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Reactive-transport modeling of fly ash–water–brines interactions from laboratory-scale column studies

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ABSTRACT

Dynamic leaching tests are important studies that provide more insights into time-dependent leaching mechanisms of any given solid waste. Hydrogeochemical modeling using PHREEQC was applied for column modeling of two ash recipes and brines generated from South African coal utility plants, Sasol and Eskom. The modeling results were part of a larger ash–brine study aimed at acquiring knowledge on (i) quantification and characterization of the products formed when ash is in contact with water–brines in different scenarios, (ii) the mineralogical changes associated with water–brine–ash interactions over time, (iii) species concentration, and (iv) leaching and transport controlling factors. The column modeling was successfully identified and quantified as important reactive mineralogical phases controlling major, minor and trace elements' release. The pH of the solution was found to be a very important controlling factor in leaching chemistry. The highest mineralogical transformation took place in the first 10 days of ash contact with either water or brines, and within 0.1 m from the column inflow. Many of the major and trace elements Ca, Mg, Na, K, Sr, S(VI), Fe, are leached easily into water systems and their concentration fronts were high at the beginning (within 0.1 m from the column inflow and within the first 10 days) upon contact with the liquid phase. However, their concentration decreased with time until a steady state was reached. Modeling results also revealed that geochemical reactions taking place during ash–water–brine interactions does affect the porosity of the ash, whereas the leaching processes lead to increased porosity. Besides supporting experimental data, modeling results gave predictive insights on leaching of elements which may directly impact on the environment, particularly ground water. These predictions will help develop scenarios and offer potential guide for future sustainable waste management practices as a way of addressing the co-disposal of brines within inland ash dams and heaps.

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1. Introduction

Leaching is considered as one of the risks in ash disposal facilities to ground water systems, and whose quantification in Eskom and Sasol coal utility plants in South Africa, was the ultimate goal of this study. Both batch and dynamic leaching studies are important as they complement each other in terms of the diverse information of interest they provide. Batch leaching experiments, performed over short durations are simple tests useful for determining the intrinsic properties of the solid waste with respect to one or several controlled parameters (De Windt and Badreddine, 2007). Batch tests can give valid information concerning the influence of various parameters, such as pH value, liquid/solid

ratio, elution agent and elution time on the mobilization of inorganic contaminants. However, a major disadvantage of all batch experiments is that they only represent a snapshot of the leaching history of the material investigated.

This work presents findings of column modeling as part of dynamic leaching studies for both Secunda and Tutuka ash disposal systems using PHREEQC code (version 2.15.0) (Parkhurst and Appelo, 1999). Results from column modeling studies are useful in enhancing further understanding of long term time-dependent leaching mechanisms and the impact on ground water pollution. They also aid in quantification of release rates and also useful for the extrapolation of laboratory results to site conditions of various characteristics such as varying solution/solid ratios, cyclic infiltration, and site specific geometry (Baranger et al., 2002; Van der Sloot et al., 2002; Tiruta-Barna et al., 2006; De Windt et al., 2007; Schiopu et al., 2008). They involve modeling of the reactive and transport mechanisms of a given system.

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Table 1
Modeled fly ash recipe composition as input in PHREEQC for Secunda and Tutuka (Hareepsad et al., 2010).

Name	Formula	Secunda ash recipe (mol/L)	Tutuka ash recipe (mol/L)	Dissolves only
Anhydrite	CaSO ₄	7.66E-03	6.90E-03	
Chromatite	CaCrO ₄	1.96E-05	3.00E-05	
Calcite	CaCO ₃	1.36E-02	6.90E-03	
Powellite	CaMoO ₄	1.32E-06	1.80E-07	
Hematite	Fe ₂ O ₃	1.41E-03	3.00E-02	TRUE
Kaolinite	Al ₂ Si ₂ O ₅ (OH) ₄	2.35E-03	5.32E-04	TRUE
Lime	CaO	6.15E-02	4.41E-02	
Millerite	NiS	1.16E-07	0.00E+00	TRUE
Mullite	Al ₆ Si ₂ O ₁₃	1.26E-05	5.00E-03	TRUE
Liebenbergite	Ni ₂ SiO ₄	2.14E-06	3.00E-06	TRUE
Periclase	MgO	4.16E-02	2.10E-02	
Pyrite	FeS	5.50E-04	3.00E-04	
SrSiO ₃	SrSiO ₃	6.09E-04	4.59E-04	TRUE
Zn ₂ TiO ₄	Zn ₂ TiO ₄	2.67E-07	2.00E-06	TRUE

Table 2
Elemental levels in brines from Secunda and Tutuka coal utility plants.

