Laboratory study on the mobility of major species in fly ash–brine co-disposal systems: up-flow percolation test

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Abstract
Apart from the generation of fly ash, brine (hyper-saline wastewater) is also a waste material generated in South African power stations as a result of water re-use. These waste materials contain major species such as Al, Si, Na, K, Ca, Mg, Cl and SO_4. The co-disposal of fly ash and brine has been practiced by some power stations in South Africa with the aim of utilizing the fly ash to capture the salts in brine. The effect of the chemical interaction of the species contained in both fly ash and brine, when co-disposed, on the mobility of species in the fly ash–brine systems is the focus of this study. The up-flow percolation test was employed to determine the mobility of some major species in the fly ash–brine systems. The results of the analysed eluates from the up-flow percolation tests revealed that some species such as Al, Ca and Na were leached from the fly ash into the brine solution while some species such as Mg, Cl and SO_4 were removed to some extent from the brine solution during the interaction with fly ash. The pH of the up-flow percolation systems was observed to play a significant role on the mobility of major species from the fly ash–brine systems. The study showed that some major species such as Mg, Cl and SO_4 could be removed from brine solution using fly ash when certain amount of brine percolates through the ash.

1 Introduction

The combustion of coal for power generation is on the increase due to the increase in demand for electricity globally. Huge amounts of fly ash are produced as a result of the increase in coal combustion. According to US Coal Combustion Product Production & Use Survey Report, US power plants produced about 60 million tons of fly ash in 2011, out of which nearly 39 % was beneficially used (ACAA 2011). South African power utilities generate significant quantities (about 40 Mt) of fly ash annually of which the power stations operated by ESKOM South Africa generate 25 Mt of the fly ash annually (ESKOM Report 2013). Out of the fly ash generate in South Africa per annum, less than 10 % is beneficially utilized. The fact remains that, despite its beneficial use for agricultural purposes, waste stabilization, additive to cement, road construction among others (Iyer and Scott 2001; Kumpiene et al. 2006; Foner et al. 1999), significant amounts of fly ash are being disposed in ash dump. Fly ash contains major and minor species such as Ca, Na, Mg, K, SO_4, Cl, Fe, As, Pb, Cu, Cr, Mo, Mn, etc., and these species could leach out in significant quantities from fly ash when in contact with aqueous solution (Ilic et al. 2003; Baba and Kaya 2004;

Polettini and Pomi 2004; Adriano et al. 1980). The disposal of fly ash has been a major concern to coal-fired power stations due to the possible release of contaminants to the surrounding soils, surface and groundwater. Apart from the fly ash generated in the power stations in South Africa, brine (a hyper-saline wastewater), is also generated in significant quantities in water treatment circuits. 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 disposal of brine is regulated due to its chemical composition thereby causing some power stations to co-dispose fly ash and brine with the aim of using fly ash to capture the species in brine. The leaching behaviour of major and minor species from coal fly ash and municipal solid waste incineration ash has been widely studied (Gitari et al. 2009; Meima and Comans 1999; Hyks et al. 2009) in order to assess the environmental implications of their utilization and disposal. Despite several studies on the release of species from fly ash when in contact with water and acid mine drainage (Baba and Kaya 2004; Polettini and Pomi 2004; Gitari et al. 2006), adequate attention has not been given to understanding the mobility of some species when fly ash is in contact with brine solution. This study is aimed at understanding the chemical interactions and mobility of major species when fly ash and brine are co-disposed. The up-flow percolation test was employed to simulate, to some extent, a co-disposal scenario where fly ash and brine are mixed to form a slurry after which brine solution is percolated through the fly ash–brine system on a continuous basis. This approach enables the evaluation of the temporal evolution of pH and the major species over a given period of time.

2 Materials and Method

2.1 Fly Ash and Brine

Fresh fly ash samples were collected from two South African coal-fired power utilities. The power utilities were coded as SC and TC. Fresh fly ash from SC power station was collected directly from the hoppers while the fly ash from TC was collected from the conveyor belt taking the ash to the ash dump. The TC fly ash used in this study was preconditioned with about 16 % brine solution to suppress dust before the ash was sampled (Fatoba et al. 2011). There was no access to the fresh fly ash directly from the hopper because of the regulations of the power station. The fly ash samples were stored in sealed plastic containers. The plastic bags were filled to the top to exclude as much air as possible and then sealed up. The plastic bags containing the fly ash samples were stored in a dark cool cupboard far away from sources of heat, out of direct sunlight and away from fluctuating temperature.

The brine sample used in this study was collected from the highly saline retentate stream of the reverse osmosis desalination plant at TC power station. The choice of the brine sample from TC power station was as a result of the higher concentration of the major elements compared to the brine generated at SC power station. The brine sample was stored in plastic containers, tightly closed and stored in the refrigerator at 4 °C.

