralogical analysis of ash samples

The morphology of the ash samples was determined using scanning electron microscopy (SEM). The energy dispersion spectroscopy (EDS) analysis was done on some spots for qualitative elemental composition. Chemical and mineralogical analyses of the fly ash samples were performed using X-ray fluorescence (XRF) and X-ray diffraction (XRD) with a Philips 1404 Wavelength Dispersive Spectrometer fitted with an Rh tube, and a Philips PANalytical instrument with a PW3830 X-ray generator operated at 40 kV and 25 mA, respectively. The samples were oven-dried at 105 °C for 12 h to remove the water content.

Total acid digestion

This test involves contacting fly ash with concentrated acids to determine the total concentration of each of the elements in the sample. This test was carried out according to Jackson and Miller (1998). 2 ml of concentrated hydrofluoric acid (HF) and 5 ml aqua regia were reacted with 0.25 g of fly ash in a digestion vessel (Parr bomb) at 200 °C for 2 h. The sample was allowed to cool after which the excess HF in the digestate was neutralized by the addition of 25 ml of saturated H_3BO_3 solution. The digestate was filtered through 0.45- μm membrane filter and the solution was diluted to 50 ml with de-ionized water.

Long-term fly ash–brine interactions experiment

The long-term fly ash–brine interaction experiment was carried out by weighing 600 g of each of the fresh fly ashes (SFA and TFA), respectively, into 1-L plastic containers. 600 mL of the brine solution ROB was accurately measured and mixed with each of the fly ash samples in the plastic containers. After the mixing of the fly ash and the brine solution in the plastic containers, the containers were closed. The mixture of fly ash and brine (1:1 wt/v) in the containers was allowed to stand for different periods ranging from 1 week to 12 months (sample for each fly ash–brine interaction period was in duplicate). After each predetermined interaction period, the excess brine on the fly ash was decanted, filtered, and stored in the refrigerator at 4 °C for analysis. The major, minor and trace elements in the decanted brine from the long-term fly ash–brine interaction tests were determined using inductively couple plasma atomic emission spectrometry (ICP-AES) (Varian Liberty) and inductively coupled plasma mass spectrometry (ICP-MS) (Agilent 7500ce). The anions were determined by the use of a Dionex DX-120 ion chromatograph (IC) with an Ion Pac AS14A column and AG14-4-mm guard column.

The fly ash–brine solid residues recovered from each experiment were oven-dried at 50 °C. The oven-dried residues were crushed, milled, homogenized, and stored in tightly closed plastic containers at room temperature for further experiments and analysis. The long-term fly

ash–brine interactions experiments were carried out in duplicate. Table 1 below gives the description of the materials used in the long-term fly ash–brine interaction experiments.

For easy identification, the residues from the fly ash–brine interaction experiments were labeled as SAC, SBC, SCC and SDC for residues of SFA fly ash–brine interactions experiments at 1 week, 1, 6 and 12 months, respectively, and TAC, TBC, TCC and TDC for residues of TFA fly ash–brine interactions experiments at 1 week, 1, 6 and 12 months, respectively.

Results and discussion

pH and EC of unreacted brine and brine decanted from the solid residues

The pH and EC values of the excess brine decanted from the solid residues at the specified time after the long-term fly ash–brine interactions experiments showed an increase compared to the pH and EC of the unreacted brine (UB) (Tables 2, 3). The increase noted in the pH of the systems could be attributed to the dissolution of alkalinity-contributing oxides such as CaO and MgO in the fly ashes. The increase in the pH of the systems could influence the reactivity of the species in the systems as high pH favors the precipitation of most of the elements. According to Gitari et al. (2009) and Ugurlu (2004), some species in fly ash precipitate as hydroxides when the pH increases to alkaline condition. For instance, at $\text{pH} > 10$, Mg could precipitate to form $\text{Mg}(\text{OH})_2$. An increase was observed in the EC of the decanted brine compared to that of UB. The significant increase observed in the EC of the excess brine decanted from the solid residues from 16.69 (UB) to a range between 27 and 35 mS/cm in the excess brine from SAC, SBC, SCC and SDC after the long-term fly ash–brine interaction experiments could be attributed to the leaching of some major species from the fly ashes during the experiments. Ugurlu (2004) related higher EC values of fly ash solution to the high ion dissolution that occurs in the fly ash system.

Chemical composition of unreacted brine and brine decanted from the solid residues

The elemental composition of the excess brine decanted from the solid residues after the long-term fly ash–brine interaction experiments and the percentage of species removed or leached from the brine solution by the fly ashes during the long-term fly ash–brine interaction experiments are presented in Tables 2 and 3. The percentage of species

Table 1 The description of the long-term SFA and TFA fly ash–brine interaction setup ($n = 2$)

SFA sample ID	TFA sample ID	Weight of fly ash (g)	Volume of brine (mL)	Contact time
SAC	TAC	600	600	1 week
SBC	TBC	600	600	1 month
SCC	TCC	600	600	6 months
SDC	TDC	600	600	12 months



Table 2 Chemical composition of UB and the excess brine solution decanted from the solid residues after the long-term SFA fly ash–brine interactions experiment; (concentration in mg/L except pH and EC (mS/cm)) ($n = 2$)

