



# Application of hydrogeochemical modelling in simulating the transportation of elements in fly ash heap under different disposal systems in South Africa



J.M. Mbugua<sup>a,b</sup>, J.C. Ngila<sup>a,\*</sup>, A. Kindness<sup>c</sup>, M. Demlie<sup>d</sup>

<sup>a</sup> University of Johannesburg, Department of Applied Chemistry, P.O. Box 17011, Doornfontein, Johannesburg 2028, South Africa

<sup>b</sup> Technical University of Kenya (TUK), Department of Chemical Sciences and Technology, P.O. Box 52428, 00200 Nairobi, Kenya

<sup>c</sup> University of KwaZulu-Natal, School of Chemistry and Physics, Westville Campus, Private Bag X54001, Durban 4000, South Africa

<sup>d</sup> University of KwaZulu-Natal, Department of Geological Sciences, Westville Campus, Durban 4000, South Africa

## ARTICLE INFO

### Article history:

Received 12 February 2014

Received in revised form 30 October 2014

Accepted 21 November 2014

Available online 4 February 2015

### Keywords:

Ash heap

Brines

Coupled transport modelling

Leachate

Groundwater pollution

## ABSTRACT

Ash heap modelling of South African fly ash from Tutuka was carried out and the duration of transportation projected for 20 years based on two disposal scenarios, namely; irrigation of ash with rainwater, and irrigation with brines. The hydrogeochemical modeling code, PHREEQC, was applied in the study which gave insights into the speciation, release and transport of elements from the water and brines–fly ash long term interactions. Tutuka ash–water heap model showed a general sharp decrease of total elemental concentrations released during the first 2.5 years simulation as the pH value dropped from 12.6 to 8.7, after which it remained constant and their concentration remained constant up to 20 years. The elements showing this trend included Ca, Mg, Al, Fe, Sr, Zn, Na, K, Li and C(4). Generally, brines caused sharp increase in released concentration of the elements Ca, Mg, S(6) and C(4) for the first 3 years of heap irrigation whereas with water irrigation an opposite trend was observed in which the elemental concentrations decreased. Much of the release chemistry of the elements was closely related to the phase dissolution/precipitation and formation as the major controlling factors. Generally therefore, the modelled leachate quality results revealed that many elements are mobile and move through the ash heap in a progressive leaching pathway. The model could therefore be used to provide reasonable leachate quality from the modelled Tutuka ash heap which may be reaching the ground water. Overall, the ash heap modelling enhanced the understanding of the environmental impacts of ash–water–brines interactions and demonstrated that leachate composition is determined by the following factors; (i) the mass flows from the pores of fly ash, (ii) the surface dissolution of the mineral phases, (iii) the various chemical reactions involved during the ash–brine and ash–water interactions, (iv) the interactions with a gas phase (atmospheric CO<sub>2</sub>), (v) the composition of the initial fly ash, and (vi) the leachate flow and hydrodynamics as captured in the conceptual model. Further model validation is recommended with lysimeters to quantitatively compare the simulated results against the experimental data and improve on the model.

© 2015 Elsevier Ltd. All rights reserved.

## 1. Introduction

Fly ash heaps and dams are potential long-term sources of contamination to surface–water sources and groundwater systems due to their possible enrichment in major and trace elements relative to normal geological materials (Donahoe, 2004). This may occur if they are released into the environment in sufficient amounts, and therefore a long-standing need to assess the release and mobilisation of elements that result from weathering of fly ash,

is important. Geochemical reactions and the mineralogical changes that occur between fly ash components and the chemical species in the brine solutions have been reported as part of the larger collaborative ash–brine project work (Gitari et al., 2009a,b; Mbugua et al., 2013; Ojo, 2010; Ojo et al., 2011, 2007; Petrik et al., 2007, 2009a,b). The interactions between the various species in the fly ash and the brine may result either in neoformed phases (as secondary phases) or in dissolution of the primary phases. The speciation, release, transport and fate of the released mobile elements were investigated. Modelling reactive transport in fly ash–water–brines systems with a view to quantify and characterise the products formed and transport mechanisms involved

\* Corresponding author. Tel.: +27 115596196; fax: +27 115596154.

E-mail address: [jcngila@uj.ac.za](mailto:jcngila@uj.ac.za) (J.C. Ngila).

has been the focus of our study. Prediction of the leachate quality when fly ash heap is subjected to brines and water irrigation was carried out using PHREEQC as the modelling tool.

Reactive-transport modelling as an emerging research field, aims at a comprehensive, quantitative, and ultimately predictive treatment of chemical transformations and mass transfers within the earth system. The field of modern geosciences is one of the fields in which reactive-transport models have had significant contribution. In their work, Regnier and co-workers (Regnier et al., 2003) noted that reactive-transport models (RTMs) provide platforms for testing concepts and hypotheses, and for integrating new experimental, observational, and theoretical knowledge about geochemical, biological and transport processes. Through numerical computation and simulation, RTMs provide the most valuable diagnostic and prognostic tools available for elucidating the inherently complex dynamics of natural and engineered environments such as our ash heap scenario. Furthermore, RTMs bridge the gap between fundamental, process-oriented research and applied research in the fields of operational modelling, environmental engineering and global change. Reactive-transport models are a recent development and modelers do not have a large body of work from which to draw. The combined capability to model flow, transport, and chemical reactions provides a systematic approach for studying ground-water processes (Parkhurst et al., 2003). For a process-based interpretation of test results and their translation to field situations, sufficient understanding is required of the geochemical and mass transfer processes that control the leaching of contaminants in a percolation regime. This understanding will form the basis of our ash heap modelling in order to determine the leaching and transport mechanism during fly ash–water and fly ash–brine interactions as well as the quality of the leachates.

Even though large uncertainties are associated with the modelling results (Ligia et al., 2004) a reactive-transport model is the only systematic method available to estimate the time dependency of the loads and fate of major and trace elements in a complex ash–brine disposal system transported down an ash heap and to assess the sensitivity of the load estimate to various chemical and physical processes.

This study therefore seeks to model the Tutuka ash heap and demonstrate the application of PHREEQC as an analytical-hydro-geochemical tool in predicting the interaction of water and brines respectively, with fly ash during their co-disposal from Eskom coal-utility plant, Tutuka.

## 2. Modelling methodology

A description of a one-dimensional advective–dispersive–reactive-transport model which is used to simulate transport of various elements down gradient of an ash heap disposal beds at Tutuka disposal facilities is presented. Model definitions include geometry and boundary conditions, initial conditions, and selection of chemical reactions. Conceptual models were developed and mechanisms involved were used as the input parameters for the PHREEQC program using a modified Lawrence and Livermore National Laboratory (LLNL) database for inorganics. A description of the conceptual model and the PHREEQC input data code used for the simulations are provided in the subsequent Sections 2.1 and 2.2 respectively. Both fly ash–water and fly ash–brine models had common input parameters except the infilling solutions. The fly ash–water model had water equilibrated with atmospheric CO<sub>2</sub> and O<sub>2</sub> gases where as the fly ash–brine model had the infilling solution of brines whose composition was as given in the ash–brine interim reports (Mbugua et al. 2009, 2010). The results for both systems are presented in a combined format and given in Section 3.