2.2 Up-flow Percolation Test

The up-flow percolation test was carried out according to European standard method prEN14405 (CEN 2003) (details in Fatoba 2010). Columns of height 30 cm and internal

diameter 5 cm were designed for the up-flow percolation test. The column, including top and bottom sections, and filters were rinsed with 1 M nitric acid and de-mineralized water consecutively. The column was packed with the fly ash sample to the height of 25 ±5 cm and then weighed to determine the weight of the fly ash in the column (Fig. 1). The column was saturated with brine using a peristaltic pump. The saturated fly ash was left standing for a period of 3 days in order to equilibrate the systems (CEN 2003). After the equilibration period, fresh brine was continuously pumped into the column using a peristaltic pump pumping at a flow rate of 12 mL/h. The outlet hose was connected to the collection bottle and samples were taken at different times for analyses over a period of time until a cumulative L/S 80 was attained. At each leachate collection, time and volume of the eluate fraction was recorded in order to calculate the liquid/solid ratio and other necessary calculations at the end of the experiment. The pH and EC of the eluate were measured immediately after the eluates were taken. Samples were thereafter preserved with dilute HNO_3 for analysis of metals by inductively coupled-mass spectrometry for major elements and un-acidified samples diluted accordingly for SO_4^{2-} and Cl^- analysis by ion chromatography. Samples were refrigerated at 4 °C until analysis. The up-flow percolation tests were carried out in duplicate.
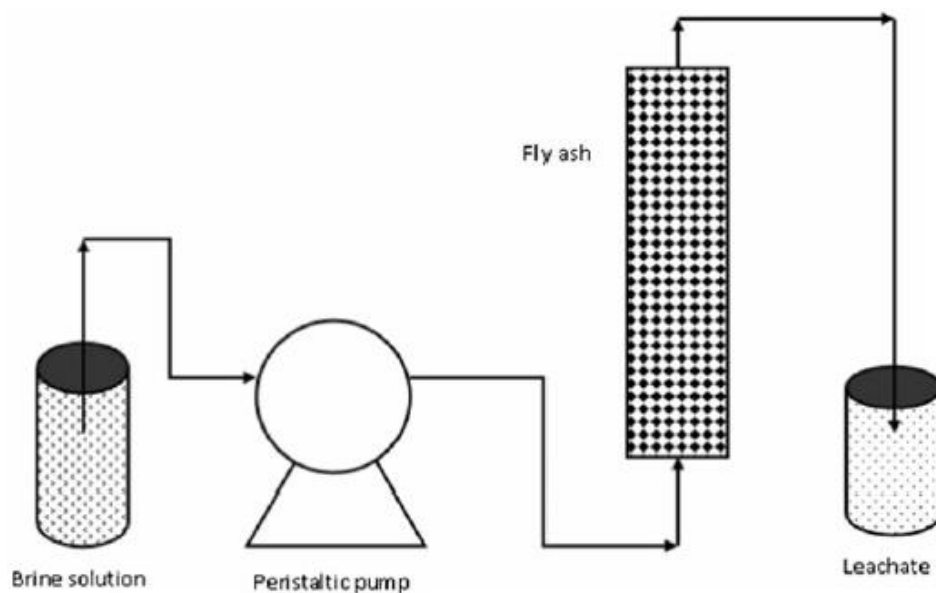

Fig. 1 Schematic diagram of up-flow percolation test

3 Results and Discussion
3.1 Major Elements in Fly Ash
The major elemental composition of the fresh fly ashes from SC and TC power stations showed that the ashes contain high concentrations of Al, Si, Ca, Mg and S (SO_4) (Table 1). The comparison of the fly ashes showed that the concentrations of the species in the fly ashes vary. For instance, the concentration of Ca and Mg in SC fly ash was found to be higher than their concentration in TC fly ash. The variation in the concentrations of Ca and Mg in the fly ashes could be due to the different types of coal burnt by the different power

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stations. The concentration and the dissolution of the oxides of Ca and Mg in the fly ash have significant effect on the pH of the fly ash system. This effect was noticed in the pH of the two fly ash systems as the pH of SC fly ash, with higher concentration of Ca and Mg, was slightly higher than that of TC fly ash (Fig. 2). The higher concentration of S and Cl in the TC fly ash compared to their concentration in SC fly ash could be attributed to the pre-conditioning of the TC fly ash with brine solution before the sample was taken.

3.2 pH and EC

The pH and EC of SC and TC fly ash–brine interactions in the up-flow percolation test are shown in Fig. 2. The pH of the unreacted brine (UB) was ≈8. After the interaction of the brine solution with the fly ashes, the pH of the fly ash–brine systems increased significantly to values >13 and >12 in SC and TC systems, respectively (Fig. 2) at the beginning of the experiments except for TC fly ash–brine system at L/S 0.1 where the pH value at the beginning of the experiment was almost the same as the pH of the UB. The high pH values observed in the leachates of the up-flow percolation systems during the first few bed volumes of flow could be attributed to the dissolution and hydrolysis of alkalinity-contributing oxides such as CaO on the surface of the fly ash particles during the 3-day equilibration period (Gitari et al. 2009; Iwashita et al. 2005; Reardon et al. 1995). After the initial increase, the pH of the systems (Fig. 2) gradually decreased over several bed volumes of flow. The gradual decrease in the pH of the systems after the maximum pH was reached at L/S 0.5 could be due to the slow release and continuous flushing out of the dissolved alkalinity-contributing components as a result of the low flow rate (12 mL/h) applied in the systems.