Elements	Secunda TRO brine (mol/L)	Tutuka RO brine (mol/L)
Ca	2.05E-02	4.30E-03
Mg	3.39E-04	8.38E-03
K	6.61E-03	4.30E-03
Na	1.09E-01	2.87E-01
CO ₃ ²⁻	4.00E-03	6.00E-03
SO ₄ ²⁻	4.54E-02	1.11E-01
Cl ⁻	4.64E-02	8.83E-02

Reactive-transport modeling aims at achieving a time-dependent, quantitative, and ultimately predictive treatment of chemical transformations and mass transfers within the porous heterogeneous ash–water–brines system.

Reactive transport modeling is a potentially valuable instrument to identify and describe the dynamic leaching processes of contaminants from waste materials which act as the source term, as well as further their rate of transport in soil and groundwater. This may form a basis for the development of realistic regulatory limits (Zhu and Anderson, 2002).

Within the set out scope, dynamic column leaching modeling was therefore undertaken in order to provide the linkage between changes in the ash chemistry and the transport properties of the fly ash from Secunda and Tutuka coal utility plants. Modeling results have been used routinely in risk assessment, remedial designs, and regulatory decisions related to ground water contamination (Zhu and Burden, 2001).

Table 3
Calculated column discretization parameters for PHREEQC transport input.

Column discretization (symbols)	Description	Secunda	Tutuka	Units
<i>Kd</i>	Normalized distribution coefficient = $q/c = pb/e$	5.0728	5.0728	
<i>R</i>	Retardation = $1 + q/c = 1 + Kd$	6.0728	6.0728	
Mixf	Mixing factor between two consecutive cells: $\Delta x < \text{Mixf} > 0$, if $N_{\text{cell}} > \text{Tot } x/\alpha_L * [(1 - 1/R)/2]$, integer For mixf > 0, if $\Delta x < [\alpha_L 2R]/(R - 1)$: $\Delta x <$ and $N_{\text{cell}} \geq$	1.20E-02 20	1.20E-02 20	m Cells
<i>V</i>	Pore water flow velocity ($Q/\epsilon A$)			
Δx	Cell length	0.0125	0.0125	m
α_L	Dispersivity	0.005	0.005	m
Tot <i>x</i>	Total column length or flowline	0.2500	0.25	m
<i>N</i> _{cell}	Number of cells = Tot <i>x</i> / Δx	20	20	Cells
Tot <i>t</i>	Total time of injection or simulation	7,776,000	7,776,000	s
Δt	For maximal value of Δt : = $\Delta x/v$ (integer value)	2792	4688	s
Timesteps	Timesteps (=Tot <i>t</i> / Δt = Nshifts, integer value): PHREEQC input	3000	2000	Shifts
Δt	Tot <i>t</i> /Nshifts: PHREEQC input	2592	3888	s

This study therefore seeks to demonstrate the application of PHREEQC code (version 2.15.0) as an analytical-hydrogeochemical tool in predicting the interaction of water and brines with fly ash during their co-disposal of the ash waste from two major coal utility plants in South Africa, Sasol and Eskom. Time-dependent release, transport and fate of the related mobile species were investigated. Modeling reactive transport in fly ash–brines–water disposal systems with a view to quantify and characterize the products formed and transport mechanisms involved, was the focus of this study. This project talks of the integrated water management where industrial waste has a bearing on the quality of groundwater.

2. Methodology and hydrogeochemical modeling tools

Description of the coupled geochemical-transport modeling and data input used in the model are highlighted in subsequent subsections, followed by a brief presentation of the simulation results. The model calibration was carried out with an attempt to demonstrate that the model and its parameter values were reasonably representative of the experimental conditions carried out by Petrik et al. (2009) with the fresh fly ash and demineralised water from Secunda situated in Mpumalanga province in South Africa.

2.1. Fly ash modeling recipes and brines

Fly ash samples were collected from Secunda (Sasol) and Tutuka (Eskom) coal-utility plants in South Africa and from where the modeling ash recipes (Table 1) were derived and modified as adopted from Hareepsad et al. (2010), and Gitari et al. (2009). The characterized brines incorporated in the model from Secunda and Tutuka are also given by Table 2. Experimental data was based on the mineralogical and chemical characterization of the fresh fly ashes and the brines carried out by Ojo (2010) and Gitari et al. (2009). Four column modeling scenarios were simulated, namely: Secunda ash with demineralized water, Tutuka ash with demineralized water, Secunda ash with brines and Tutuka ash with brines.

