

Inorganic contaminants attenuation in acid mine drainage by fly ash and fly ash-ordinary portland cement (OPC) blends: Column Experiments

W. M. GITARI¹, L. F. PETRIK², O. Etchebers², D. L. KEY³, C. OKUJENI⁴

¹Dep. of Ecology and Resources Management, School of Environmental Studies, University of Venda, Private Bag, X5050, Thohoyandou, South Africa, mugera.gitari@univen.ac.za; mugeraw@gmail.com

²Environmental and Nano Sciences Group, Dep. of Chemistry, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa, lpetrik@uwc.ac.za, oetchebers@uwc.ac.za.

³Dep. of Chemistry, University of the Western Cape, dkey@uwc.ac.za,

⁴Dep. of Earth Sciences, University of the Western Cape, Private Bag X17, Bellville, 7535, South Africa, cokujeni@uwc.ac.za.

Abstract One of the environmental impacts of coal mining is generation of acid mine drainage (AMD) in mine voids. Mitigation of AMD in a backfill scenario in a mine void was simulated by addition of AMD to Fly ash (FA), Solid Residues (SR), SR + 25 % FA and SR + 6 % Ordinary Portland Cement (OPC) packed columns over a 6 month period. Acidity neutralization in AMD was achieved over the study period, with acidification of the leachates occurring stepwise. The interaction of FA and its derivatives generated near neutral to alkaline pH levels which induced several contaminant attenuation mechanisms such as precipitation, co-precipitation and adsorption. PHREEQC modeling indicated that precipitation of ferrihydrite, Al-hydroxides, Al-oxyhydroxysulphates, gypsum, ettringite, manganite, rhodochrosite contributed to the low levels of contaminants observed at alkaline pH. The leaching of the toxic trace elements and attenuation of the contaminants was observed to strongly depend on the pH regime generated and acidity of the AMD which means that the success of the application will be site specific.

Key Words Fly Ash, Acid Mine Drainage, Column leaching, Solid Residues (SR), Backfilling, Acidity, Inorganic contaminants.

Introduction

Coal mining and coal combustion for generation of electricity produces various types of wastes such as, acid generating coal discards, acid generating mine tailings, acid mine drainage (AMD) and fly ash (FA) that require a form of management and remediation. FA is a by-product obtained during the combustion of coal in coal burning power generation plants. South Africa coal burning power stations generate 26 Mt of FA per annum (Kruger, 2003). Only a small portion is put into beneficial use mainly as a cement extender, the rest is stockpiled or slurried to ash dams near the power plants (Krüger, 2003). There is need to develop high volume disposal and utilization technologies for FA and other coal combustion by-products. AMD is characterized by high acidity (pH 2–4), high sulphate concentrations (1–20 g/L) and often contains high concentration of heavy metals such as Fe, Mn, Al, Cu, Ca, Pb, Mg, Na and Ni (Gitari et al., 2006). Management of mine water pollution demands a range of active and passive remediation engineering technologies to minimize its impact on ground and surface waters which can incur significance expense. Recent studies by Gitari et al (2006) have shown that fly ash can effectively neutralize AMD and reduce significantly the concentration of major inorganic contaminants. However large volumes of solid residues (SR) will be generated that would require disposal. One of the proposed disposal technique for the SR as backfill in coal mine voids. The main objective of this study was to evaluate the effect of the SR interacting with AMD in a backfill scenario and validating the proposed disposal technique.

Materials and methods

Sample characterization and column assembly

FA and AMD was sampled at a coal combustion plant and a coal washing plant respectively in Mpumalanga, South Africa. The SR were generated by reacting the fly ash and AMD in a S/L of 1:3 using a 150 litre capacity agitator. The mixture was agitated until a pH of 9.2 was achieved. The mixture was allowed to settle and the liquid phase drained. The SR after air drying were then crushed and mixed thoroughly with the required portion of either fresh FA or OPC to attain homogeneity and thereafter placed in columns.