Table 1 Major elements in SC and TC fly ashes

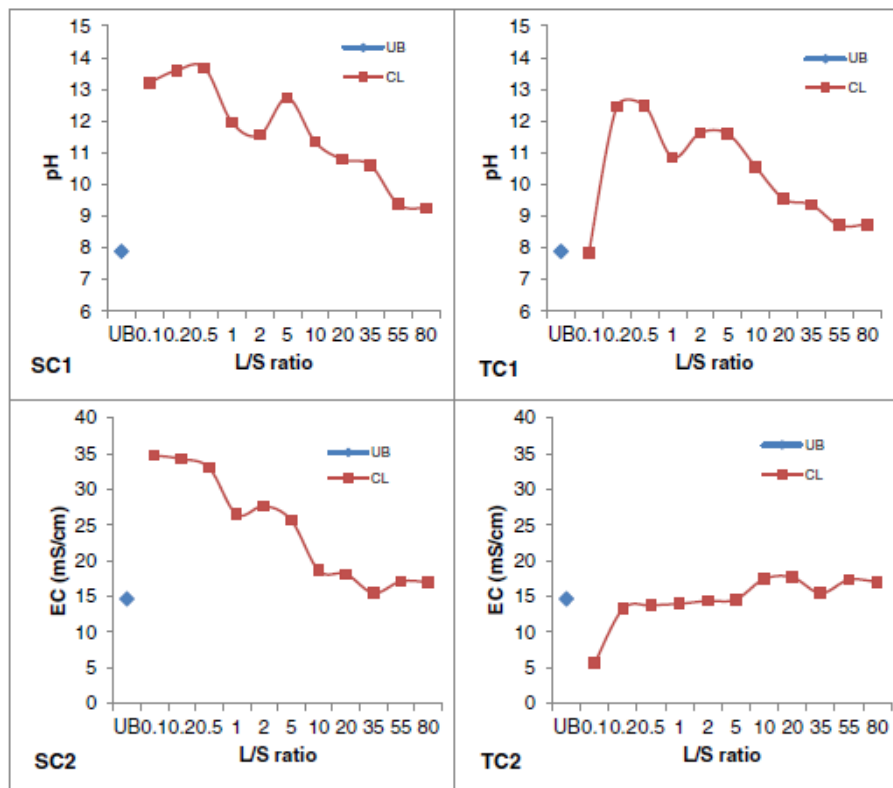| Major species (ppm)	Al	Ca	Mg	Na	Si	S	Cl
SC fly ash	137,751	66,467	13,572	4,525	231,787	1,378.35	73.89
TC fly ash	129,495	42,096	8,204	2,151	242,352	7,025.05	730.26

Fig. 2 pH (SC1 and TC1) and EC (SC2 and TC2) profiles of up-flow percolation tests as a function of L/S ratio: *UB* = unreacted brine, *CL* = fly ash–brine leaching trend

After the 3-day equilibration period, the EC of TC systems (Fig. 2 (TC2)) was initially considerably lower (5.6 mS/cm) than the EC of the unreacted brine solutions (UB) at the beginning of the test. Thereafter, the EC of TC systems increased rapidly to 13.23 mS/cm at L/S 0.2 after which a gradual and steady increase was observed until the end of the test except at L/S 35 where a slight decrease in the EC values of the fly ash–brine systems were observed. On the other hand, the EC of SC systems (Fig. 2 (SC2)) increased from ≈15 mS/cm to the maximum of between 30–35 mS/cm at the beginning of the percolation test (after the equilibration) after which a gradual decrease from 35 to 15 mS/cm in the EC trends was observed for the fly ash–brine systems. The low EC values observed in TC systems at the beginning of the test could be attributed to the removal of some major species such as Na, Cl and SO_4 from the fly ash–brine systems upon the initial contact of the fly ash with brine which was confirmed by the analysis of the eluate. The initial removal observed could be as a result of transient precipitation of some elements or formation of secondary mineral phases due to the super-saturation of these species in the systems. The rapid increase observed in the EC thereafter could be attributed to the dissolution of the transient phases or the dissolution of major components from the matrix of the fly ash that were released over time as the pH decreased. In contrast to the TC systems where the EC increased steadily, the EC of SC systems decreased steadily from about 35 to 15 mS/cm. The high EC observed at the beginning of the test, in the case of the SC system (Fig. 2 (SC2)), could be accounted for by the dissolution of highly soluble components of the fly ash during the 3-day equilibration period. The gradual decrease in the EC as observed in SC

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system could indicate the steady flushing out of the dissolved species from the ash or the precipitation of some of the dissolved species due to super-saturation promoted by continuous and gradual flow of fresh brine solution in the systems. The almost stable EC observed at the end of the tests (Fig. 2) could be attributed to the steady and continuous dissolution of components locked up in the aluminosilicate matrix that are released over time.