Previous ash–brine project work (Gitari et al., 2009a,b; Mbugua et al., 2013; Ojo, 2010; Ojo et al., 2011, 2007; Petrik et al., 2007, 2009a,b), provided relevant experimental data for acid neutralization capacity, (ANC), ash and brines characterisation, column dynamic leaching data, water flux and composition data, porosity and permeability data and conceptual model of brines flow in the heaps, all of which were used for the modelling as part of the initial modelling conditions. The flow rates, the volumes of the leachates and the specific solid/liquid (S/L ratio) were imposed at the laboratory scale. In the aforesaid project work, fly ash is reported as the dust-like material that results from the combustion of either hard (bituminous) coal or brown coal (lignite) in a wide variety of combustion processes. Fly ash particles are generally very fine (silt size, 0.074–0.005 mm) and spherical in shape (Ferguson, 1993; Berry et al., 1990; Mehta, 1985). Coal fly ash is a dark grey fine-grained material which is mostly made up of spherical, glassy particles. Mineralogical characterisation of two South African fresh fly ashes (Secunda and Tutuka ashes) indicated the presence of mullite, quartz, hematite, magnetite, maghemite, anhydrite, portlandite, lime, periclase and titanium oxides as the major phases (Hareepsad et al., 2010; Petrik et al., 2009a,b; Matjie et al., 2005; Mahlaba et al., 2011).

### 2.1. Conceptual model

Initial conceptual model of Tutuka ash heap entailed capturing the wet disposal method involving irrigating the heap with water to mimic rainwater as well as irrigation with brines as a method for co-disposal of ash and brines. The Tutuka fly ash composition and that of brines (Tables 1 and 2) were based on the work of Hareepsad et al. (2010) and Ojo (2007) respectively.

The water was equilibrated with atmospheric CO<sub>2</sub> and O<sub>2</sub> gases. In our model a heap height of 12 m was considered. For simplicity, the ash heap was considered as a 12 m column which was cylindrical in section and represents an element of volume within the heap. The column was discretized into 10 cells of equal lengths (1.2 m each) with 4000 shifts and a time step of 157,680 s. It was assumed that there was no diffusion (diffusion coefficient = 0) while a dispersivity of 0.8 m was imposed as adapted from Appelo and Postma estimates (Appelo and Postma, 2005); the general trend is that macrodispersivity is about 10% of the travelled distance. These assumptions and estimates which gave a more realistic and reasonable values of pH and total elemental concentrations which compared well with some results of the core

**Table 1**  
Modelled mineralogical composition of Tutuka fly ash (am or A = amorphous, mC = microcrystalline, Csh = C–S–H).

Mineral phase	Moles (L)	Mineral phase	Moles (L)
Al(OH) <sub>3</sub> (mC)	0.00E+00	Kaolinite	5.32E–04
Anhydrite	6.90E–03	Lime	4.41E–02
Brucite	0.00E+00	Magnesite	0.00E+00
Bunsenite	0.00E+00	Millerite	0.00E+00
CaCrO <sub>4</sub>	3.00E–05	Mullite	5.00E–03
Calcite	6.90E–03	Ni(OH) <sub>2</sub>	0.00E+00
CaMoO <sub>4</sub>	1.80E–07	Ni <sub>2</sub> SiO <sub>4</sub>	3.00E–06
Celestite	0.00E+00	NiCO <sub>3</sub>	0.00E+00
Cr(OH) <sub>3</sub> (A)	0.00E+00	Periclase	2.10E–02
CSH_1.4	0.00E+00	Portlandite	0.00E+00
Csh_gel_0.8	0.00E+00	Pyrite	3.00E–04
Csh_gel_1.1	0.00E+00	SiO <sub>2</sub> (am)	0.00E+00
Csh_gel_1.8	0.00E+00	Sr(OH) <sub>2</sub>	0.00E+00
Diaspore	0.00E+00	SrSiO <sub>3</sub>	4.59E–04
Ettringite	0.00E+00	Zincite	0.00E+00
Fe(OH) <sub>3</sub> (am)-CF	0.00E+00	Zn(OH) <sub>2</sub> (gamma)	0.00E+00
Gypsum	0.00E+00	Zn <sub>2</sub> TiO <sub>4</sub>	2.00E–06
Hematite	3.00E–02		

**Table 2**  
Elemental levels in Reverse Osmosis (RO)-generated brines from Tutuka power plant.

Elements	Ca	Mg	K	Na	CO <sub>3</sub> <sup>2-</sup>	SO <sub>4</sub> <sup>2-</sup>	Cl <sup>1-</sup>
Moles (L)	4.30E-03	8.38E-03	4.30E-03	2.87E-01	6.00E-03	1.11E-01	8.83E-02

samples obtained from the UWC ash brine report (Petrik et al., 2009a,b). Bulk density of fly ash (2.21 g/cm<sup>3</sup>) and UWC's hydraulic data was adapted in the model in which Darcy flow rate of 0.0002 cm/s and hydraulic conductivity of 0.00015 cm/s were used in the model. Porosity of 0.3 and flow rate of 2 ml/min was also used. The above parameters notwithstanding, the reality however on the ground is usually different in the way the ash heap is designed. A basement layer of about between 10 and 20 m high is usually established after which a track is built on this raised mound. Subsequent mound is constructed on the first, adding up to a total height of about 20 m. Fresh ash was considered for the model which therefore dictated the initial conditions for the model. A single layer approach was considered as opposed to the two layer approach which presents complicating factors with respect to the weathering patterns. Cation exchange reactions were incorporated in the model from UWC data on cation exchange as given by Petrik et al. (2009a,b). Effects of soil and plant growth were not factored into the construction of a conceptual site model. Runoff from the site was considered minimal and therefore inconsequential. Water balance on the fly ash dump irrigated with water or brines can be visualised in Fig. 1 as adapted from the ash-brine report (Steyl et al., 2010).

Fig. 1 shows the root (where vegetation growth occurs for remediation purposes), vadose, compacted, as well as the saturated zones of an ash heap. Accounting for the water balance considers the amount of rainfall, water percolating through the stated zones of the ash heap, surface runoff and evapotranspiration (ET).

## 2.2. Input parameters

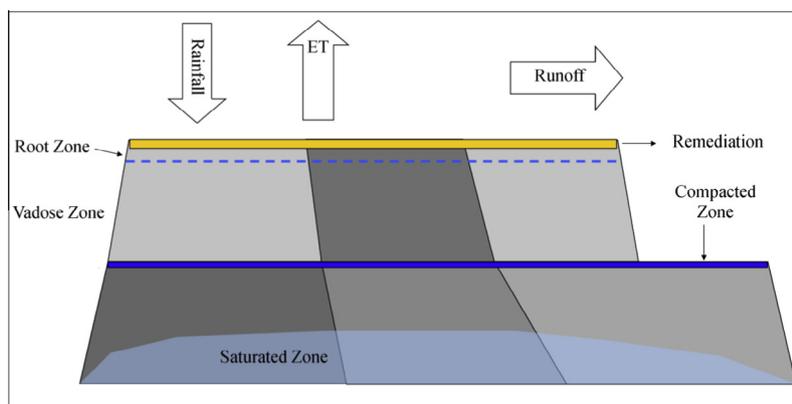
The fly ash mineral phases and brine composition were as given in preceding ash-brine project work Hareeparsad et al. (2010) and Mbugua et al. (2009, 2010, unpublished reports). Additional aspects are the incorporation of atmospheric air (O<sub>2</sub> and CO<sub>2</sub> gases at fugacity values of 10<sup>-3.5</sup> and 10<sup>-7</sup> respectively) in equilibrium with the fly ash and also ion exchange as per the UWC cation exchange capacity data (Petrik et al., 2009a,b). Third-type or Cauchy flux boundary conditions (flux flux) were used for both ends of the 1D-model. Other parameters are as described in the conceptual model in Section 2.1.