2.2. Column parameters and discretization

The column experimental parameters were adopted from the work of Ojo (2010) and Hareepsad et al. (2010). Other column parameters and hydraulic property calculations were performed in programmed spreadsheets by MS EXCEL and formed part of the input column and hydraulic parameters (Table 3) in PHREEQC code (version 2.15.0). Flux-type boundary conditions (also known as third type or Cauchy boundary condition) were employed. The

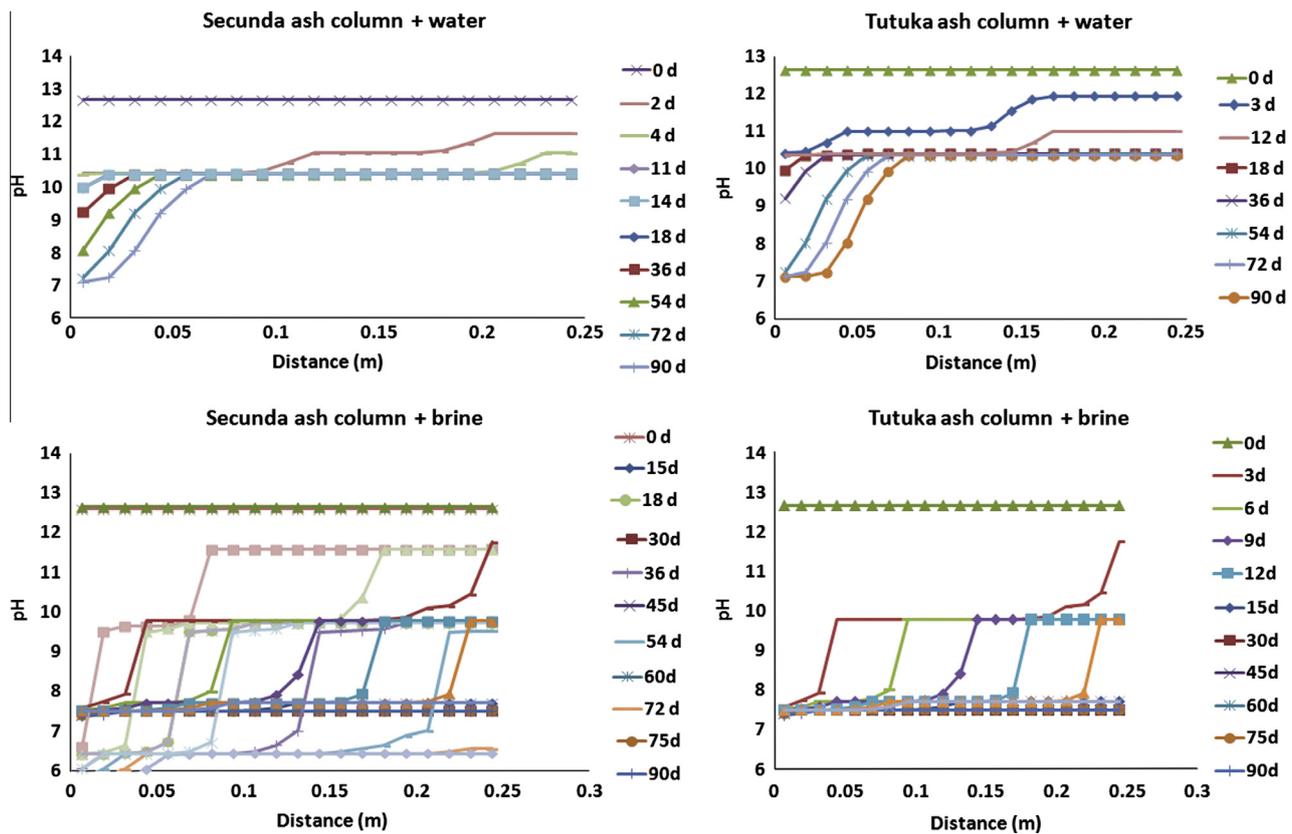


Fig. 1. The pH versus column distance at different days for Secunda and Tutuka ash–demineralized water and brines scenarios. (NB. d stands for days in all subsequent graphs in this paper).

one dimensional (1D) column (0.25 m) was discretized into 20 cells of cell length of 12.5 cm each. The total time of the simulation calculated was 90 days. The respective column geometry and hydraulic parameters, and column discretization and transport parameters were fed into the PHREEQC input file and ran accordingly.

