

## **Influence of Tracer Composition on Estimated Hydraulic Properties in Fly Ash**

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**Abstract** The study of fine fly ash as a waste product has given rise to two fundamental problems. Firstly, the chemical retention in the fine fly ash matrix and the subsequent release of retained salt load to the environment. Secondly, the rate of release of the salt to the environment is of critical importance. Fly ash dams in South Africa are typically located on mine tenements and water produced from these facilities could drain into underground mine workings. One of the main methods to evaluate the chemical retention in fly ash is to conduct standard leach tests. In most instances only one leaching solution is used and subsequently, parameters such as hydraulic conductivity and leaching characteristics are assessed. In the current paper a number of core samples were obtained from a fly ash dam and the leaching behaviour of these samples were determined under different leaching solutions. In addition the use of conservative tracers was evaluated (NaCl, KCl and LiCl). It became clear that the use of conservative tracers in the lab led to varying results. The selection of tracer composition impacted the chemical and hydrogeological properties of the fly ash.

**Keywords** fly ash, salt retention, tracer tests, groundwater management

### **Introduction**

Coal combustion products (CCPs) originate from the combustion of coal at power stations and petroleum refineries. Coal remains an abundant and widely dispersed source for energy generation and synthesis gas (van Dyk et al. 2001, Sajwan et al. 2006). Fly ash, bottom ash, flue-gas desulphurisation residue (synthetic gypsum) and boiler slag are the predominant residues from these processes (Kayoncu 1998). The current worldwide production of fly ash is more than 700 million tons per annum (Lokeshappa and Dikshit 2011).

At present, the disposal of fly ash is either by wet disposal or dry disposal in landfills or storage lagoons (USDT 1998, Di Gioia and Nuzzo 1972). Water contained in the ash material at deposition can leach constituents from the ash dump and transport these to the surrounding environment. Rainfall may also supplement the interstitial water and contribute to the leaching of elements. The water migrates through the dump and either daylight along the edge of the ash dump (seepage faces) and enter the surrounding environment as surface water, or migrate to the bottom and enter the soil underlying the dump from where it can recharge into the aquifers (Troskie 2005).

In the current paper a number of core samples were obtained from a fly ash dam and the leaching behaviour of these samples were determined under different leaching solutions. In addition the use of conservative tracers was evaluated (NaCl, KCl and LiCl) as these methods are commonly used to estimate hydraulic parameters.

### **Methodology**

Mineral identification was done by powder X-ray diffraction (PXRD) and scanning electron microscopy (SEM). Fresh ash samples were analyzed using a Bruker D8 Advance powder diffractometer with Cu radiation source, a göbel mirror and a Vantec-1 detector. The spectra were then matched with the crystallographic open database on EVA.DIFFRAC.SUITE™ (EVA) Software. SEM analysis was done using a JEOL JSM-6610 scanning electron

microscope with a Thermo Scientific Ultra dry EDS detector and an accelerating voltage of 20 kV and a live time of 60 seconds per analysis.

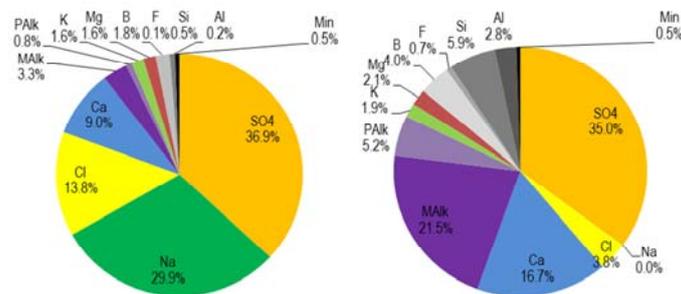
Chemical analysis was performed on the leachate using inductively coupled plasma – optical emission spectrometry (ICP-OES) to evaluate the mobility of selected elements leached from the ash and to determine the matrix response to other salts introduced to the matrix. A constant head permeameter with a fraction collector are some of the apparatus that were used as part of this study.

Initial leaching experiments were performed over a weekly time period, however release of chemical components stabilised in the first six hours of the experiment. Experiments were performed in triplicate to verify results and average data is reported in this paper.