## 3. Results and discussion

Simulation data obtained in this study showed predicted release and mobility of major and trace elements in fly ash heaps subjected to rainwater irrigation and another scenario subjected to brine irrigation. This ultimately gave the quality of the leachate down the modelled ash heap. Important physico-geochemical changes occurring during the weathering of fly ash-water-brine systems were captured in the representative profiles from the simulated data.

### 3.1. pH – depth profile of the ash heap at different times

The variation of pH against the Tutuka ash heap depth (of 11.4 m) over the simulation time of 20 years irrigated with water and brine is given by Fig. 2. For the ash heap-water scenario, the pH dropped from 13 to between 8 and 8.8 after 2.5 years at the ash heap depth of 1 m. The pH was then observed to increase slightly to a maximum of 8.8 at a depth of 1–4 m down gradient and remained constant at 8.8 for the first 2.5 years. This could be interpreted to be the depth at which the greatest weathering of fly ash was taking place. Under such weathering conditions (described in the conceptual model in Section 2.1), the fly ash mineral phases were undergoing transformation in which neutralization reactions were taking place as a result of acidic rain (due to atmospheric CO<sub>2</sub>) interacting with alkaline fly ash. Similar pH-depth profiles were recorded for the subsequent years (5, 7.5 and 20 years) with negligibly small differences in the pH values at various ash heap depths as shown in Fig. 2. For the ash heap-brines scenario, a similar trend was observed as that of the fly ash heap-water scenario, although pH values dropped to 7.7 at 2 m after 2.5 years. There after the pH increased slightly at subsequent depths to pH 8 at the depth of 5 m down gradient and remained constant up to 20 years. The results compared well with the UWC cores data analysis in which the lowest pH of the pore water was observed at the top layer 0.55–3.00 m and immediately after the water level (Petrik et al., 2009a,b). This observation indicates that the greatest weathering of the fly ash had occurred at the top layer of the ash heap (0.55–4 m) upon contact with water or brine. Below this depth of 4 m, the pH of the pore fluid was



**Fig. 1.** Conceptual model of Tutuka ash heap adapted from (Steyl et al., 2010).

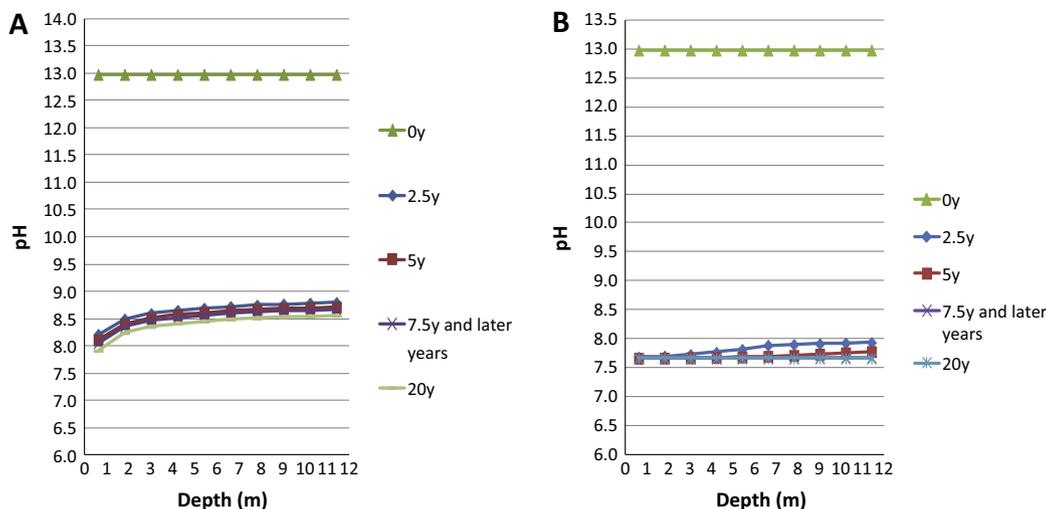


Fig. 2. Graph showing variation of pH against the Tutuka ash heap depth for varying number of years of irrigation with: (A) water, and (B) brine. (0 y, 2.5 y, ... 20 y indicate 0–20 years).

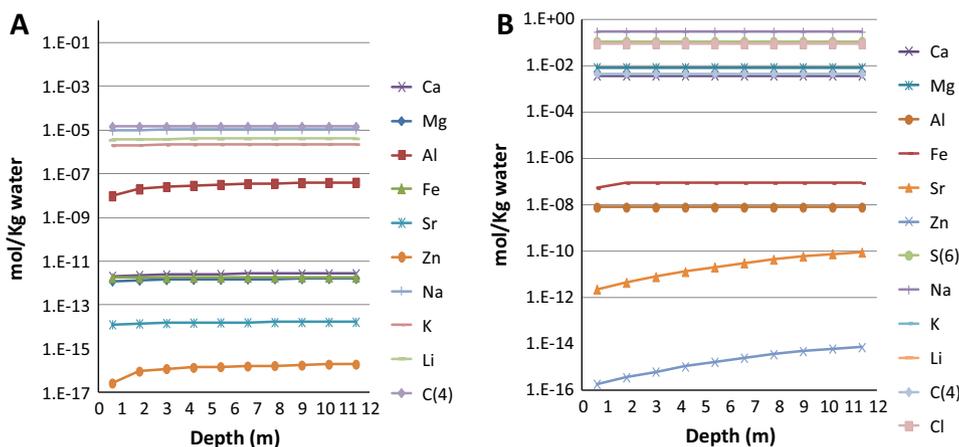


Fig. 3. Total elemental concentrations in leachates after 20 years against the depth down the ash heap irrigated with: (A) water, and (B) brine; (NB. Legend symbols different for A and B).

persistent for the rest of the subsequent years. After depth of about 4 m, pH was maintained around 7.5–8 for ash irrigated with brine and at about 9 for ash irrigated with rainwater. This means that the high pH of Tutuka ash gets lowered with time due to weathering, resulting to self regulating of the ash–brine–water system.

The simulation results for the total elemental concentration down gradient the two modelled ash heap scenarios are presented in Fig. 3. Further supplementary results on elemental concentrations are given in Appendix A (Fig. A.1). The following observations can be noted from each of the modelled scenarios.

### 3.2. Ash heap irrigated with water

- (i) Zinc (Zn) and Aluminium (Al) concentrations increased between 0.55 and 2 m depth. Below this depth their respective concentrations remained constant. In the case of Al, it is considered to be a conservative element in coal ash (Katz et al., 2011; Shoham-Fridera et al., 2003) hence its concentration was not expected to change. The amounts in the leachate were however relatively small, indicating much of the elemental content had not been leached before the 20 years. The leaching pattern of Zn and Al could be deduced as adsorption controlled. In this type of leaching pattern (adsorption-controlled release), the concentration of metals

in pore fluid continually changes, because the metal concentrations in the solid and liquid phase are controlled by the partition coefficients. Adsorption-controlled release corresponds to an equilibrium condition where desorption occurs instantaneously. Leaching could also have occurred through chemical dissolution of the respective element-containing mineral phases from the fly ash–water interactions, followed by precipitation or adsorption onto particles (Shoham-Fridera et al., 2003).