3.3 Major Elements in the Fly Ash–Brine Leachates

The concentration of Al in the leachate samples collected from SC up-flow percolation systems (Fig. 3 (SC3)) was between 1 and 2 mg/L after the equilibration whereas the concentration of Al in the unreacted brine solutions at the beginning of the up-flow percolation tests was almost zero. This indicates that Al was released from fly ash upon equilibration with brine. The concentration of Al in SC leachate (Fig. 3 (SC3)) thereafter reduced to a minimum at L/S 1 and 2 whereafter an increase to about 4 mg/L was observed at L/S 10 after which the concentration of Al gradually decreased in the systems for the remaining L/S ratio. The release of Al in leachates samples of TC systems (Fig. 3 (TC3)) was higher (about 18 mg/L) thus more Al was released from the TC fly ash after equilibration at the beginning of the test. After the increase observed during equilibration, a gradual decrease in Al concentration was observed in TC leachates (Fig. 3 (TC3)) and continued until the end of the up-flow percolation tests. The leaching patterns of Al could be attributed to the dissolution of its oxides as a result of flushing out of Al due to continuous inflow of brine solution. The slight increase observed in the concentration of Al in SC3 leachates at the beginning of the tests could be attributed to the dissolution of amorphous aluminosilicates in the fly ash. In fly ash systems, it was argued that after the rapid dissolution of CaO and other soluble salts, the mineral phase most susceptible to weathering are amorphous glassy aluminosilicates and silica (Seoane and Leirós 2001). The decrease observed at L/S 1 to 5 in SC3 could be as a result of formation of transient phases (Hyks et al. 2009; Georgakopoulos et al. 2002; Tiruta-Barna et al. 2006) due to high pH of the up-flow percolation systems.
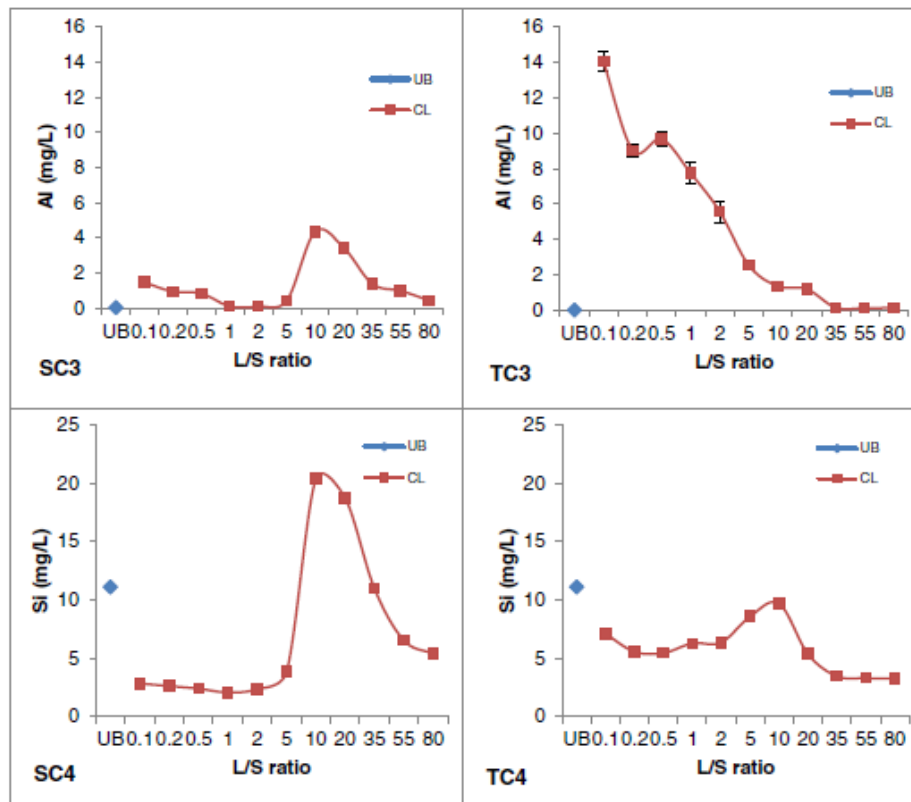
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Fig. 3 The concentrations of Al (SC3 and TC3) and Si (SC4 and TC4) released from the up-flow percolation tests as a function of L/S ratio: *UB* = unreacted brine, *CL* = fly ash–brine leaching trend

The sudden increase observed at L/S 10 in SC3 could be accounted for by the dissolution of the transient or by further dissolution of the glassy Al phases. The difference observed in the leaching trend of Al in TC systems (TC3) compared to that of SC systems (SC3) could be as a result of the lower pH of the former due to the dust suppression pretreatment it underwent before the sample was taken. The higher concentration of Al in TC systems (TC3) at the beginning of the tests could be as a result of the greater solubility of the amorphous glassy or crystalline Al phases in the fly ash due to the lower pH of TC systems.