2.3. Coupled geochemical-transport modeling and data input

In the PHREEQC simulation, the ash is modeled as a collection of pure mineral phases which come to equilibrium with the water or brine liquid phases. Modified LLNL database was used for all the simulations which involved inorganics (mineral phases and brines). Closed system was imposed in order to minimize the effect of atmospheric CO₂ and other gases. Input parameters for Secunda and Tutuka ash recipes were similar except that the ash composition differed quantitatively for the mineral phases. The infilling solution was demineralized water at default conditions of temperature (20 °C), pH (7) and electron activity (pe, 4). The solution in the column was modeled to be containing mobile cations of alkali metals of Na, K and Li in small quantities (0.010, 0.002 and 0.004 mol/L originally in the fly ashes) respectively. Dispersivity value of 0.005 m was adopted from Appelo and Postma (2005) as obtained from field experiments for porous media which closely resembled that of fly ash. The flow rates, the volumes of the leachates and the specific solid/liquid (S/L ratio) were imposed at a laboratory scale.

3. Results and discussion

PHREEQC simulations generate enormous amount of data depending on the specific interests and objectives of the modeller, among which the most significant simulation results to be

discussed are the pH, elemental total concentrations in the leachate, mineralogical changes as well as porosity the in the column against time, pore volumes and also distance.

3.1. pH changes along the column distance at different time

The pH trend for both scenarios of Secunda and Tutuka ash recipes with water was similar (Fig. 1). It was also observed to be similar for fly ash–brine model scenarios for the two ash recipes (Secunda and Tutuka). Initial pore chemistry reflected the pH values of the ash recipes (about 12.6) before the interactions commenced. The same trend recorded in pH confirms the similar mineralogy associated with the two ash recipes, only differing quantitatively. Great pH variation was observed between the influent point and 0.05 m of the column for up to 90 days during which time pH fluctuations were registered for different days along the column. This could be due to the equilibration reactions taking place when fly ash comes into contact with the water. At 0.05 m the pH drops from 12.6 to 10.4 after which it remains constant until 54 d after and then it starts to fall reaching 9.7 after 90 days. These changes in pH are an indication of the chemistry that is occurring at the point of first contact with water and also brines, resulting to dissolution of certain mineral phases that form leachates of lower pH values and which move down the column advectively. Significant pH-fronts change for different days for the first column distance of between 0.05 m and 0.25 m were observed. Between this column distance, some chemical changes could be occurring since a small decrease (2 or 3) in pH value over time can increase the solubility and decrease the adsorption of metals by many orders of magnitude, (Gitari et al., 2009). If the pH decreases over time, the concentration of metals in the leachate is expected to increase over time as well. Same trend of pH along the column was observed for both ash recipes with brines. Fly