Simulated AMD and column drainage

Model solution simulating AMD was formulated using soluble salts of the major elements found in AMD (Fe, Al, Mn and SO_4^{2-}). The simulated AMD was added to each column over a period of several minutes. The drainage was done after 7 days for the first 53 days and thereafter 14 days until stoppage of the experiment at 165 days. A total of 16 batches (350mL and 450mL) were added for each column. Effluents from previous drainage were collected before the next drainage. The columns were drained at intervals

Results and discussion

Chemical characterisation of fly ash, solid residues and Ordinary Portland Cement

OPC primarily consists of calcium, silicon and aluminium compounds and this is reflected in the high SiO_2 , Al_2O_3 and CaO content. The SR and FA was observed to have high weight % of SiO_2 , Al_2O_3 which reflected the main components of FA, quartz, mullite and aluminosilicate matrix. An enrichment of Fe, Al, Mn and P probably as phosphate was observed in the SR as a result of the removal of these elements from AMD. Trace elements observed to be enriched in the SR included Mo, Sr, Co, Cr and Zn. Pb, Ni and Ba were observed to decrease in the SR indicating leaching from the FA.

Temporal evolution of pH in the column effluents

Results of pH evolution with S/L ratio for FA, SR, SR + 25 % FA and SR + 6 % OPC blends are presented in Figure 2. Stepwise acidification of all the column residue cores was observed as the drainage progressed (Fig1). Several buffer zones: pH 11–11.5, pH 8.5, pH 8.5–9.5, pH 6.3–6.7, pH 4–4.5 and pH 3.5–4 were exhibited by the various cores. The SR core appeared to have a significant buffering capacity, maintaining a neutral to slightly alkaline pH in the effluents for an extended period of time (Fig 1). The use of OPC as a binder reduced the neutralization capacity of SR (Fig 1).

Contaminant attenuation trends in acid mine drainage as a function of pH and L/S ratio

This section will only present contamination attenuation trends for SR and SR + 6 % OPC columns due to space limitations of four pages. The reader is referred to our upcoming publication (Gitari et al., 2010). Figure 2 shows the concentration of Ca, Fe, Al, Mn and SO_4^{2-} in the leachates as a function of L/S ratio and pH for SR and SR + 6 % OPC packed columns. Only results for SR + 6 % OPC column are discussed.

Solid Residues + 6 % OPC column

The SO_4^{2-} concentration in the leachates drops from 2875.8mg/L at L/S of 0.4 to a steady value at L/S of 0.7–1.5 (1767–1906 mg/L) (Fig 2f). Hydration of OPC releases Ca^{2+} and OH^- ions, Ca^{2+} and SO_4^{2-} precipitates out as either gypsum or ettringite in presence of Al, while Fe, Al and Mn will precipitate out as metal hydroxides with corresponding adsorption of SO_4^{2-} . At a L/S ratio of 1.85 a sharp increase in concentration was observed. This coincided to a pH drop to below 5.5 (Fig 2e),