The release of Si in both SC and TC systems (Fig. 3 (SC4 and TC4)) followed nearly the same trend. The concentration of Si at the beginning of the tests (L/S 0.1–2) was observed to be lower than the Si concentration in UB which indicates that Si was removed from the brine solution during equilibration. The removal of Si at the beginning of the tests could be due to the formation of transient amorphous Si-bearing mineral phases. Georgakopoulos et al. (2002) suggested that the presence of Al and Si in solution at high pH could lead to the formation of amorphous Al hydroxides and Si-rich mineral phases such as gehlenite ($Ca_2Al_2SiO_73SiO_5$) and hatrurite (Ca_3SiO_5). The formation of these phases may be possible due to the significant concentration of Ca released into the up-flow percolation systems. A rapid increase in Si concentration was observed at L/S 5–20 and 2–10 in SC and TC systems, respectively (Fig. 3 (SC4 and TC4)), with more Si released from SC fly ash ($\approx$15 mg/L) than TC fly ash ($\approx$6 mg/L). The increase in both systems could be accounted for by the dissolution of the probable transient secondary mineral phases formed or as a result of

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the further dissolution of the silica matrix of the fly ash (Jankowski et al. 2006; Ward et al. 2009) in case of SC systems (SC4). In the case of TC systems (TC4), the dissolution of some transient amorphous silica containing phases formed at the beginning of the tests could possibly account for the increase at L/S 5 and 10. This assumption was based on the fact that despite the increase in the concentration of Si at L/S 2–10 in TC systems (TC4), the concentration of Si in TC systems remained lower than its concentration in the UB.

The concentration of Ca in UB was about 91 mg/L while SO_4 levels in UB were exceptionally high, being nearly 9,000 mg/L (Fig. 4). The concentration of Ca in leachates from both SC and TC up-flow percolation systems (Fig. 4 (SC5 and TC5)) increased after equilibration at the beginning of the tests (L/S 0.1) compared with its concentration in the unreacted brine solutions. The concentration of Ca in the leachates gradually increased until a maximum of about 500 and 350 mg/L was reached at L/S 55 and 5 in SC and TC systems, respectively. The trend of Ca released from the fly ash–brine systems showed that apart from the initial dissolution of readily soluble Ca-rich phases such as CaO, the dissolution of Ca-rich phases locked in the fly ash matrix contributed significantly to the gradual increase in Ca concentration. The fluctuation in the concentration of Ca in the SC systems and the gradual decrease observed in TC systems (Fig. 4 (TC5)) after the maximum was reached at L/S 5 could be as a result of depletion of Ca-bearing phases by flushing with brine solution or due to precipitation and dissolution of transient Ca-rich mineral phases in the fly ash–brine systems (Georgakopoulos et al. 2002; Hjelmar 1990). Steenari et al. (1999) suggested that the presence of other species such as SO_4 in alkaline fly ash systems could produce Ca-hydrated mineral phases such as gypsum and calcite. Ca in fly ash occurs mainly as lime (CaO), anhydrite ($CaSO_4$) and in the glass matrix, and these anhydrous phases are very reactive when exposed to aqueous solution. Therefore, the solubility and reactivity of Ca with other species could be responsible for the trend of Ca observed in leachates in the up-flow percolation systems.