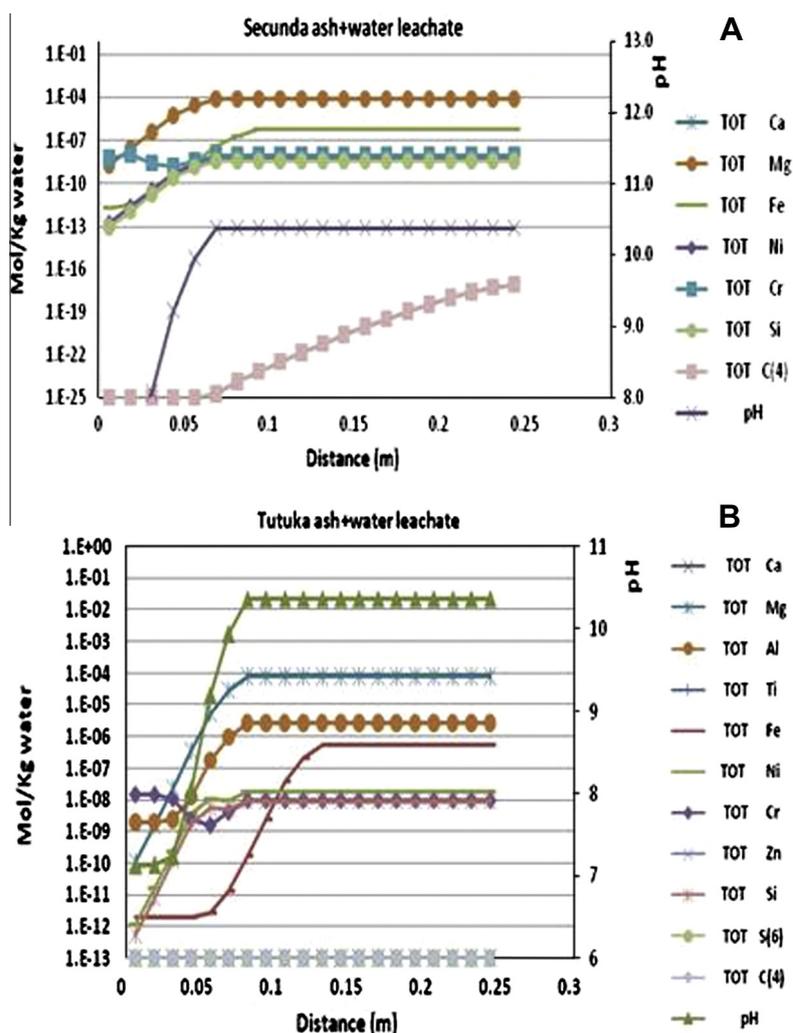


Fig. 2. Total elemental concentrations along the column distance after 90 days for major and trace elements for: (A) Secunda ash–water and (B) Tutuka ash–water.

ash–brines interaction results in marked change in pH over time, the initial alkaline pH of fly ash leachate with brine was lowered upon weathering to a final pH of about 6.5 for Secunda ash and 7.5 for Tutuka ash in 150 pore volumes. The difference could be attributed to the quantitative variations in the modeled ash recipes and different levels of brine constituents emanating from each of the coal utility plants of Sasol and Eskom. These results illustrated the distinctive general chemistry of the ash recipes (Hareeparsad et al., 2010) used in the model under different scenarios, with ash–brine systems exhibiting marked but similar trends between the two ash recipes but at a different time along the column distance.

3.2. Total concentration of major and trace elements (water soluble components in leachate) versus column distance and pH after 90 days

Column simulations results gave the breakthrough curves shown in Figs. 2 and 3. The results are those of Secunda and Tutuka fly ash interactions with water (Fig. 2) and brines (Fig. 3) along a column after 90 days. Both ash–water scenarios (for Secunda and Tutuka) showed similar trends for individual elemental concentrations in the leachate after the 90 days but only differ in quantities and magnitude of change. The major and trace elements considered were as listed in Fig. 2. The highest change in concentrations of the elements in the leachate was recorded between column

distance of 0.05 m and 0.1 m, except for Fe which exhibited the change of about 0.125 m for Tutuka ash–demineralized water column model. In the case of the two ash recipes with brines (Fig. 3), some of these elements were eluted at constant concentration along the column. These elements were Ca, Mg, S(VI), Na, K and C. The element Fe increases in concentration progressively up to about 0.075 m of the column after which it levels up to a constant value up to the end of the column as shown in Fig. 3. In these figures, Al was shown to have its concentration being pH-controlled as it showed a decrease in concentration within the first 0.05 m of the column as the pH increased within this distance.

3.3. Moles of mineral phases present versus distance along the column at end of simulated time (90 days)

The results of the mineral phase amounts along the column distance during the 90 days simulation were presented in Figs. 4 and 5. Secunda and Tutuka ash–water systems showed that the major mineral phases remaining after 90 days were hematite, nickel silicate, amorphous hydrous ferric oxide (HFO), amorphous chrome and brucite. Hematite amounts remained constant at all column positions whereas between 0.07 m and 0.15 m a general increase of brucite and amorphous HFO was recorded. Amorphous chrome showed no significant change in Secunda ash–water system but with Tutuka, its neoformed phase occurred at about 0.02 m