- (ii) The concentrations of the rest of the major and minor elements (Ca, Mg, Fe Sr, Na, Li, K and C) did not show any significant variation down gradient of the ash heap irrigated with water. The amounts are however within a range of 1–4 orders of magnitude lower than those of the ash heap irrigated with brines (for Zn it was lowered by 1 order of magnitude, C and Sr lowered by about 3, Na, K, Li by about 4, whereas Fe was lowered by 5 and Mg about 9 orders of magnitude).

### 3.3. Ash heap irrigated with brine

- (i) Iron (Fe) showed slight increase in concentration for 1–2 m down gradient while Sr and Zn showed steady increase up to 11.4 m in both ash heaps. This could be due to slow

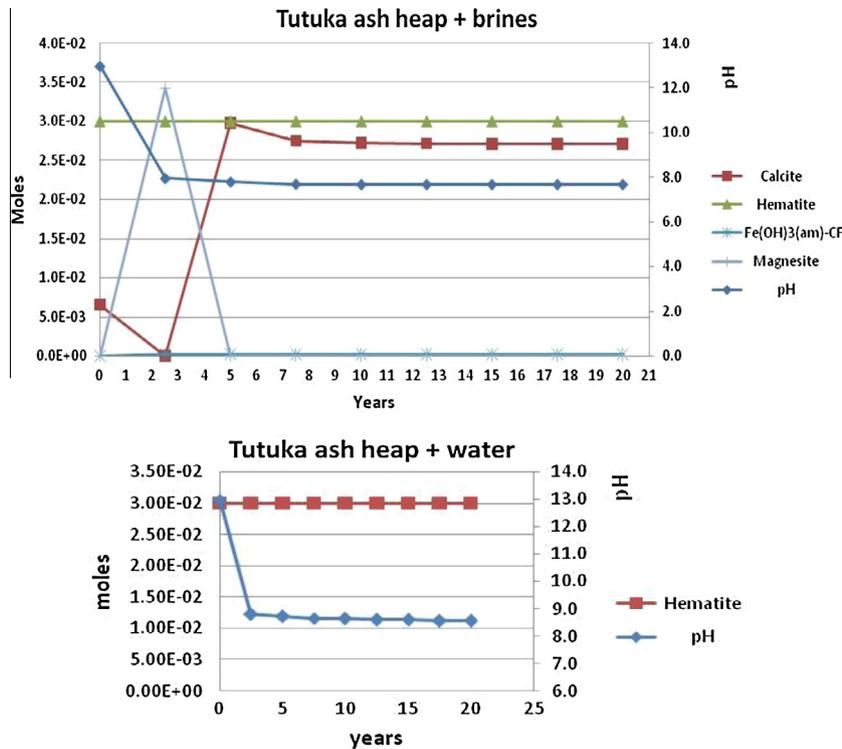


Fig. 4. Major mineral phases present against time and pH after ash heap irrigation with brine and water over a 20-year period.

dissolution of minerals associated with these elements (Hematite, Pyrite for Fe,  $\text{SrSiO}_3$  for Sr and  $\text{Zn}_2\text{TiO}_4$  for Zn) down gradient or possible desorption of the elements taking place.

- (ii) The concentrations of the rest of the major and minor elements were constant down gradient the ash heap. This may suggest that the release pattern for metals from the fly ash heap–water scenario and that of ash heap with brine appeared to be adsorption-controlled. Concentrations of most of the elements were in higher orders of magnitude in leachate collected from the fly ash heap irrigated with brine than those from ash heap with water.

The quantitative mineralogical changes occurring down gradient the ash heap scenarios against pH and time are presented in Fig. 4. The mineral phases that showed significant change in the fly ash–brine heap over 20 years of brine irrigation were calcite, hematite,  $\text{Fe(OH)}_3(\text{am})\text{-CF}$  and magnesite. However amounts of  $\text{Fe(OH)}_3(\text{am})\text{-CF}$  were negligibly small throughout the years. Any other minerals particularly the silicon based minerals such as mullite and quartz were assumed to have undergone insignificant chemical changes but got flushed down gradient the ash heap. (This could also explain why not much quantitative mineralogical data was obtained from the ash heap irrigated with water). For the ash heap irrigated with brines, the amount of calcite decreased in the first 3 years, as the pH value decreased from 13 to 8 then followed by a sharp increase in amounts occurring up to 5 years. This showed the dissolution and precipitation of calcite was pH-controlled. This variation of the mineral calcite could explain the variation of the Ca metal concentration in the leachate over the years. A slight decrease in calcite was recorded up to about 8 years within which the pH also showed some slight decrease and then remained constant up to 20 years. Hematite amount remained constant over the 20 years while magnesite was formed as a new phase up to 2.5 years after which it dissolved progressively up to 5 years and then got depleted.

Generally, brines caused sharp increase in concentrations (mol/kg of water) of the elements Ca, Mg, S(6) and C(4) for the first 3 years of heap irrigation (Fig. 5) whereas with water irrigation an opposite trend was observed in which the elemental concentrations decreased. The increased trend is due to the brine composition which contains most of these elements and hence causes elevated concentrations. With both brine and water irrigation systems, a reduction in elemental concentration in the leachate was registered for Al and Fe. This could be due to precipitation and adsorption of these elements down gradient of ash heap. After 3 years the amounts remained constant up to 20 years for all elements. A general sharp decrease of the element's concentration for Sr, Zn, Na, K and Li was recorded for ash heap–water scenario for the first 3 years, but with brines, Sr, Na and K showed slight increase for the first 3 years due to flushing and then a progressive decrease up to 20 years. Zn showed a steady decrease in concentration. This sharp decrease in concentration of the elements could be due to flushing of the dissolved elements down gradient whereas for Zn some precipitation or possible adsorption could be occurring down gradient of the ash heap. These results show that concentration of metals in leachate was controlled not only by solubility but other factors such as adsorption and precipitation processes.

The results of the modelled fly ash heap irrigated with water were presented in Fig. 6 and those of the ash heap irrigation with brine were presented in Fig. 7. In order to interpret the results obtained, the following information must be noted for the two modelled scenarios.