Species	Conc. in unreacted brine (CUB)	SAC(L)		SBC(L)		SCC(L)		SDC(L)	
		Conc. in decanted brine (CDB)	% removed/leached	Conc. in decanted brine (CDB)	% removed/leached	Conc. in decanted brine (CDB)	% removed/leached	Conc. in decanted brine (CDB)	% removed/leached
Al	0.016	0.057	−256.3	104.9	−655,525	141.5	−884,275	132.15	−825,838
As	0.0036	0.0015	58.3	0.027	−650	0.044	−1,122.2	0.101	−2,705.6
B	1.39	BDL	100	0.58	58.3	BDL	100	3.47	−149.6
Ba	0.029	0.22	−658.6	0.17	−486.2	0.094	−224.1	0.037	−27.6
Ca	101.27	977.52	−865.3	245.57	−142.5	5.24	94.8	8.062	92.04
Co	0.0072	BDL	100	0.0013	81.9	BDL	100	0.0026	63.9
Cr	0.0063	1.55	−24,503.2	1.29	−20,376.2	0.38	−5,931.7	0.161	−2,455.6
Cu	0.1004	BDL	100	0.0054	94.6	0.0049	95.1	0.0086	91.4
Fe	0.043	0.098	−127.9	0.24	−458.1	0.104	−141.9	0.55	−1,179.1
K	56.37	143.92	−155.3	181.6	−222.2	232.1	−311.7	244.16	−333.1
Mg	75.44	0.109	99.9	0.13	99.8	0.03	99.9	BDL	100
Mn	0.043	0.00049	98.9	0.0061	85.8	0.0026	94	0.017	60.5
Mo	0.019	0.38	−1,900	0.67	−3,426.3	1.28	−6,636.8	1.61	−8,373.7
Na	4,475.07	4,411	1.4	4,372.05	2.3	3,658.36	18.3	2,935.2	34.4
Ni	0.057	0.046	19.3	0.062	−8.8	0.031	45.6	0.04	29.8
Pb	0.00093	0.00037	60.2	0.00066	29	0.00035	62.4	0.00023	75.3
Si	7.27	0.56	92.3	71.11	−878.1	48.2	−563	399.57	−5,396.1
Sr	2.93	50.58	−1,626.3	10.75	−266.9	1.96	33.1	0.16	94.5
Zn	0.051	0.013	74.5	0.027	47.1	0.048	5.9	0.022	56.9
Cl	2,424	2,089.05	13.8	1,950	19.6	1,730	28.6	1,780	26.6
SO ₄	8,858	4,835.18	45.4	1,000	88.7	652	92.6	705.33	92
pH	7.75	12.54		12.3		12.98		12.46	
EC(mS/cm)	16.69	34.75		34		32.84		27.68	

Negative (−) values indicate % leached from fly ash

CUB, unreacted brine solution; SAC(L), excess brine decanted from SAC, (1 week); SBC(L), excess brine decanted from SBC (1 month); SCC(L), excess brine decanted from SCC (6 months); SDC(L), excess brine decanted from SDC (12 months)

leached or removed from the brine solutions was calculated using Eq. 1.

$$\text{Percentage(\%)leached or removed} = \frac{\text{CUB} - \text{CDB}}{\text{CUB}} \times 100 \quad (1)$$

where CUB and CDB are concentration of species in the UB solution and concentration of species in the decanted brine solution, respectively.

Despite the static and closed (no access to the atmosphere) conditions of the long-term fly ash–brine interaction tests, some species such as Al, Si, Ca, K, Ba, Sr, Fe, As, Cr and Mo were significantly leached out of the fly ashes (SFA and TFA) into the brine solutions after a year thereby causing an increase in the concentrations of these species in the decanted brine solutions at different contact times compared with their concentrations in the UB (Tables 2, 3). In SFA, the percentage of Al, Si, Fe, As, Cr and Mo leached from the fly ash into the brine after a year of fly ash–brine

interaction was 825,838, 5,396.1, 1,179.1, 2,705.6, 2,455.6 and 8,373.7 %, respectively (Table 2), while the percentage of most of these species leached from TFA after a year was 40,088 % Al, 266.7 % Si, 261.1 % As, 24,186 % Cr and 6,215.8 % Mo (Table 3). The leaching of Al and Si could be attributed to the dissolution of the soluble phases of these species on the surface or aluminosilicate matrix of the fly ash. It was observed that the leaching of Al and Si increased with an increase in the interaction period showing the metastable nature of the ash matrix. This implies that these species could continuously leach from the fly ash into the brine solution even when the fly ash–brine systems are left undisturbed. The very significant release of Cr into the brine solution, especially in the case of TFA, could be attributed to the dissolution Cr-bearing phase(s) in the fly ash. Cr(VI) has been reported to be easily available in solution at high pH (Koukouzas et al. 2010; Tiruta-Barna et al. 2006). The release of Mo could be as a result of high solubility and mobility of Mo in alkaline systems (Gitari et al. 2009;



Table 3 Chemical composition of unreacted brine and the excess brine solution decanted from the solid residues after the long-term TFA fly ash–brine interactions experiment; (concentration in mg/L except pH and EC (mS/cm)) ($n = 2$)

Species	Conc. in unreacted brine (CUB)	TAC(L)		TBC(L)		TCC(L)		TDC(L)	
		Conc. in decanted brine (CDB)	% removed/leached	Conc. in decanted brine (CDB)	% removed/leached	Conc. in decanted brine (CDB)	% removed/leached	Conc. in decanted brine (CDB)	% removed/leached
Al	0.016	0.43	−2,588	4.73	−29,463	3.29	−20,463	6.43	−40,088
As	0.0036	0.0087	−141.7	0.015	−316.7	0.015	−316.7	0.013	−261.1
B	1.39	0.14	89.9	0.84	39.6	BDL	100	0.8	42.4
Ba	0.029	0.17	−486.2	0.16	−451.7	0.12	−313.8	0.18	−520.7
Ca	101.27	194.72	−92.3	73.87	27.1	110.18	−8.8	95.32	5.9
Co	0.0072	0.0028	61.1	0.0027	62.5	0.0018	75	0.002	72.2
Cr	0.0063	2.087	−33,027	2.7	−42,757.1	2.56	−40,535	1.53	−24,186
Cu	0.1004	0.015	85.1	0.016	84.1	0.007	93	0.018	82.1
Fe	0.043	0.067	−55.8	0.29	−574.4	0.13	−202.3	0.042	2.3
K	56.37	147.88	−162.3	147.36	−161.4	154.55	−174.2	145.89	−158.8
Mg	75.44	1.47	98	0.14	99.8	0.13	99.8	0.065	99.9
Mn	0.043	0.00081	98.1	0.0043	90	0.00072	98.3	0.0012	97.2
Mo	0.019	0.79	−4,057.9	0.98	−5,057.9	1.034	−5,342.1	1.2	−6,215.8
Na	4,475.07	3,639.29	18.7	3,273.57	26.8	3,607.78	19.4	3,240.41	27.6
Ni	0.057	0.091	−59.6	0.11	−92.9	0.087	−52.6	0.096	−68.4
Pb	0.00093	0.00085	8.6	0.00064	31.18	0.00025	73.1	0.0009	3.2
Si	7.27	9.01	−23.9	16.78	−130.8	20.98	−188.6	26.66	−266.7
Sr	2.93	9.053	−208.9	4.47	−52.6	7.39	−152.2	5.79	−97.6
Zn	0.051	0.01	80.4	0.031	39.2	0.016	68.6	0.011	78.4
Cl	2,424	1,608.08	33.7	1,860	23.3	1,797.51	25.8	1,768	27.1
SO ₄	8,858	6,161.83	30.4	5,388	39.2	5,770.41	34.9	5,112	42.3
pH	7.75	11.07		11.46		12.11		11.5	
EC(mS/cm)	16.69	15.44		17.52		12.67		16.4	