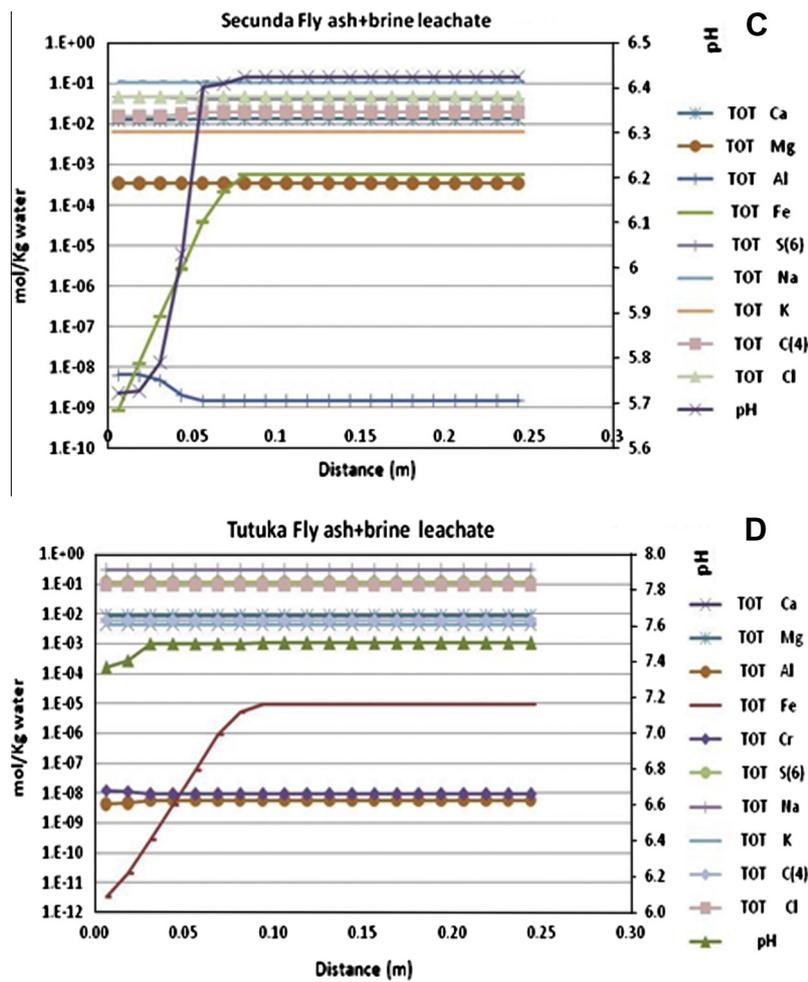


Fig. 3. Total elemental concentrations along the column distance after 90 days for major and trace elements for: (C) Secunda ash-brine and (D) Tutuka ash-brine.

(though very small amounts) and same amounts remained up to the end of the column. From the Secunda and Tutuka ash-water model, brucite formed at a point closer to the column inflow for Secunda compared to that of Tutuka. Calcite started being formed at 0.05 m and the amount increased rapidly to about 2.5 mol/kg water after which slight fluctuations within 2 and 2.5 mol were recorded up to the end of the column after 90 days. While calcite is precipitating and thus increasing in amount at this column distance, gypsum amounts are decreasing, implying dissolution of the mineral is taking place during the Secunda ash-brine system. After about 0.075 m all the gypsum will have dissolved while the precipitation reaction of calcite will have reached a steady state, thereby amount present remaining constant up to the column outflow position. The dissolution of calcite accounts for the marked increase of the concentrations of Ca and S(VI) in the leachate within 40–90 days as depicted in Figs. 2 and 3. However the amounts were not sufficient enough to cause oversaturation of gypsum for it to precipitate. In the case of ash-brines scenario, calcite initial amounts remained constant for the first 0.02 m for Secunda and Tutuka after which the amount increased in both ash-brine systems, recording about 2.5 mol/kg water (Secunda); about 0.085 mol/kg water of calcite within the first 0.05 m column distance. The increased amounts could be attributed to the presence of Ca and S(VI) in the brines which cause precipitation of the calcite, (Freyssinet et al., 2002; Koukouzas et al., 2009). At the initial stages of ash-brine interaction, gypsum is precipitated as the brines provide sufficient amounts of Ca and S(VI) to make gypsum

oversaturated and hence precipitates for Secunda and Tutuka ash-brine systems. A further amount of Ca in solution is available by the dissolution of CSH_gel_0.8 (Calcium silicate hydrate gel) particularly within the first 0.05 m column distance. CSH_gel_0.8 mineral also responded to changes in pH by taking the same trend as shown by pH and exhibited a dissolution. The formation of ettringite and then dissolving in the Secunda ash-brine system may have been controlled by the CSH_gel_0.8 mineralogical changes. The respective initial amounts of hematite were constant throughout the 90 days for all Secunda and Tutuka modeled systems. The results showed most of the other mineral phases may have dissolved or were present in negligible amounts over the 90 days period along the column distance.