### 3.3.1. Fly ash heap irrigated with water

- (i) At zero (0) years: There is no contact between fly ash and water hence the elemental concentrations represented in Fig. 6 are those in the fresh fly ash down gradient the 11.4 m ash heap. Irrigation of the ash heap with water caused a general decrease of elemental concentration to lower levels than the initial amounts in the ash heap. This

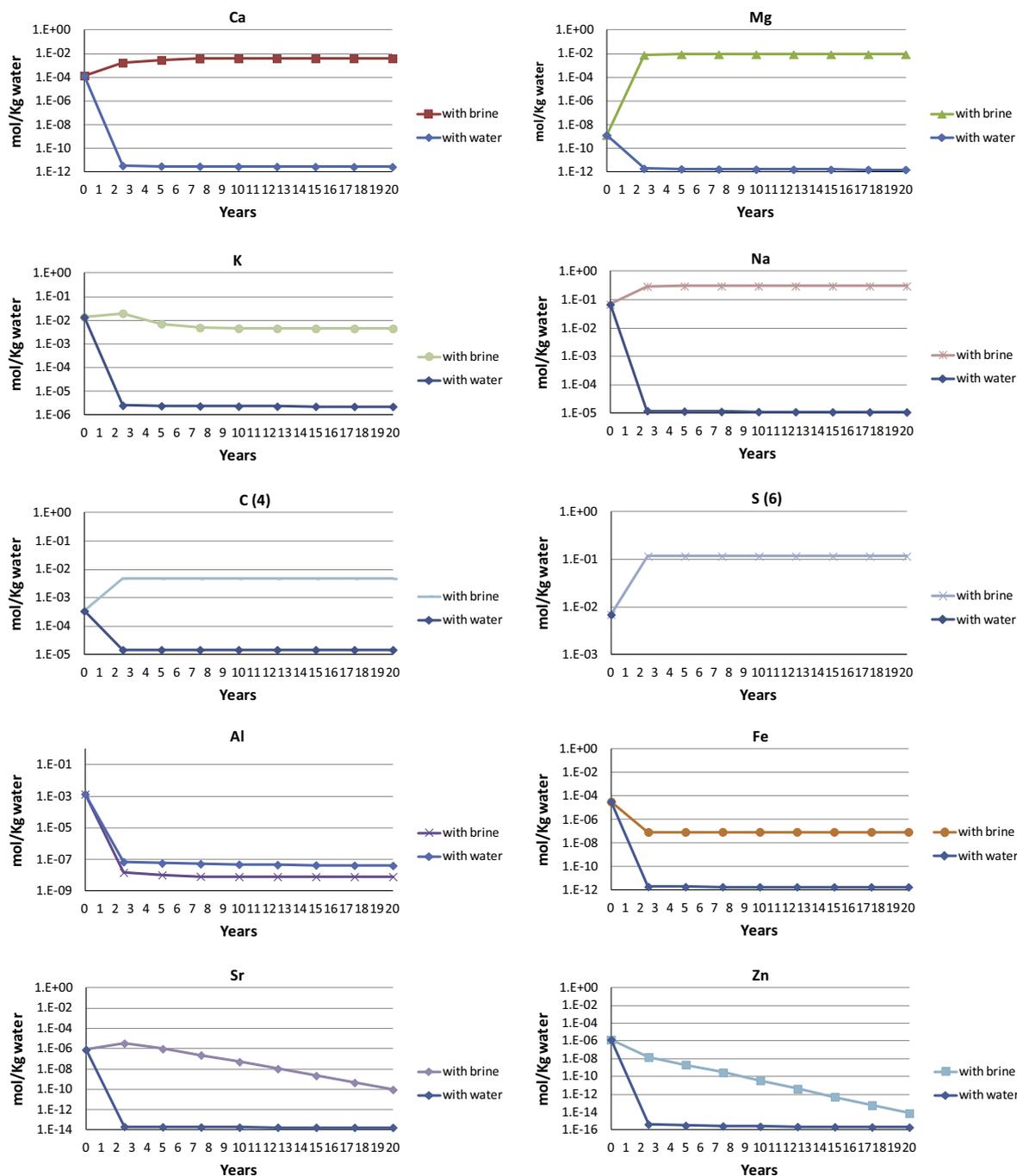


Fig. 5. Comparison of total major and minor elements released from ash heap irrigated with rainwater and that irrigated with brines over a period of 20 years. (Leachate quality at 11.4 m depth of the ash heap in both scenarios).

is a clear indication that over time the fly ash–water interactions resulted in leaching of the major and minor elements down gradient the ash heap.

- (ii) After 2.5 years, when the ash and the rain water have interacted, the concentration of most of the elements Ca, Mg, Na, Fe, Sr, K, Li, C and Cl showed insignificant changes down gradient of the ash heap and implied resistance to weathering. The concentration of these elements in the subsequent years (5, 7.5, 10, 12.5 and 20 years) showed the same trend down gradient the ash heap as shown by the superimposition of the respective profiles on each other.
- (iii) The elements Al and Zn showed some increased concentration vertically down the ash heap in the first 2 m of the

inflow position of ash depth. After the 2 m depth the concentration remained constant throughout the rest of the ash heap depth of 11.4 m. The trend was the same vertically down gradient of the ash heap after each of the modelled years (2.5, 5, 7.5, 10, 12.5, 15, 17.5 and 20 years).

### 3.3.2. Fly ash heap irrigated with brine

- (i) At zero (0) years: There is no contact between fly ash and brine hence the elemental concentrations represented are those in the fresh fly ash down gradient of the 11.4 m ash heap. Irrigation of the ash heap with brines caused the elevation of the elemental concentration levels above the initial amounts.