Negative (−) values indicate % leached from fly ash

CUB unreacted brine solution, TAC(L) excess brine decanted from TAC (1 week), TBC(L) excess brine decanted from TBC (1 month), TCC(L) excess brine decanted from TCC (6 months), TDC(L) excess brine decanted from TDC (12 months)

Jankowski et al. 2006). Ca was leached from the SFA into the brine solution at 1-week and 1-month interaction periods, but the leaching of Ca into the brine was at 1-week and 6-month interaction periods in the case of TFA. At some stage, Ca was removed from the brine solution. Ca exists as soluble salt on the surface of the fly ash as well as forming part of the main components of the aluminosilicate glass fractions, along with other major element like Al (Choi et al. 2002). The leaching of Ca could be as a result of the dissolution of its soluble salts on the fly ash surface while its removal could indicate the formation of Ca-containing secondary mineral phase in the systems after the initial leaching. On the other hand, some species were removed to some extent from the brine solutions by the fly ashes during the fly ash–brine interactions experiments. For instance, species such as Co (63–100 %), Cu (91–100 %), Mg (99–100 %), Mn (60–99 %), Zn (6–75 %), Cl (13–29 %) and SO₄ (45–93 %) were removed from the brine solutions by SFA during the long-term fly ash–brine interactions

experiments but the removal was time dependent with some species showing higher removal over the longer time. Although Na (34.4 %) and Ni (29.8 %) were removed from the brine solution over a year by SFA, the concentration and the percentage removed were lower than those of other species mentioned above (Tables 2, 3). In the case of TFA systems, B (39–90 %), Co (61–75 %), Cu (82–93 %), Mg (98–100 %), Mn (90–98 %), Na (18–28 %), Zn (39–80 %), Cl (23–34 %) and SO₄ (30–42 %) were removed from the brine solution by the fly ash (TFA). Pb was initially removed from the brine solution by the interaction with fly ash but later leached back into the brine solution at 1- and 6-month interaction periods for SFA and TFA long-term interactions, respectively. Ni, which was removed from the brine solution by SFA, was leached from TFA into the brine solution (Tables 2, 3). The inconsistent removal of these species from the brine solution could be as a result of precipitation, co-precipitation or adsorption processes in the fly ash–brine systems. The % removal of



Mg from the brine solutions by SFA and TFA ranged between 98 and 100 % (Tables 2, 3) at different interaction periods. In alkaline solution, the formation of insoluble $\text{Mg}(\text{OH})_2$ (Bhattacharyya et al. 2011) could be responsible for the removal of Mg from the brine solution. The removal of B from the brine solutions was in the range of 39 and 100 % (Tables 2, 3). Due to the high concentration of Ca leached into the brine at the beginning of the experiment, coprecipitation of B with CaCO_3 in the systems could account for the removal of B from the brine solution (Jankowski et al. 2006). However, the possible formation of ettringite ($\text{Ca}_6\text{Al}_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) in the highly alkaline solutions ($\text{pH} > 11$) due to the availability of its components (Al, Ca and SO_4) in the brine solution can also reduce the concentration of B (Iwashita et al. 2005; Dermatas and Meng 2003). Mn was removed significantly from the brine solutions in percentages ranging between 60 and 98 % (Tables 2, 3), but the removal was gradually reduced with an increase in the interaction period. The removal of Mn could be associated with the possible formation of Mn oxyhydroxides in the alkaline systems (Blissett and Rowson 2012). The percentage removal of Cu, Co and Zn from the brine solutions was found to range between 82 and 100 %; 61 and 100 %; and 5 and 80 %, respectively, at different interaction periods (Tables 2, 3). The removal of Co, Cu and Zn from the brine could be attributed to their adsorption on the Mn oxyhydroxides in the systems or as a result of the adsorption of these species on the negatively charged surfaces of the fly ash particles (Alinnor 2007; Papandreou et al. 2007). The relatively low removal of Na (1–34 %) and Cl (13–34 %) from the brine during the long-term fly ash–brine interaction experiments could be due to the formation of transient Na- and Cl-containing mineral phases in the systems over time. The percentage removal of SO_4 was found to be in the range of 30 and 93 % (Tables 2, 3). SO_4 removal could be as a result of the precipitation of SO_4 -rich mineral phases such as CaSO_4 , SrSO_4 , Na_2SO_4 and BaSO_4 during the long-term fly ash–brine interactions experiments. The % removal of Na, Cl and SO_4 from the brine solution by the fly ashes increased with an increase in the static interaction periods. This indicates that the period of static interaction at L/S 1:1 could have a positive effect on the removal of Na, Cl and SO_4 from the brine solution if the fly ash–brine system is left undisturbed for a longer period of time with a limited volume of brine applied. Comparison of the removal capacity of the two fly ashes showed that SFA could remove more SO_4 than TFA while on the other hand, TFA showed higher removal capacity for Na and Cl than SFA. After 1 month of the fly ash–brine interactions, the concentrations of Ca, Ba and Sr decreased in the excess brine decanted indicating that these species initially released into the systems from the fly ash were removed gradually from the systems. The removal of these species from the brine over time indicates the possible

interactions with other species such as SO_4 in the brine solution to form transient secondary mineral phases. The formation of SO_4 -rich mineral phases such as CaSO_4 , BaSO_4 and SrSO_4 could be responsible for the decrease in the concentrations of Ca, Ba and Sr, respectively. The decrease in the concentration of SO_4 in the excess brine and the increase observed in the % removal of SO_4 from the brine solution (Tables 2, 3) by the fly ashes after 1 month of interactions support this assumption.