The very high concentration of SO_4 in the leachates from both SC and TC systems showed a very significant decrease after equilibration at the beginning of the up-flow percolation tests compared to the concentration of SO_4 in the unreacted brine solutions (UB) (Fig. 4 (SC6 and TC6)). This indicates that SO_4 was significantly removed from the brine during and after the equilibration until 1 bed volume of brine had percolated. The concentration of SO_4 removed from the brine solution by the fly ashes immediately after equilibration (at L/S 0.1) was between 6,000 and 8,000 mg/L. After the very low concentration of SO_4 observed in the leachates at the beginning of the tests, the SO_4 concentration increased again until a maximum (between 7,000 and 8,000 mg/L) was observed at L/S 20 and 10 in SC and TC up-flow percolation systems, respectively (Fig. 4 (SC6 and TC6)).
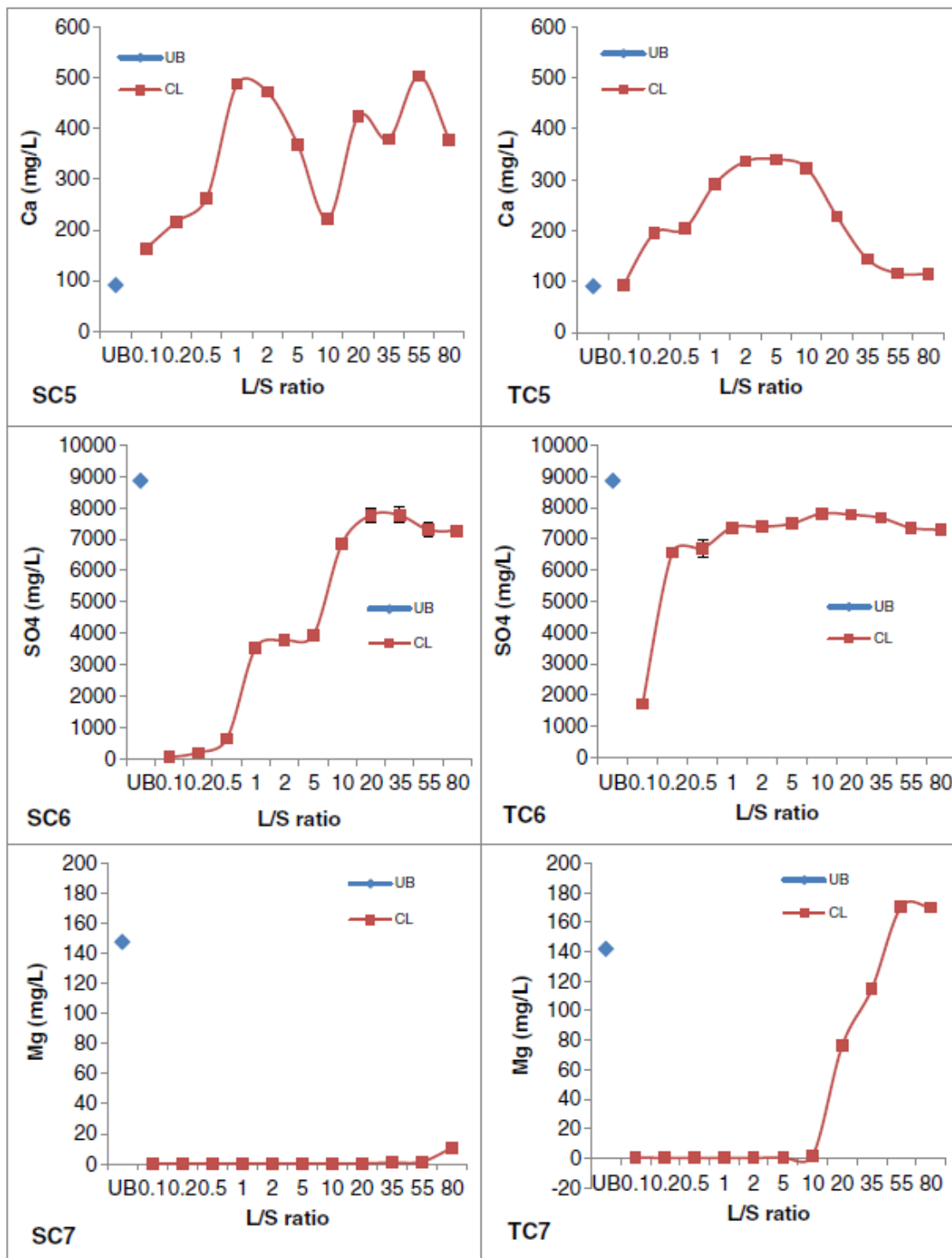
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Fig. 4 The concentrations of Ca (SC5 and TC5), SO₄ (SC6 and TC6) and Mg (SC7 and TC7) released from the up-flow percolation tests as a function of L/S ratio: *UB* = unreacted brine, *CL* = fly ash–brine leaching trend

The trends of SO_4 showed that SO_4 the brine solutions by the fly ashes as a result of precipitation of SO_4 bearing phases. According to Bock (1961), in a system containing considerable concentration of Ca and SO_4, the precipitation of gypsum ($CaSO_4 \cdot 2H_2O$) could control the release of SO_4 but when the solution contains excess of Na or KCl,

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the precipitation of anhydrite is possible only at high temperature. The removal of SO_4 from the fly ash-brine systems especially at the beginning of the tests could be attributed to the formation of transient $CaSO_4$-rich mineral phases such as gypsum (Gitari et al. 2009). The significant amounts of SO_4 present in the brine solution could interact with the Ca released from the fly ashes during equilibration to form transient $CaSO_4$-rich mineral phases. Gypsum is moderately soluble in water or in aqueous solution. The gradual dissolution of the transient hydrated $CaSO_4$-rich phase formed at the beginning of the tests (during equilibration period) could be responsible for the increase in the concentration of SO_4 in the leachates after the initial minimum concentration. This shows that the mineral phases formed are unstable and subject to continuous weathering if an excess of brine (more that L/S 1) is percolated through the ash system.

The concentration of Mg in the UB was approximately 140 mg/L (Fig. 4 (SC7 and TC7)). The concentration of Mg in the leachates of the up-flow percolation systems indicates the immediate and constant removal of approximately 140 mg/L Mg from the brine solutions during the interactions with the fly ashes despite the continuous inflow of the fresh brine solutions (Fig. 4 (SC7 and TC7)). An increase in the concentration of Mg was observed at L/S 55 and 10 in SC (SC7) and TC (TC7) up-flow percolation systems, respectively. The low concentration of Mg which indicates its continuous removal by the fly ash in the system could be attributed to the formation of Mg-rich mineral phases such as $Mg(OH)_2$ due to the alkaline pH of the systems which favours the formation of such mineral phases. The hydrolysis of MgO in fly ash in alkaline condition has been observed to form sparingly soluble brucite ($Mg(OH)_2$) (Tiruta-Barna et al. 2006; Warren and Dudas 1984), and this could account for the low level of Mg in the leachates of the up-flow percolation tests. Apart from MgO present on the surface of fly ash, Mg is also present in the slowly dissolving glassy phase (Mattigod et al. 1990), and this could account for the gradual increase observed in Mg concentration in the leachates above levels found in UB over time at L/S 55 in TC (TC7) systems.