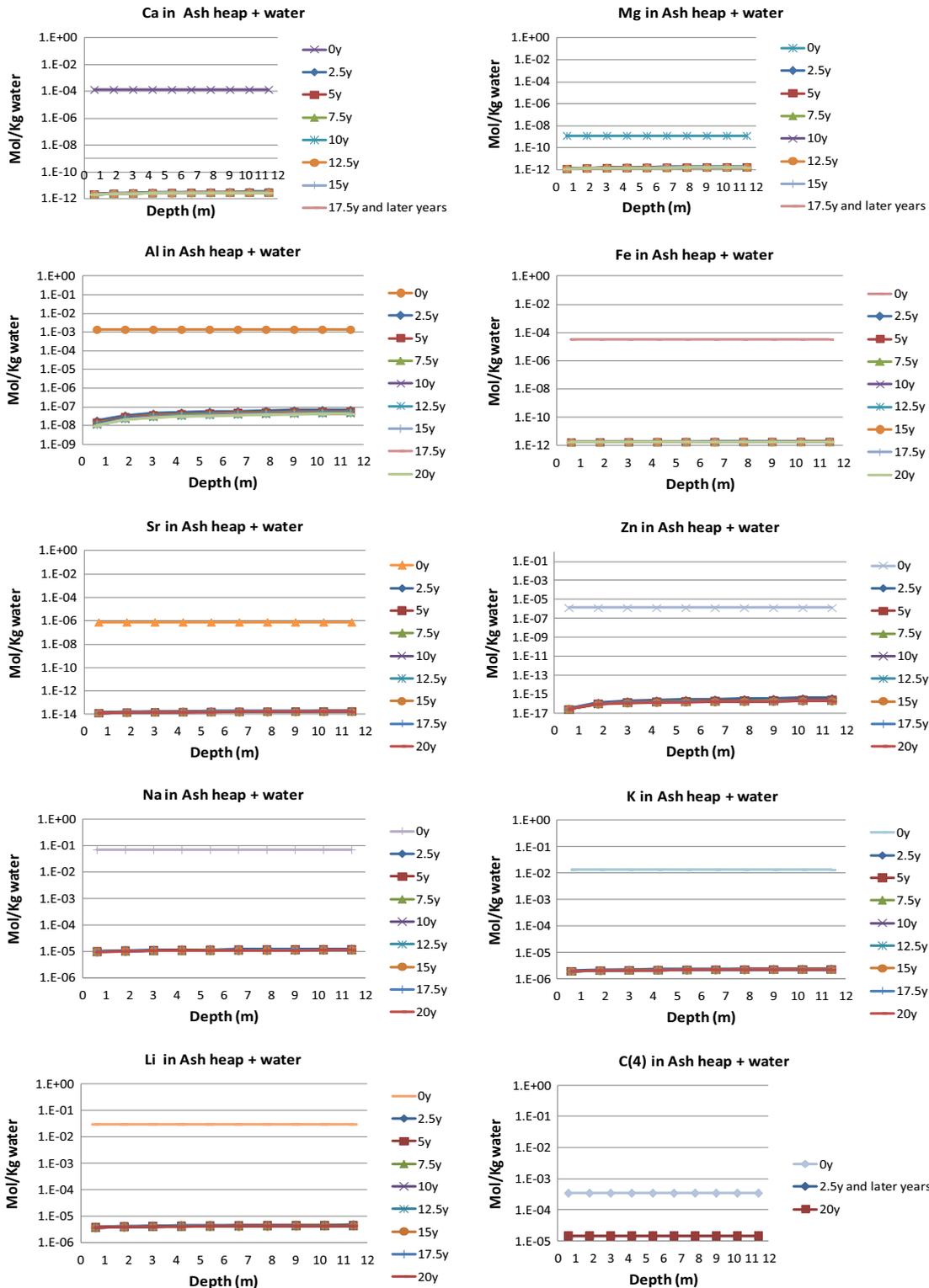


Fig. 6. Total elemental concentration of major and minor elements in the leachate, against the depth at certain years of ash heap irrigation with water.

(ii) After 2.5 years, when the ash and the brine solution have interacted, the concentration of the elements Na, Fe, Al, Cl, C and S showed no significant changes down gradient the ash heap and which showed some conservative behaviour. The concentration of these elements in the subsequent years (5, 7.5, 10, 12.5 and 20 years) showed the same trend down gradient the ash heap as shown by the superimposition of the respective profiles on each other (Fig. 7). Some elements

namely, Ca, Mg, Sr, Zn, Li, K, showed some significant variations of concentration vertically down the ash heap at different depths. Calcium (Ca) and Mg concentration remained constant up to a depth of 4 m and then a gradual decrease followed up to a depth of 11.4 m. The elements Sr, Zn, Li, and K showed a progressive increase of concentration vertically down gradient after each of the modelled years (2.5, 5, 7.5, 10, 12.5, 15, 17.5 and 20 years).

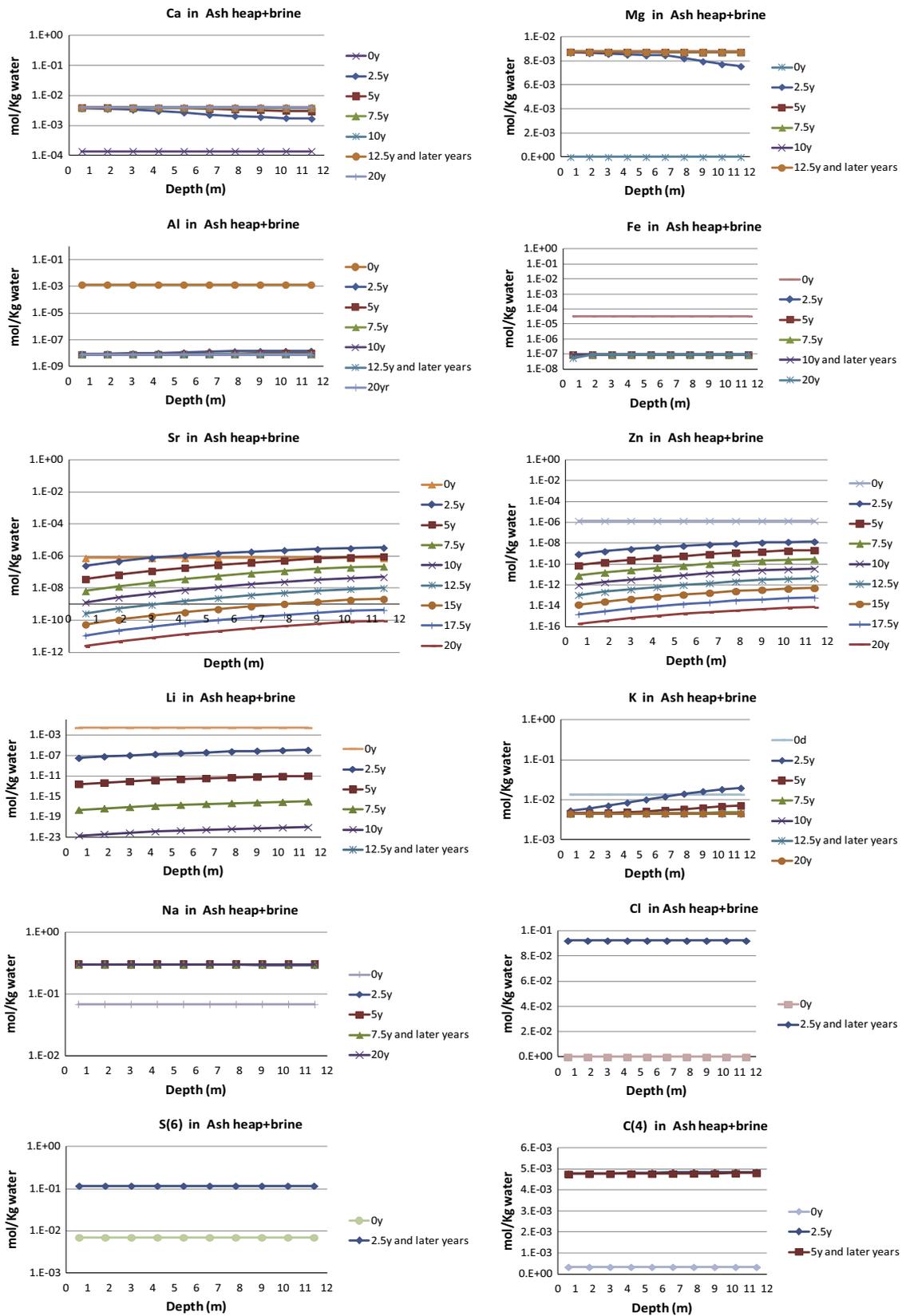


Fig. 7. Total elemental concentration of major and minor elements in leachate against the depth, at certain years of ash heap irrigation with brine.