Morphological composition of fresh fly ash and fly ash–brine interaction solid residues

The analysis of the solid residues using SEM–EDS gave insight into the morphological changes and showed the presence of some elements associated with some specific mineral phases in the solid residues (Figs. 1, 2). SEM is one of the most widely used characterization techniques to determine the morphology and physical appearance of fly ash (Vassilev and Vassileva 2005). Two spots were analyzed on each of the SEM micrographs by EDS. The EDS analysis was used for a qualitative determination of constituent elements in the solid residues to establish whether some morphological features were associated with specific elemental composition.

The SEM micrographs showed that the surfaces of most of the particles of SFA were smooth and spherical in shape (Fig. 1) while some agglomerated and irregular-shaped particles characterized the morphology of particles of TFA (Fig. 2). The interactions of the fresh fly ashes with the brine solution at different contact times were observed to have had an effect on the surfaces of the fly ash particles. The observed roughened surfaces of the ash particles after the interactions experiment [Fig. 1 (SAC, SBC, SCC and SDC)] and [Fig. 2 (TAC, TBC, TCC and TDC)] could be attributed to the dissolution of the soluble phases on the surface of the fly ash particles upon contact with brine over time. Apart from the rough surface of the fly ash particles, agglomeration of particles and irregularly shaped amorphous particles were observed, which could be as a result of inter-particle cementing (Kutchko and Kim 2006) during the interactions experiments.

The EDS of the analyzed spots with specific morphological features showed Al, Si, Ca and O as the predominant major elements while elements such as Mg, K, Na, Fe and Ti were determined in minor amounts in both fresh fly ashes (SFA and TFA) and the solid residues. The presence of the major elements such as Al and Si at the analyzed spots in the fresh fly ashes (SFA and TFA) confirmed the aluminosilicate composition of the ash. Some analyzed spots showed the absence of S and Cl, which does not indicate that these species were not present in the fresh fly ash but may be present in small amounts. The analyzed



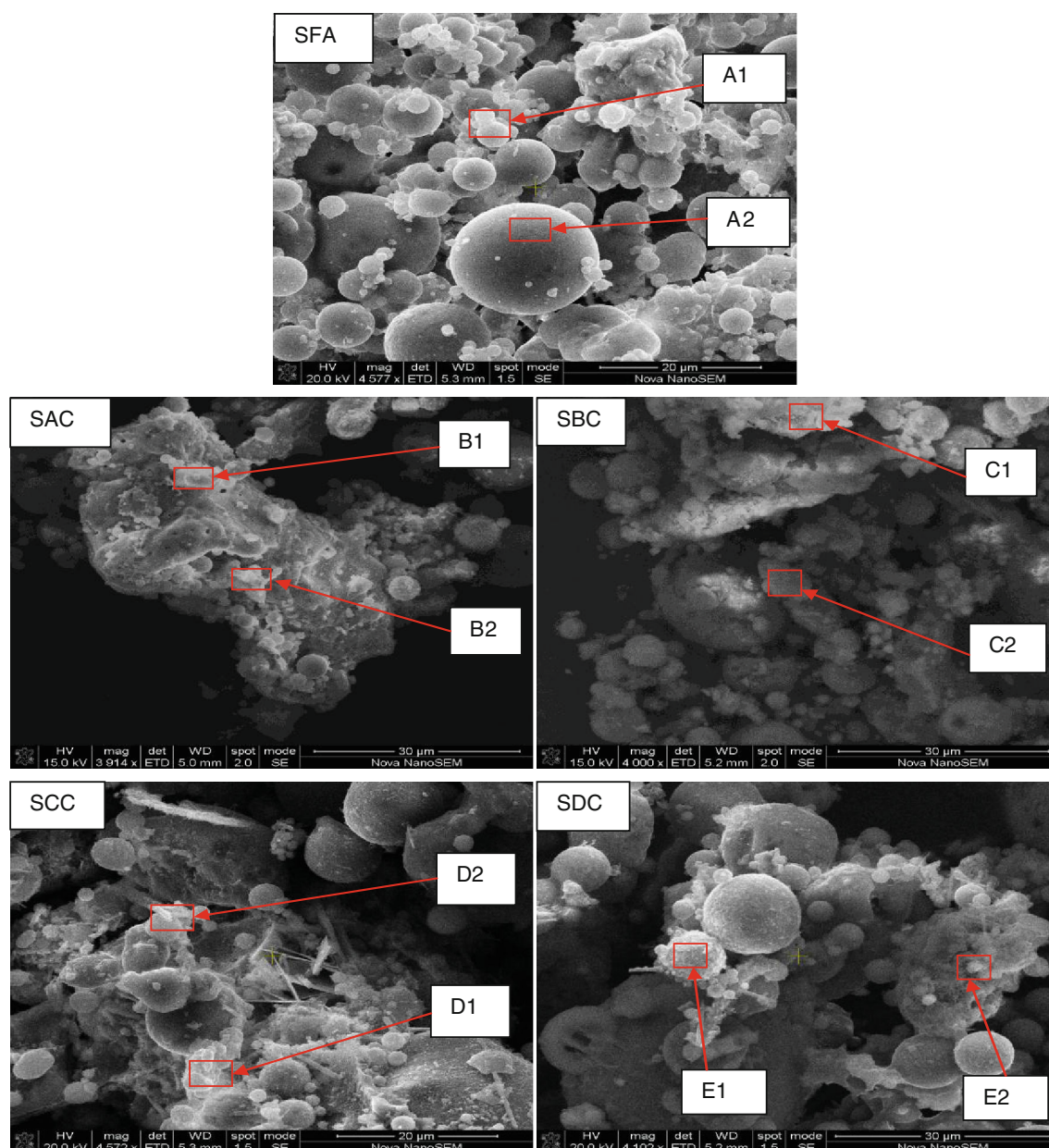


Fig. 1 SEM-EDS micrograph of fresh fly ash and fly ash–brine interaction solid residues showing the spots for EDS analysis; SFA—fresh ash; SAC—solid residue at 1 week; SBC—solid residue at 1 month; SCC—solid residue at 6 months; SDC—solid residue at 12 months