### General Sample Properties

XRD spectra of a sample of fly ash before and after leaching indicated that the material had undergone only minor mineralogical changes and correlated with SEM analysis. This result indicated that the material was stable under leaching conditions and no major mineralogical change was expected during tracer testing. It should be noted that fly ash may consist of a large component of amorphous glass which does not have regular arrays of atoms that produce definitive peaks in XRD patterns. This amorphous glass component may also be a major host within the ash for adsorbed trace elements, which may be leached to the surrounding environment.

The first leachate solutions were found to be high in  $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ; whereas the last leachate samples were much more alkaline ( $\text{HCO}_3^-$ ,  $\text{CO}_3^{2-}$ ) and Ca-rich (fig. 1). This can be explained by the rapid release of highly soluble halite and sulphate species from the system ( $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\text{CaCl}_2$ ) which are then replaced by carbonate and sulphate species ( $\text{CaCO}_3$ ,  $\text{Ca}(\text{HCO}_3)_2$  and  $\text{CaSO}_4$ ).



*Fig. 1 Change in average composition from the first and last leachate samples for major components.*

An overall decrease in hydraulic conductivity is observed over time, ultimately reaching a steady state. However, changes in hydraulic conductivity were generally low for the samples and ranged from 1 ~ 9 m/d.

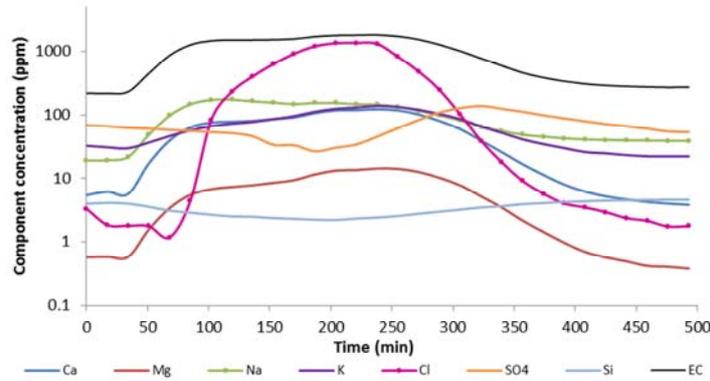
### Hydraulic and transport properties during tracer tests

The application of tracers in the environment is heavily reliant on the assumption that the injected material would be able to move with the flowing water instead of adsorbing onto the matrix (Davis et al. 1980). Fly ash has a high reactive surface due to the combustion process, however as noted previously it is expected that the system would obtain a stable leachate profile over a short timeframe.

In order to investigate this property, a set of tracer solutions (NaCl, KCl and LiCl) were prepared to assess tracer properties. The following section contains the results from tracer solutions and how it relates to the chemical stability of the fly ash matrix.

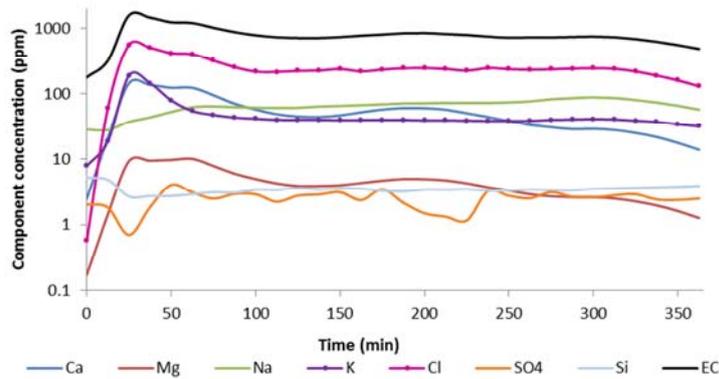
**Tracer test results**

Sodium chloride is the most commonly used tracer in hydrogeological investigations. The tracer did not perform as expected and two main observations from fig. 2 can be made. Firstly, sodium breakthrough is not observed at the same time as chloride species. Instead an increase in sodium, potassium, calcium and magnesium concentrations is observed which is associated with carbonate species. Chloride breakthrough only occurs after an hour (fig. 2) which includes a decrease in sulphate concentration. A similar trend is observed for the silicon concentration which could indicate that silicate dissolution is suppressed by chloride species. In this instance NaCl is not behaving as a conservative tracer but instead activates the matrix of the fly ash to release additional species into solution.