Na concentration was very high in UB, being approximately 4,323 mg/L while Cl level was also high (2,424 mg/L). Two different trends were observed for the release of Na into the leachates from SC and TC up-flow percolation systems (Fig. 5 (SC8 and TC8)). A slight increase in the concentration of Na (approximately 5,000 mg/L) was observed in SC systems (SC8) after equilibration while initially, at L/S 0.1, a significant decrease to about 1,000 mg/L in Na concentration was observed in TC (TC8) systems immediately after equilibration and at the beginning of the up-flow percolation tests. After the initial increase in the concentration of Na in SC system, a slight and slow decrease (only slightly lower than the levels in UB) was observed and this concentration (>4,000 mg/L) was maintained throughout the period of the tests. On the other hand in the TC systems, the concentration of Na increased abruptly at L/S 0.2 from approximately 1,000 mg/L to 4,000 mg/L and was almost equal to its

concentration in UB throughout the percolation tests with small fluctuation except at L/S 35 where a slight decrease in the concentration was observed. The slight increase of Na at L/S 0.1 in SC systems when compared with the concentration in UB could be attributed to the leaching of Na from the fly ash during the 3-day equilibration period while the initial decrease in Na concentration in TC systems immediately after the equilibration period may be as a result of the formation of transient Na-containing phase upon contact with fly ash due to the super-saturation of Na in the brine containing systems. The nearly immediate dissolution of the transient Na-containing phase or the exhaustion of the capacity of the fly ash to capture more Na from the brine due to continuous flow of brine may account for the increase in Na concentration in TC systems at L/S 0.2. These trends indicate that after the initial removal of Na, the capacity of the fly ashes to remove more Na from the brine solutions during the tests reduced as a result of continuous flow of fresh brine solution. This shows that the removal of Na from the brine solution is insignificant.

The concentration of Cl in the leachates after contact with fly ash was lower than the concentration in UB throughout the period of the up-flow percolation tests (Fig. 5 (SC9 and TC9)). This indicates that some Cl was continuously removed from the brine solution throughout the period of the up-flow percolation tests.
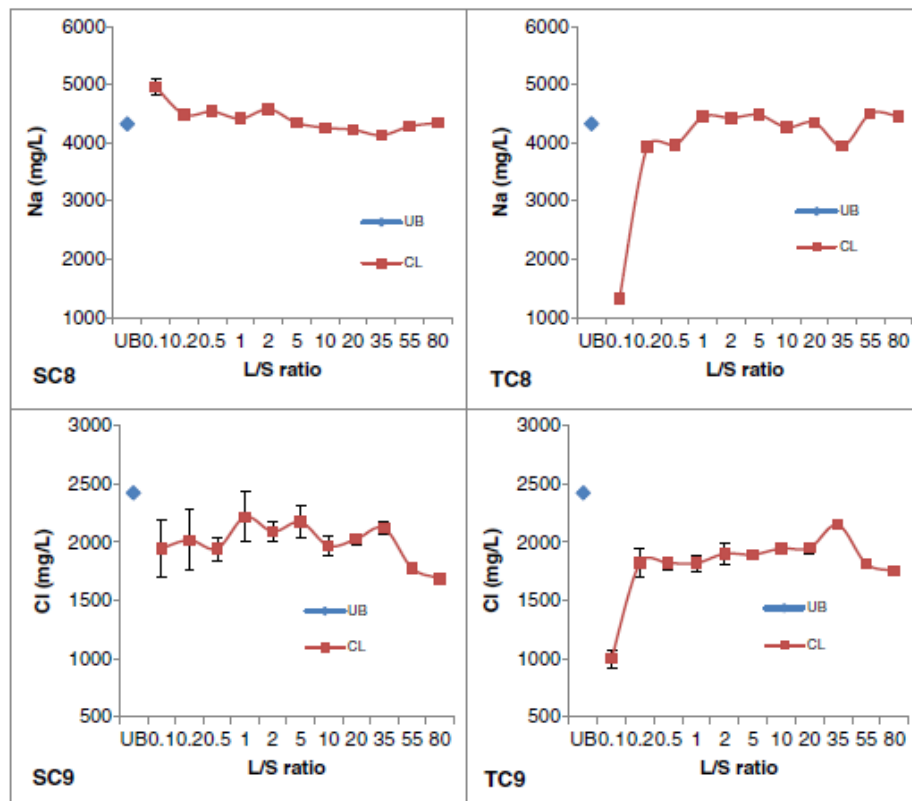

Fig. 5 The concentrations of Na (SC8 and TC8) and Cl (SC9 and TC9) released from the up-flow percolation tests as a function of L/S ratio: *UB* = unreacted brine, *CL* = fly ash–brine leaching trend

Cl was initially removed from the brine solution in TC systems after equilibration. Between L/S 0.1 and 0.2, a proportion of the Cl removed from TC systems was redissolved and the levels increased from about 1,000 mg/L to about 2,000 mg/L for the duration of the experiments with small fluctuation. The removal patterns of Cl in TC systems correlated with those of Na indicating that the removal of Cl from the systems could be controlled by the formation of a transient halite (NaCl) phase at the beginning of the tests. Due to the sufficient concentration of Ca and Al in the up-flow percolation systems as a result of matrix dissolution of fly ash, the probable formation of Friedel's salt $[Ca_4Al_2Cl_2(OH)_{12} \cdot 4H_2O]$ could also account for the reduction in the concentration of Cl after the initial stages in the systems (Hyks et al. 2009; Suryavanshi and Swamy 1996; Bothe and Brown 2004).