spots in the solid residues showed, in some cases, high concentration of Ca and S which could suggest the precipitation of Ca–S-rich phases. Cl was associated with higher concentration of Na at spots B1, B2 and H3 indicating the presence of Na–Cl salt in the solid residues. The presence of Cl and increased Na concentration in the analyzed spots of the residues could indicate the possible formation of Na and Cl-containing mineral phases in the fly ash residues during the interaction experiments. On the other hand, the presence of Ca, Mg, S and Na suggests the formation of Ca–Mg–S-rich or Na-rich phases embedded in the amorphous particles. The crystal-like and agglomerated

particles on the solid residues (D1, D2, I1 and I2) showed high concentration of A, Si and O with lesser amounts of Ca and Mg. The elements present in the analyzed spots in the solid residues suggest aluminosilicate phases mixed with Ca–Mg-rich or Ca–S-rich phases.

Mineralogical composition of the fly ash–brine interaction solid residues

The mineralogical composition of the fresh fly ashes and the solid residues from the fly ash–brine interaction experiments was determined using XRD (Figs. 3, 4). Peaks

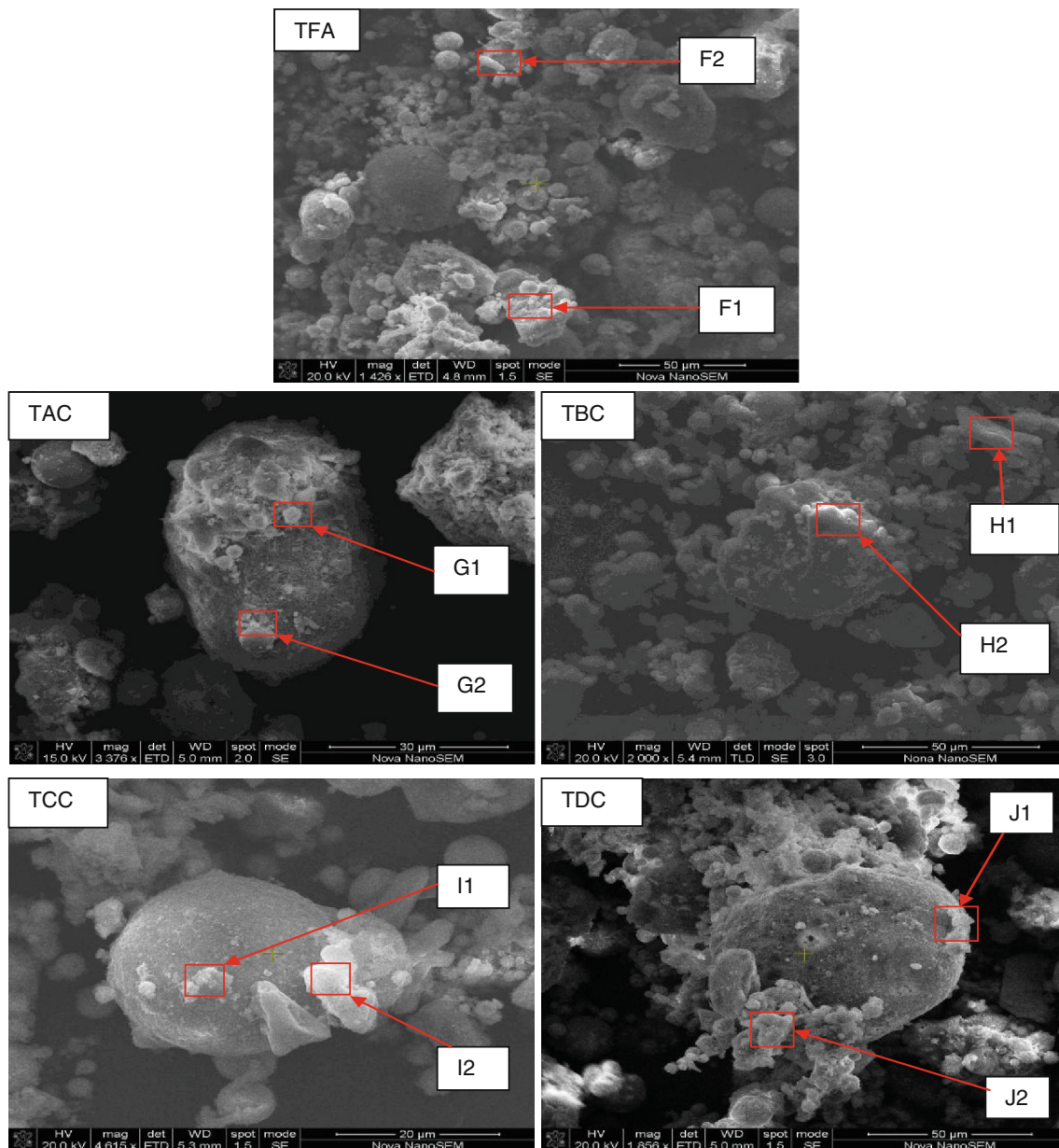


Fig. 2 SEM-EDS micrograph of fresh fly ash and fly ash–brine interaction solid residues showing the spots for EDS analysis; TFA—fresh ash; TAC—solid residue at 1 week; TBC—solid residue at 1 month; TCC—solid residue at 6 months; TDC—solid residue at 12 months