*Fig. 2 NaCl tracer test showing the chemical composition of the resulting.*

It was expected that the use of KCl would introduce the same tracer behaviour as that observed for NaCl. However, in this instance only minimal interference could be observed from the matrix (fig. 3). The peak in EC values is mimicked by both potassium and chloride species. An increase in Mg, Ca and to a lesser extent Na was observed. Most problematic was the increase in Ca concentrations which was in a similar order as that of K. The potassium tracer behaved in a classical manner with a steady increase to a peak value followed by an expected decay curve. In this instance the arrival time links up with the EC curve and it could be expected that transport properties can be assessed.



*Fig. 3 KCl tracer test showing the chemical composition of the resulting.*

Finally, lithium chloride was used as a tracer (fig. 4); it caused similar behavior as to that observed for potassium chloride. In the samples that were tested the response from the matrix was reduced. However, lithium concentration levels did not reduce to background values, which could indicate that higher absorption ratios compared to other tracers are possible. In addition since only calcium concentrations have significantly increased, it is assumed that the impact of lithium on the structural properties of the matrix is reduced compared to other tracers.

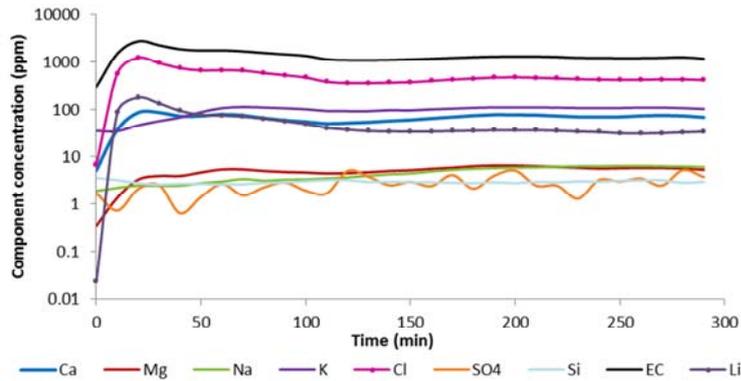


Figure 4 LiCl tracer test showing the chemical composition of the resulting.

Mass balance assessments were performed to determine the amount of tracer solution that was either absorbed or retarded due to tortuosity of fluid flow. The results are reported in Table 1 and the highest cation recovery observed is from either sodium or lithium tracer tests.

Sodium does leach from the fly ash matrix for all samples and this could artificially increase the recovery values of sodium. Furthermore, a similar trend in potassium concentration levels can be observed for the sodium and lithium tracer tests which could indicate that recovery on the potassium chloride tracer could be overestimated. The lithium tracer test also resulted in significant releases of calcium and potassium but interestingly only minimal amounts of sodium were produced.

In all instances (table 1), the injection of a tracer solution resulted in the release of calcium and potassium from the fly ash matrix. This effectively excludes potassium as a viable tracer for fly ash in these systems. The sodium chloride solution has a similar issue related to potassium release and possible sodium interference from the matrix which cannot be excluded. This observation is further supported by the general chemical composition of leachate and EC profile of the tracer test (fig.2).

Table 1 Recovery of tracer from leachate solution, percentage recovery in brackets.

		NaCl	KCl	LiCl
Applied	Cation / Anion	275 / 425	420 / 380	98 / 502
	Ca	62	89	64
	Mg	6	7	4
Recovery	Na	161 (59)	54	3
	K	73	106 (25)	59
	Li	-	-	60 (61)
	Cl	357 (84)	422 (111)	458 (91)

## **Conclusions**

The application of readily available trace solutions (NaCl, KCl and LiCl) was investigated. The most non-reactive tracer was lithium chloride. Sodium and potassium chloride tracers had inherent issues with release of tracer species. This in effect caused a mismatch between EC and tracer cation profiles.

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