3.4 Mass Balance

The percentage of species leached from the fly ashes or removed from the brine solution (UB) at selected L/S ratios during the up-flow percolation tests are presented in Tables 2 and 3. The percent leached or removal of the species was calculated using the following equation;

$$\% \, Removal/Leached = \frac{CUB - CL}{CUB} \times 100 \qquad (1)$$

where

CUB   is the concentration of species in the unreacted brine (UB)

CL   is the concentration of species in the leachate that percolated through the ash

The calculated mass balance (Tables 2 and 3) revealed that the removal of Na, mostly at the beginning of the experiment, was low, in the range of 2.3 % except in the TC fly ash–brine system where 69.4 % was only observed at L/S 0.1. The removal of Mg, Cl and SO_4 was in the range of 92–100, 8.5–30.3 and 12.3–99.4 %, respectively, in SC fly ash–brine system, while in the TC fly ash–brine system, the percentage removal of Mg, Cl and SO_4 was in the range of 99.7– 100, 19.5–58.8 and 12.3–80.7 %, respectively, at different L/S ratios. The removal of some species from the brine solution at specific L/S ratio could be attributed to the precipitation process in the up-flow percolation systems. However, Ca and Al were leached out of the fly ashes into the brine solution in significant percentages irrespective of the L/S ratio.

Table 2 Chemical composition of brine and the percentage of major elements leached from fly ash or removed from brine during the up-flow percolation tests on SC fly ash and brine at selected L/S ratios (All values are in percent except UB = milligram per litre)

Parameter	UB	L/S ratio					
		0.1	1	5	20	55	80
Al	0.01	−13,016.3	−742.7	−3,698.8	−30,671.8	−8,634.9	−3,803.8
Ca	91	−79.7	−435.1	−304.6	−365.2	−452.3	−315.1
Mg	147.5	99.9	100	99.9	99.8	100	92.8
Na	4,323.2	−14.9	−2.1	−0.5	2.3	0.9	−0.4
Si	11.1	74.6	81.5	65.7	−68.9	41.1	51.6
Cl	2424	19.7	8.5	10.3	16.3	26.6	30.3
SO$_4$	8,858	99.4	60	55.6	12.3	17.6	18.1

Negative (−) values indicate percent leached from the fly ash into the brine solution while the positive values indicate percent removal from the brine during the up-flow percolation tests

The removal capacity of the two fly ashes varied slightly. The percentage of some species such as Mg, Si and SO$_4$ removed from the brine solution by SC fly ash was higher than the percentage removed by TC fly ash in most cases. The increase in the removal capacity of SC fly ash could be attributed to its slightly higher pH than TC fly ash. The TC fly ash removed more Na and Cl from the brine solution than SC fly ash, which could be attributed to the effect of the super-saturation of these species bearing in mind that the TC fly ash had been moistened with brine before sampled.

4 Conclusion
The removal and subsequent leaching of some species in the systems could be as a result of precipitation followed by dissolution of the transient secondary mineral phases formed during the interactions. The release of Ca, Al and Na throughout the period of the percolation tests indicates that these species would continuously leach from the fly ashes by contact with brine flows. The trends observed in the release of the major species from the up-flow percolation systems showed that the removal capacity of the fly ashes could be exhausted at a stage due to continuous inflow of brine thereby overwhelming the removal of some species by the fly ashes.

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Table 3 Chemical composition of brine and the percentage of major elements leached from fly ash or removed from brine during the up-flow percolation tests on TC fly ash and brine at selected L/S ratios (All values are in percent except UB = milligram per litre)

Parameter	UB	L/S ratio					
		0.1	1	5	20	55	80
Al	0.01	−126,062.4	−69,417.1	−22,863.1	−10,734.6	−1,080.4	−1,186
Ca	91	−2.2	−220.6	−273.3	−150.2	−27.4	−26.4
Mg	147.5	99.8	99.9	99.7	100	100	100
Na	4,323.2	69.4	−2.8	−3.6	−0.6	−4.1	−3.2
Si	11.1	35.9	43.6	22.7	51.8	70.5	70.8
Cl	2,424	58.8	24.9	21.8	19.5	25	27.7
SO$_4$	8,858	80.7	16.9	15.5	12.3	17	17.8

Negative (−) values indicate percent leached from the fly ash into the brine solution while the positive values indicate percent removal from the brine during the up-flow percolation tests

Apart from the reduction in the capacity of the fly ash to remove species from brine, metals held in the fly ash matrix could be released over time by brine flowing continuously through the ash system thereby increase the leaching of some species. The trend of the mobility of the major species in the fly ash–brine systems gives an insight into the long-term environmental effect of co-disposal technique. Hence, the co-disposal of brine with fly ash would require a careful consideration of the bed volume of brine that goes into the ash systems.

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