assigned to quartz (SiO_2), mullite ($\text{Al}_6\text{Si}_2\text{O}_{13}$) and calcite (CaCO_3) were easily identified in the diffraction patterns of SFA and TFA as well as the fly ash–brine interaction residues. Some poorly defined peaks were identified as wairakite [$\text{CaAl}_4\text{Si}_4\text{O}_{12} \cdot 2(\text{H}_2\text{O})$], charlesite [$\text{Ca}_6(\text{Al},\text{Si})_2(\text{SO}_4)_2\text{B}(\text{OH})_4(\text{OH},\text{O})_{12} \cdot 26(\text{H}_2\text{O})$] and spinel (MgAl_2O_4) in fly ash–brine interaction residues SAC, SBC, SCC and SDC (Fig. 3); and celestine (SrSO_4) was identified in the case of TAC, TBC, TCC and TDC (Fig. 4). Quartz, mullite and calcite are known to be the major mineral phases in fresh fly ash (SFA and TFA) while phases such as wairakite, charlesite, spinel and celestine identified in the solid residues

could be attributed to the interactions of the fly ash and brine species. Comparison of the fresh fly ashes (SFA and TFA) with the fly ash–brine interaction residues at different contact times revealed the possible formation of secondary mineral phases over time during the interaction experiments.

The formation of secondary mineral phases in the solid residues after the fly ash–brine interaction experiments indicates that some readily soluble species in the fly ash may have interacted with the species in the brine during the extended period of interaction. Thus, any secondary mineral phase formed may be soluble under hydraulic flows. Due to the high concentrations of species such as Na and Cl in the



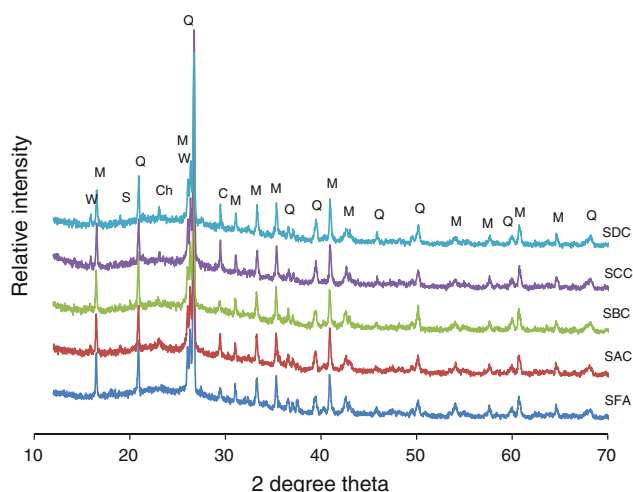


Fig. 3 X-ray diffractograms for SFA—fresh ash; SAC—solid residue at 1 week; SBC—solid residue at 1 month; SCC—solid residue at 6 months; SDC—solid residue at 12 months. Peaks labeled are M (mullite), Q (quartz), C (calcite), W (wairakite), Ch (charlesite) and S (spinel)

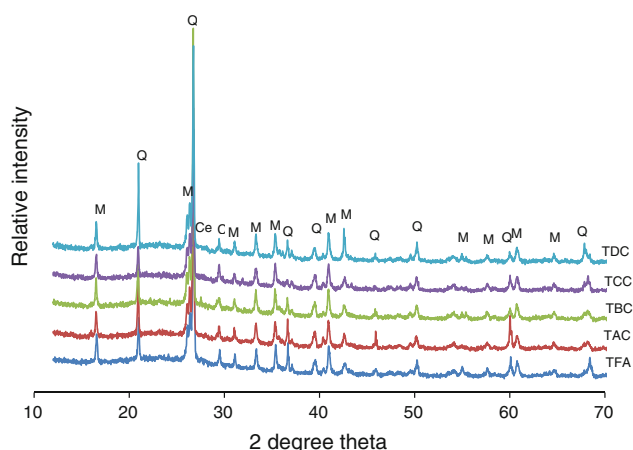


Fig. 4 X-ray diffractograms for TFA—fresh ash; TAC—solid residue at 1 week; TBC—solid residue at 1 month; TCC—solid residue at 6 months; TDC—solid residue at 12 months. Peaks labeled are M (mullite), Q (quartz), C (calcite) and Ce (celestine)

brine solution, the mineral phase(s) containing these species were expected to be identified by the XRD analysis in the solid residues after the fly ash–brine interactions, but were not identified, which might be due to their low abundance or the limit of the resolution of the XRD analysis. Some mineral phases could be present in amorphous forms in the solid residues and may not be detectable by the XRD.

Chemical composition of the fly ash–brine interaction solid residues

The total elemental composition of the fresh fly ashes (SFA and TFA) and the solid residues recovered from the long-

term fly ash–brine interactions experiments carried out at different contact times ranging from 1 week (SAC and TAC), 1 month (SBC and TBC), 6 months (SCC and TCC) and 12 months (SDC and TDC) are presented in Fig. 5. The results of the total elemental compositions of SFA, TFA and the solid residues from the long-term fly ash–brine interactions experiments were determined by the XRF analytical technique except As and Mo which were determined by the total acid digestion tests (experimental details in “Total acid digestion” section). The results represent the mean of the triplicate analysis.

The XRF results showed that the concentrations of major elements in the fresh fly ashes (SFA and TFA) were high with Al having 129,495–137,751 mg/kg; Ca, 42,096–66,467 mg/kg; Fe, 16,506–37,907 mg/kg; Si, 231,787–242,352 mg/kg and Mg, 8,204–13,572 mg/kg (Fig. 5a–f). Species such as Na, Ba, Sr, K, Cl and SO_4 (as S) in the SFA are 4,525, 2,292, 3,268, 6,724, 74 and 1,378 mg/kg, respectively, while the concentration of these species in TFA are, respectively, 2,151, 984, 1,164, 6,890, 730 and 7,025 mg/kg. The concentration of the trace elements such as As, Co, Cu, Mo, Ni, Pb and Zn in the fresh fly ashes (SFA and TFA) are below 150 mg/kg except for Mn which has a concentration of approximately 400 mg/kg. The high concentration of toxic species in the fresh fly ashes gives an indication that fly ash, if not properly handled, could be a major source of metal contamination in the environment.