3.4. Effect of geochemical reactions on porosity

The geochemical reactions that involve dissolution and precipitation of mineral phases do affect the porosity of the fly ash. Fig. 6 shows that precipitation and new-phase formation caused a decrease in porosity while dissolution led to increased porosity of fly ash. The porosity of the fly ash increased sharply during the first 30 pore volumes. This was also the period in which fast geochemical reactions were taking place as evidenced by the sharp decrease in the pH from 12.4 to about 9, and equilibrium trying to be attained. Between pore volumes of 30 and 60, the porosity remains constant at about 0.835, within which period the pH also remained constant at about 9. Sharp increase in porosity to about

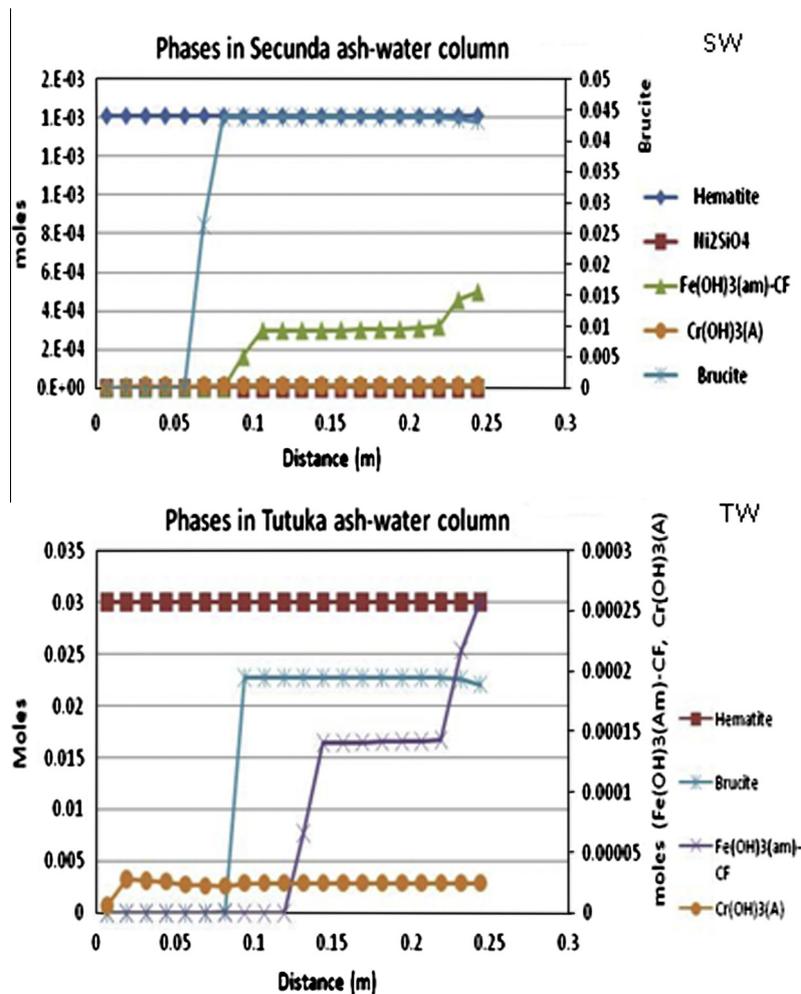


Fig. 4. Amount of mineral phases remaining along the column after 90-days ash-brine dynamic interaction for Secunda and Tutuka ash columns: SW-Secunda ash and water, TW-Tutuka ash and water (NB. Legend symbols different).

0.91 was then recorded between pore volume of 60 and 90. During the leaching process of a solid material, the concentration of the chemical species present in the interstitial solution is expected to decrease. The chemical equilibrium initially established is then upset and more soluble mineral phases in the fly ash dissolve successively in order to restore the equilibrium. Therefore, further leaching results in an increase in porosity due to the dissolution of mineral phases (Berry et al., 1990). Modification of the transport properties of the fly ash in the column would therefore be taking place in turn. From pore volume 90 downwards, a decrease of porosity was recorded, as the pH values further reduced to about 6. Though some dissolution of mineral phases was still occurring, the formation of neo-formed phases or precipitation previously given in Figs. 4 and 5; (e.g., hematite, $\text{Fe}(\text{OH})_3(\text{am})\text{-CF}$, pyrite, calcite, brucite, $\text{Cr}(\text{OH})_3(\text{A})$ and gypsum) could contribute to the decrease in the porosity which could have interfered with the flow rates in the column. Geochemical reactions do therefore affect the mineralogy of the fly ash and consequently may affect the porosity of the fly ash, (Larsson and Jarvis, 1999). Modeling porosity evolution within mixing regions of fly ash-brine interactions (during reactive transport) may have important applications in several environmental and engineering problems, (Berry et al., 1990). This information could give some useful insights in making certain engineering decisions on possible improvement on the reuse of fly ash in the road construction industry (Mahlabi et al., 2011).