(iii) After the first 2 m closer to the inflow position of the ash heap the concentration of the elements Ca, Mg, Fe, Zn, Sr, K and C(4) decreased after 2.5 years and there after

remained constant up to the outflow position when ash heap was irrigated with water. The same trend was observed for the subsequent years. This shows that a lot of the

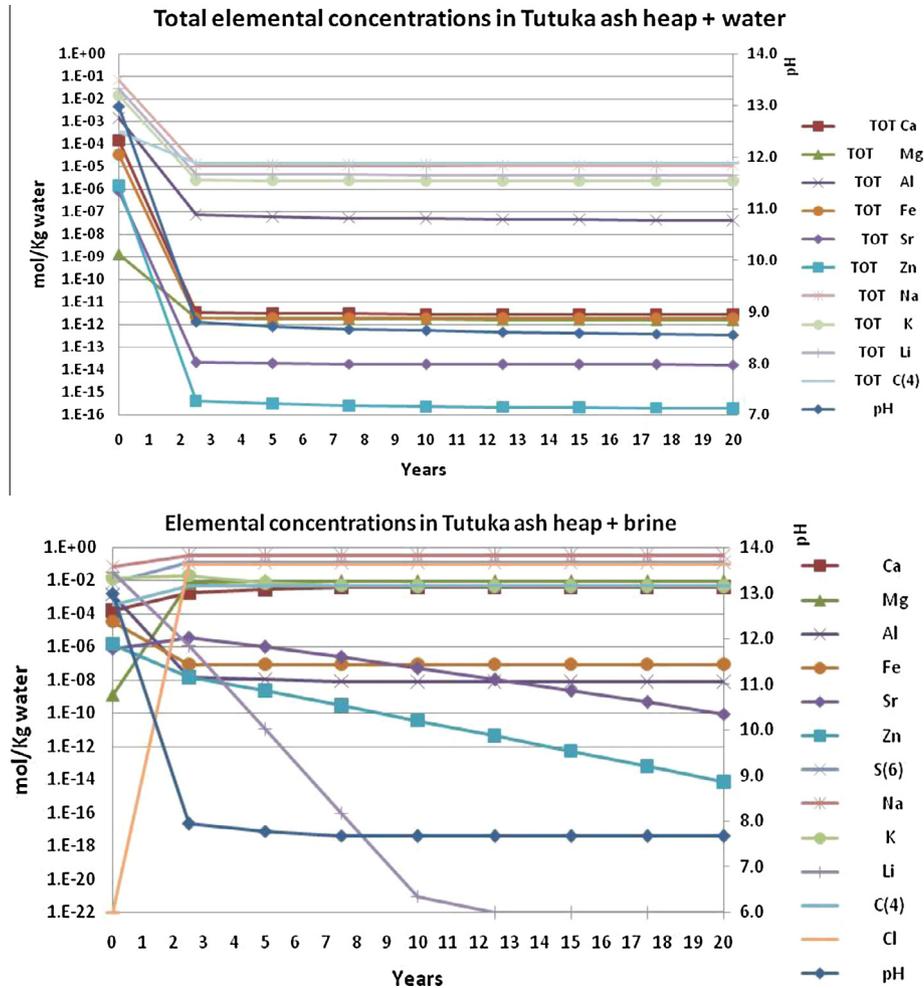


Fig. A.1. Total elemental concentrations against time in Tutuka ash heap with water and with brine irrigation.

geochemical reactions and leaching chemistry occurred during the initial 2.5 years after fly ash contact with brines. Transformational processes of the mineral phases leading to precipitation could be attributed by the decrease in the elemental concentrations. This could also be due to flushing of the elements particularly the very soluble ones such as K and Sr as well as possible precipitation reactions that could have taken place.

- (iv) Zn showed some distinct profiles for each of the years simulated as depicted in Fig. 7. At about 1 m the concentration reduced after which there was a steady increase of the concentrations down gradient up to 11.4 m. For each of the subsequent years this trend was maintained but at different lower concentrations. Similar trend was recorded for Sr, Li and K though with quantitatively different amounts. The same trend was observed for these elements at 1 m down gradient up to 2.5 years. The concentration then increased after 2.5 years and then remained constant up to 11.4 m down gradient. For the rest of the subsequent years the same trend was observed down gradient the ash heap.

The release patterns of the major and minor elements from the ash–water and ash–brine interactions were deduced to be a possible combination of solubility control, adsorption–desorption, precipitation and chemical exchange processes (Donahoe, 2004; Freyssinet et al., 2002; Mendoza et al., 2006; Mizutani et al., 1996; Shoham-Fridera et al., 2003).

Overall, the ash heap modelling enhanced the understanding of the ash–brines interactions and demonstrated that leachate composition is determined by the following factors; (i) the mass flows from the pores of fly ash, (ii) the surface dissolution of the mineral phases, (iii) the various chemical reactions involved during the ash–brine and ash–water interactions, (iv) the interactions with a gas phase (atmospheric  $\text{CO}_2$ ), (v) the composition of the initial fly ash, and (vi) by the leachate flow and hydrodynamics as captured in the conceptual model. These findings from the modelling work went further to support the works of Schiopu et al. (2009).

When comparing the mineralogical results from the leached residue with those in the original modelled ash recipe, the mineral differences in the ash residue exhibited in Tutuka ash heap indicate different dissolution kinetics of the minerals containing similar cations or anions and which govern the solution behaviour of those ions. This means that as much as the leaching takes a particular dissolution pathway, down gradient the ash heap, the dissolution of the mineral phases in the fly ash is also a function of time.

#### 4. Conclusion

Simulations of reactive transport were performed for a period of 20 years of seepage by rain water and brines irrigation into the ash heap. Because this is a forward model, the modelling results are predictions of the future and cannot be compared to field data 'per se'. However attempts have been made to have the modelling

conditions and parameters as close as possible to the field disposal site conditions as described by the conceptual model.

The modelling results revealed that the weathering of ash either irrigated with rainwater or with brine is pH dependent. Initial high pH causes dissolution of some mineral phases that are amphoteric such as Al and Zn. When comparing the mineralogical results from the leached residue with those in the original mineral sample, the mineral differences in the residue minerals indicate different dissolution kinetics of the minerals containing similar cations or anions and which govern the solution behaviour of those cations.

The modelling studies have demonstrated that reaction kinetics is important in governing chemical exchanges for depth scales up to 11.4 m for a period of 20 years ash weathering under different scenarios. The modelling would have given a more realistic scenario if some aspects were incorporated such as sorption capacities of fly ash and use of lysimeters on the ground. Future research should focus on incorporation of sorption chemistry in the model and further validation by use of field data.

### Conflict of interest

There is no conflict of interest.

### Acknowledgements

The authors are grateful for project funding by the Pollution Research Group (PRG) at the University of KwaZulu Natal (UKZN) and tuition fee exemption by the UKZN for the first author. The Technical University of Kenya (TUK) is also acknowledged for granting him study leave and supplementary support during the study period. The authors acknowledge the contribution by Dr. Wilson Gitari, Prof. Leslie Petrik and Ojo O. Fatoba of the University of Western Cape for availing the laboratory experimental data in Phase I, used for model calibration during the initial stages.

### Appendix A. Total elemental concentrations of leachates at break through volumes over a 20-year period of ash heap weathering irrigated with water and brines

See Fig. A.1.