The results of the XRF analysis carried out on the solid residues recovered after the long-term fly ash–brine interaction experiments showed that the concentration of some of the elements in the fly ash–brine residues increased over time depending on the ash source while the concentration of other elements were reduced (Fig. 5). For instance, the concentrations of species such as Cu, Pb, (Fig. 5e) Na and S (Fig. 5c) in the fly ash–brine solid residues (SAC, SBC, SCC and SDC) increased after long-term contact with a fixed volume of brine compared with their concentrations in the fresh fly ash (SFA). This indicates that these species were slightly removed from the brine solution by the fly ash as a result of the interaction. The concentrations of Al, Ba, K, Si and Zn in the solid residues were observed to decrease compared with their concentrations in SFA indicating significant leaching while there was no significant change observed in the concentrations of Ca, Mg, Sr, Fe, Mn, Co and Ni in the solid residues compared with the fresh fly ash (Fig. 5a, c, e). Similar trends were observed when the concentrations of species in TFA were compared with the concentrations of species in the solid residues recovered from the long-term fly ash–brine interactions experiments (Fig. 5b, d, f). The concentrations of Na and S (Fig. 5c, d) and Cl (Fig. 5d) in the solid residues increased over time compared with their concentrations in the fresh fly ash. There was inconsistency in the trends of Cu and Pb. The



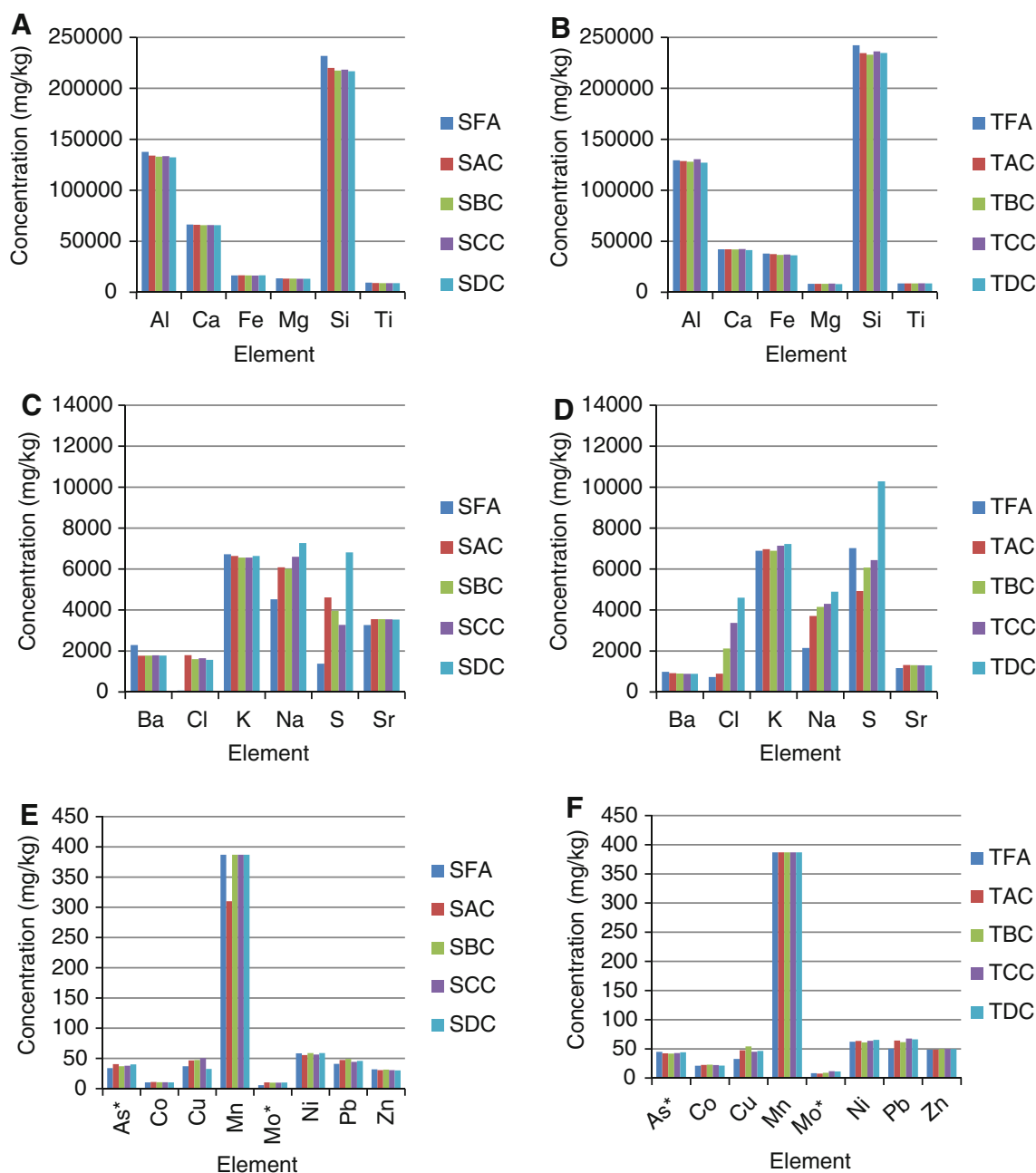


Fig. 5 Concentrations (mg/kg) of major and minor species in SFA, TFA and solid residues recovered from fly ash–brine long-term interactions experiments; SAC and TAC = solid residue at 1 week,

SBC and TBC = solid residue at 1 month, SCC and TCC = solid residue at 6 months, SDC and TDC = solid residue at 12 months; ($n = 2$); *Data from total acid digestion tests

concentrations of Al, Ba and Si were observed to reduce in the solid residues recovered from the long-term interaction experiments indicating dissolution. Since Al and Si are the major components of the fly ash matrix, their solubility has implications for all other metals locked in the fly ash matrix which will be released as the ash matrix decomposes.