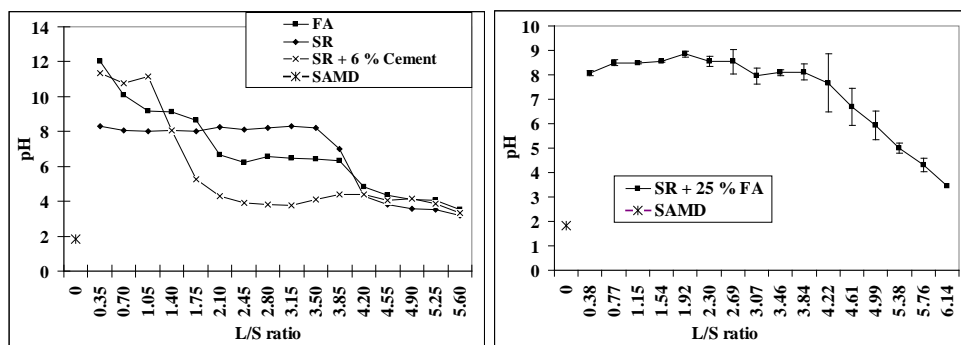


Figure 1 Evolution of effluent pH with cumulative L/S ratio

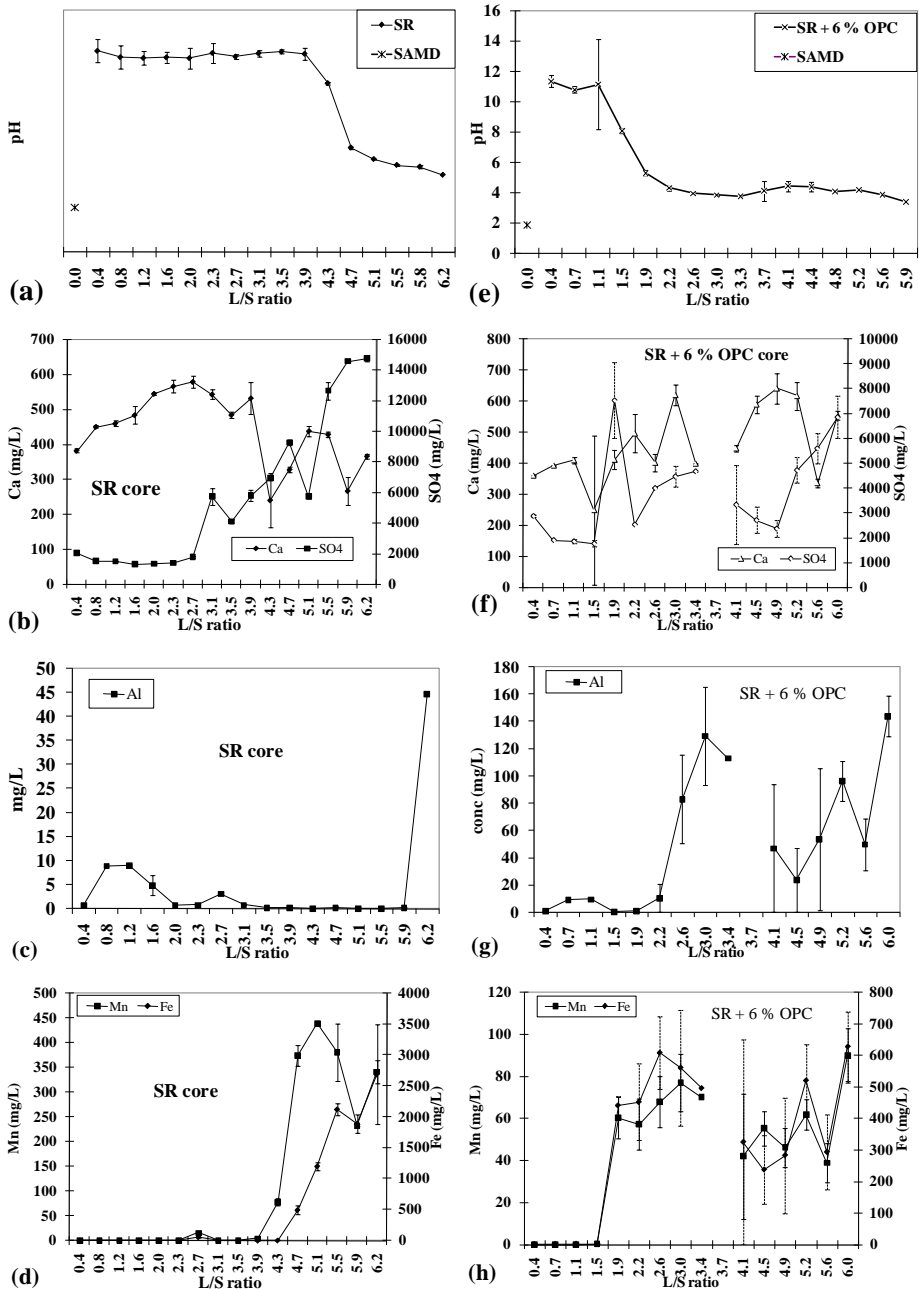


Figure 2 Concentration of Ca, SO_4^{2-} , Al, Fe and Mn in leachates as a function of L/S ratio and pH for SR and SR + 6 % OPC columns (error bars represent 1 SD above and below the mean)

the high concentration probably results from the re-solubilization of previously formed precipitates due to the pH drop. The concentration of SO_4^{2-} at a L/S ratio of 4.44 is below 3000 mg/L, a low concentration compared to other columns which is a strong indication that SR + 6 % OPC column has a high capacity to adsorb or incorporate SO_4^{2-} at highly acidic conditions. The concen-

tration of Mn remains below 0.35 mg/L upto a L/S ratio of 1.48 while Fe maintains a value below 2.07 mg/L (Fig 2h). The low concentration observed was attributed to precipitation of metal hydroxides at the high pH and possible incorporation in the resulting CSH gel. A sharp increase in concentration for both elements was observed at L/S ratio of 1.87 (Fig 2f) when the pH was observed to drop to below 6.