4. Conclusion

Column modeling was successfully developed and revealed information on the time-dependent leaching and transport chemistry of the species in ash-water and ash-brine interactions. The simulation results demonstrated identification and quantification of reactive mineralogical phases, controlling the element release. Alteration of the geochemistry of fly ash was shown to be effected during the ash-water or ash-brine interaction over time. Interaction of fly ashes with water and brines result in mineralogical alterations of the original fresh ash through dissolution and precipitation. Part of the mineralogical transformation also involved formation of new phases that were not originally present in the ash recipe. The largest mineralogical transformation took place in the first 10 days of ash contact, with either water or brines, and within 0.1 m from the column inflow. The mineralogical transformations are caused by the many and complex geochemical reactions in fly ash-water-brines systems. These geochemical reactions that involve dissolution and precipitation of mineral phases do affect the porosity of the fly ash. This information could give some useful insights in making certain engineering decisions on possible improvement on the reuse of fly ash in the road construction industry. Leach column modeling undertaken successfully provided the linkage between changes in the ash-brine-water interaction chemistry and the transport mechanisms involved during co-disposal. This will have some bearing on the leachate

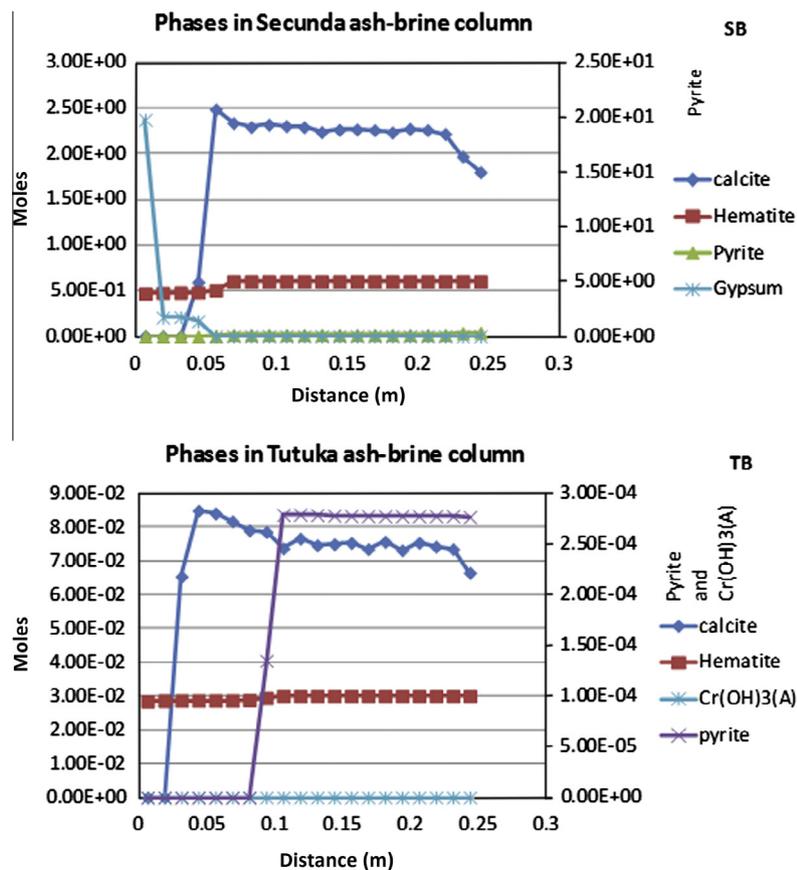


Fig. 5. Amount of mineral phases remaining along the column after 90-days ash-brine dynamic interaction for Secunda and Tutuka ash columns: SB-Secunda ash and brine, TB-Tutuka ash and brine (NB. Legend symbols different).

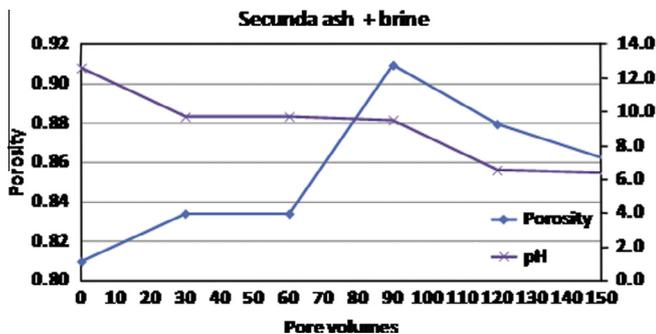


Fig. 6. Porosity changes against pore volumes and pH of Secunda ash and brine.

quality reaching the ground water in the long term, and hence adverse effects on the quality of ground water systems found within the vicinity of the fly ash heaps.

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