The increase in the concentrations of species such as Na, S, Cu and Pb in the solid residues must have resulted from their removal from the brine solution (Tables 2, 3) and the subsequent uptake by the fly ashes either by adsorption or

precipitation processes. The trends were supported by the results of the chemical composition of the excess brine decanted from the solid residues after the long-term interactions experiments which showed that the concentrations of the above-mentioned species were lower than what was measured in the unreacted brine solution (UB) (Tables 2, 3). The results showing the chemical composition of the excess brine decanted (Tables 2, 3) coupled with the results of the solid residues (Fig. 5) give evidence that species such as Na, Cl and S could be removed from a fixed



volume of brine solution by the fly ashes during the static long-term interactions experiments over a period of 12 months. On the other hand, the increase in the concentrations of Al, Ba, K and Si in the excess brine decanted from the solid residues coupled with concomitant decrease in the concentrations of these species in the solid residues showed that these species were extensively leached from the fly ashes into the brine solution under static conditions and with a limited amount of brine during the long-term fly ash–brine interactions experiments over a period of 12 months. The leaching of Al and Si into the brine solution indicates the instability of the major matrix of the fly ash. Although the concentrations of species such as Ca, Fe and Sr in the solid residues were expected to decrease significantly due to their high solubility when in contact with water, but only a slight change was observed in their concentrations in the solid residues compared to what was observed in the fresh fly ashes. In the process of decanting the excess brine from the systems after the interaction periods, brine solution was trapped in the pore volume of the ash residue which was later oven-dried. The leached species contained in the trapped brine could account for the slight difference observed in the above-mentioned species. Apart from this, the formation of secondary mineral phases after the leaching of Ca and Sr into the system under the long-term static conditions could also account for the slight change in the concentrations of these species in the solid residues compared to their concentrations in the fresh fly ashes (SFA and TFA). The formation of secondary mineral phases is possible in the fly ash–brine systems due to the interactions of these species with other species such as SO_4 contained in the brine solution. The assumption of the formation of secondary mineral phases was supported by the decrease observed in the concentrations of Ca, Ba and Sr species in the excess brine decanted from the solid residues at different interaction periods after the initial observed increase (Tables 2, 3) even though these phases were not visible by the XRD. The formation of Fe and Mn oxyhydroxides after the leaching of these species from the fly ashes could also account for the stable Fe and Mn concentrations in the solid residues.

Apart from the high pH (Tables 2, 3) of the fly ash–brine interactions systems that could favor the precipitation of some secondary mineral phases, the fact that the experiments were carried out in closed and static systems with a fixed volume of brine over an extended period of time gave sufficient contact time for various species to interact and form secondary mineral phases. Ahmaruzzaman (2010) suggested that the adsorption of heavy metals by fly ash depends on the pH, initial concentration of heavy metals and the contact time. Studies on the application of fly ash in wastewater treatment revealed the potential of fly ash to remove some species from the wastewater due to its major

chemical components, which include alumina, silica, ferric oxide, calcium oxide, magnesium oxide and carbon, and its physical properties such as porosity, particle size distribution and surface area (Ahmaruzzaman 2010). Investigation also revealed that metal ions such as Ni, Pb, As, Cu, Zn and Cd can be removed by fly ash from wastewater by adsorption process (Rao et al. 2002; Bhattacharya et al. 2006; Bayat 2002). Therefore, the removal of species such as Cu, Pb, Co and Ni in this study could be attributed to adsorption process in the long-term fly ash–brine systems. The slight decrease in the concentrations of species such as Al, Ca and Ba in the solid residues could be attributed to the dissolution of the easily soluble phases of these species contained in the fly ashes into the brine solution. Significant quantities of these species that may be present in their easily soluble phases could dissolve when in contact with an aqueous solution.

The concentration of Na, Cl and S in the solid residues was observed to increase with increase in the contact time of the static long-term interaction experiments. This revealed that the interaction periods could affect the leaching of species from the fly ash as well as the removal of species from the brine solution by the fly ash. This observation was in agreement with what was observed in the chemical analysis of the excess brine decanted from the solid residues where the % removal of Na, Cl and SO_4 (Tables 2, 3) in the brine solution increased with an increase in the interaction periods. This indicates that the longer the interaction periods of fixed ratios of the fly ashes and the brine solution in closed and static conditions, the higher the amount of Na, Cl and SO_4 that could be removed from the brine solution. However, the mineral phases formed during the interaction are soluble salts, so the flow of water through the dump should be strictly avoided and only a very limited amount of brine must be applied to prevent the dissolution of the phases.

Conclusion

The interaction of species in fly ash and brine system is not only a function of the pH of the system, but also a function of the interaction period, and the concentration of species available in the system, which depends on the type and source of the fly ash and brine. The removal capacity of the SFA was shown to be higher than that of TFA fly ash during the long-term interaction experiments which was attributed, among other factors, to the slightly higher pH of the former when in solution. The results of the chemical composition of the decanted brine solution and the solid residues revealed that some species such as Na, Cl and SO_4 , which are major constituents of the brine solution, can be removed by the SFA and TFA fly ashes to a certain extent from the brine solution when the fly ash–brine systems is allowed to stay undisturbed



for some times. This study also shows that despite the removal of some species from the brine solution, a cleaner brine solution may not be obtained due to the significant leaching of some species such as Ca, Ba, Al, Si, Cr and Mo from the fly ash during the static fly ash–brine interaction. However, the stability and the re-dissolution of the species captured by the fly ashes when in contact with rain water or solutions of different pH is a major concern which will be addressed in the second part (Part II) of this study.

Acknowledgments This study was funded by ESKOM and SASOL, South Africa. The authors are very grateful to Ms. Riana Rossouw at the ICP-MS Laboratory, University of Stellenbosch, South Africa for the multi-element analysis.

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