### References

- Appelo, C.A.J., Postma, D., 2005. *Geochemistry, Groundwater and Pollution*. A.A Balkema Publishers, Amsterdam.
- Berry, E.E., Hemmings, R.T., Cornelius, B.J., 1990. Mechanisms of hydration reactions in high volume fly ash pastes and mortars. *Cement Concr. Compos.* 12 (4), 253–261.
- Donahoe, R.J., 2004. Secondary mineral formation in coal combustion byproduct disposal facilities: implications for trace element sequestration. *Geol. Soc. Lond. Spec. Publ.* 236 (1), 641–658.
- Ferguson, G., 1993. Use of self-cementing fly ashes as a soil stabilization agent. *Fly ash for soil improvement*. *Geotech. Spec. Publ.* 36, 15.
- Freyssinet, P.P., Azaroual, M., Itard, Y., Clozel-Leloup, B., Guyonnet, D., Baubron, J.C., 2002. Chemical changes and leachate mass balance of municipal solid waste bottom ash submitted to weathering. *Waste Manage.* 22 (2), 159–172.
- Gitari, M.W., Fatoba, O.O., Nyamihingura, A., Petrik, L.F., Vadapalli, V.R.K., Nel, J., October, A., Dlamini, L., Gericke, G., Mahlaba, J.S., 2009. Chemical Weathering In A Dry Ash Dump: An Insight From Physicochemical and Mineralogical Analysis Of Drilled Cores. In: *World of coal Ash (WOCA) Conference*. Lexington, WOCA, pp. 23.
- Gitari, W.M., Fatoba, O.O., Petrik, L.F., Vadapalli, V.R.K., 2009b. Leaching characteristics of selected South African fly ashes: effect of pH on the release of major and trace species. *J. Environ. Sci. Health* 44 (Part A), 206–220.
- Hareparsad, S., Tiruta-Barna, L., Brouckaert, C.J., Buckley, C.A., 2010. Quantitative geochemical modelling using leaching tests: application for coal ashes produced by two South African thermal processes. *J. Hazard. Mater.* 186 (2–3), 1163–1173.
- Katz, G.E., Berkowitz, B., Guadagnini, A., Saaltink, M.W., 2011. Experimental and modeling investigation of multicomponent reactive transport in porous media. *J. Contam. Hydrol.* 120–121, 27–44.
- Ligia, T., Apichat, I., Radu, B., 2004. Long-term prediction of the leaching behavior of pollutants from solidified wastes. *Adv Environ Research* 8 (3–4), 697–711.
- Mahlaba, J.S., Kearsley, E.P., Kruger, R.A., 2011. Effect of fly ash characteristics on the behaviour of pastes prepared under varied brine conditions. *Miner. Eng.* 24 (8), 923–929.
- Matjie, R.H., Ginster, M., Alphen, C.V., Sobieck, A., 2005. *Detailed Characterisation of Sasol Ashes in World of Coal Ash (WOCA)*. WOCA, Lexington, Kentucky, USA.
- Mbugua, J.M., Ngila, J.C., Kindness, A., Buckley, C., Demlie, M., 2009. Hydrogeochemical modeling of fly ash co-disposed with brines and organics: Effects of Organics and Brines on ANC of Coal Ash, in towards the Development of Sustainable Salt Sinks: Fundamental Studies on the Co-Disposal of Brines within Inland Ash Dams (unpublished Sasol-Eskom Ash-Brine Project- 2009 Q3&4 Quarterly Interim report, Phase 2), University of KwaZulu-Natal (UKZN), Durban (South Africa), pp. 33.
- Mbugua, J.M., Ngila, J.C., Kindness, A., Buckley, C., Demlie, M., 2010. Hydrogeochemical modeling of fly ash co-disposed with brines and organics: Column and ash heap modeling of Secunda and Tutuka fly ashes and the effect of brines on the leaching chemistry of fly ashes, in towards the Development of Sustainable Salt Sinks: Fundamental Studies on the Co-Disposal of Brines within Inland Ash Dams (unpublished Sasol-Eskom Ash-Brine Project-2010 Q1-4 Interim report, Phase 2). University of KwaZulu-Natal (UKZN), Durban (South Africa), pp. 108.
- Mbugua, J.M., Ngila, J.C., Kindness, A., Demlie, M., 2013. Reactive-transport modeling of fly ash–water–brines interactions from laboratory-scale column studies. *J. Phys. Chem. Earth*. <http://dx.doi.org/10.1016/j.pce.2013.09.016>.
- Mehta, P.K., 1985. Influence of fly ash characteristics on the strength of portland-fly ash mixtures. *Cem. Concr. Res.* 15 (4), 669–674.
- Mendoza, T., Hernández, O.A., Abundis, M., Nestor, J.M., 2006. Geochemistry of leachates from the El Fraile sulfide tailings piles in Taxco, Guerrero, southern Mexico. *Environ. Geochem. Health* 28 (3), 243–255.
- Mizutani, S., Yoshida, T., Sakai, S., Takatsuki, H., 1996. Release of metals from MSW I fly ash and availability in alkali condition. *Waste Manage.* 16 (5–6), 537–544.
- Ojo, F.O., 2007. *Chemical Compositions and Leaching Behaviour of Some South African Fly Ashes*. Chemistry. Western Cape, University of Western Cape. Unpublished MSc Thesis, pp. 216.
- Ojo, O.F., 2010. *Chemical Interactions and Mobility of Species in Fly ash–Brine co-disposal Systems*. Department of Chemistry University of the Western Cape. Western Cape, University of the Western Cape. Doctor of Philosophy in Chemistry Thesis.
- Ojo, F.O., Petrik, L.F., Gitari, W.M., Iwuoha, E.I., 2011. Fly ash–brine interactions: removal of major and trace elements from brine. *J. Environ. Sci. Health Part A* 46 (14), 1648–1666.
- Parkhurst, D. L., Stollenwerk, K.G., Colman, J.A., 2003. *Reactive-Transport Simulation of Phosphorus in the Sewage Plume at the Massachusetts Military Reservation Cape Cod, Massachusetts*. Massachusetts, Water-Resources Investigations Report 03, pp. 40.
- Petrik, L., Gitari, W., Etchebers, O., Kumar Vadapalli V., Nel, J., Fatoba, O., Nyamihingura, A., Antonie, M., 2007. *Towards the Development of Sustainable Salt Sinks*. Unpublished 3rd Interim Progress Report, University of the Western Cape (UWC).
- Petrik, L., Gitari, W.M., Nel, J., Fatoba, O., Nyamihingura, A., Akinyemi, S.A., 2009. *Towards the Development of Sustainable Salt Sinks*. Fundamental Studies on the Co-Disposal of Brines within Inland Ash Dams. Unpublished Report, Western Cape, University of the Western Cape, pp. 55.
- Petrik, L., Gitari, W.M., Nel, J., Fatoba, O., Nyamihingura, A., Akinyemi S.A., 2009. *Towards the Development of Sustainable Salt Sinks: Fundamental Studies on the Co-Disposal of Brines within Inland Ash Dams*. Unpublished Sasol-Eskom Phase II 4th Quarter Interim Report 2009. Western Cape, University of the Western Cape, pp. 179.
- Regnier, P., Jourabchi, P., Slomp, C.P., 2003. Reactive-transport modeling as a technique for understanding coupled biogeochemical processes in surface and subsurface environments. *Netherlands J. Geosci./Geologie en Mijnbouw* 82 (1), 5–18.
- Schiopu, N., Tiruta-Barna, L., Jayr, E., Méhu, J., Moszkowicz, P., 2009. Modelling and simulation of concrete leaching under outdoor exposure conditions. *Sci. Total Environ.* 407 (5), 1613–1630.
- Shoham-Fridera, E., Shelef, G., Kressa, N., 2003. Chemical changes in different types of coal ash during prolonged, large scale, contact with seawater. *Waste Manage.* 23 (2), 125–134.
- Steyl, G., Nel, J.M., van der Merwe, C., Gomo, M., Teboho, S., Leketa, K., 2010. *Eskom-Sasol Phase II Sustainable Salt Sinks*. Unpublished Inception Report. Bloemfontein, University of the Free State. 1, pp. 63.