Peaks in concentration for both elements are then observed at 2.62 and 5.24 L/S ratio respectively, a phenomena observed with other elements such as Zn, Ni and Cu. These peaks in concentration are attributed to re-solubilization of previously formed precipitates as the pH drops to below 6 and 4 respectively. At a L/S ratio of 5.99 both elements show a sharp increase in the leachates corresponding to the pH drop to below 4 (Fig 2e and 2h). The Al attenuation was highly efficient upto a L/S ratio of 2.25 with concentration remaining below 9.33 mg/L (Fig 2g). An initial increase in concentration is observed at L/S ratios (0.75–1.12) (9.01–9.33 mg/L). This corresponds to the high pH buffer region and formation of soluble $\text{Al}(\text{OH})_4^-$ will dominate. A peak in concentration is observed at a L/S ratio of 2.99 (129.4 mg/L), a phenomena attributed to the re-solubilization of previously formed precipitates. A sharp increase in concentration is observed at L/S ratio of 5.99 as the pH drops to below 4. The concentrations at the close of the drainage are higher than for SR column which indicates that apart from precipitation other mechanisms are involved in attenuation of Al in this column.

Inorganic contaminants attenuation and solubility controls

In the SR + 6 % OPC column cores two mechanisms for attenuation of SO_4^{2-} were identified as the column core acidified: (a) Ettringite formation at the high pH generated by OPC hydration in presence of Al and SO_4^{2-} from SAMD, (b) Gypsum formation. Analysis of the ettringite crystal by SEM and SEM-EDX revealed that they were coated by C-S-H gel which resisted dissolution under the acidic regime SEM and SEM-EDX identified the presence of gypsum crystals. Precipitation of Al-hydroxysulphates and jarosite type phases could also have contributed to low levels of both SO_4^{2-} and Al. Calculated SI indicated the leachates to be saturated or super-saturated with ferrihydrite at pH > 5, with boehmite, diaspore and gibbsite at pH 4–12, rhodochrosite, manganite, pyrolusite and nsutite at pH 8–11.5

Conclusions

Stepwise acidification was observed as the drainage progressed. All the columns exhibited high contaminant attenuation efficiency at neutral and circum-neutral pH levels. However the SR + OPC column exhibited high attenuation efficiency even as the leachates became acidic suggesting different attenuation mechanisms compared to FA, SR and SR + 25 % FA columns. The near neutral to alkaline pH levels generated, induced several contaminant attenuation mechanisms such as precipitation, co-precipitation and adsorption reactions. Leaching of toxic trace elements such B, Cr, Zn, Mo, Ni, Cu, Co, Se, V, and Cd was observed. The results clearly indicate that the success of the application will be site specific.

Acknowledgements

The authors wish to express their gratitude to the Water Research Commission (WRC), Coaltech 2020 Consortium, and the National Research Foundation (NRF), CSIR and ESKOM, for their support. Chemistry Department of the University of the Western Cape for the assistance provided during this study.

References

- Gitari M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E and Okujeni, C (2006) 'Treatment of acid mine drainage with fly ash: Removal of major contaminants and trace elements', J of Environ Sci and Health-Part A. Vol. A41 Issue 8, 1729–1747.
- Krüger, J.E (2003) 'South African fly ash: A cement extender', A South African Coal Ash Association publication.
- W. M. Gitari., L. F Petrik., D. L Key and C. Okujeni. (2010) 'Inorganic contaminants attenuation in acid mine drainage by fly ash and its derivatives: Column Experiments', Int. J. Environment and Waste Management, in press.