

Stability of Brine Components in Co-disposed Fly Ash-Brine Solid Residue

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Abstract

Fly ash and hyper-saline wastewater (brine) are generated by power stations in South Africa. Fly ash and brine require adequate and safe disposal due to their chemical composition. The constraints in keeping the concentration of elements in brine to a minimum level before disposal has caused some South African power stations to co-dispose brine and fly ash. This study investigated the removal of brine component by fly ash, and the stability of brine components in fly ash/brine residue when in contact with solutions of different pH values. Comparison of the elemental composition of fresh fly ash and the solid residue showed that some elements such as Na, Cl, SO₄, Co, Cu, Pb and Zn in the solid residue increased in concentration. This indicates that some elements were removed from the brine solution by fly ash. The Acid Neutralization Capacity (ANC) test which was carried out to investigate the stability of the elements captured in the fly ash/brine residue showed that most of the captured elements were released with decrease in the pH of the leaching solution. However, Na and Cl were released in high concentration irrespective of the pH of the leaching solution. This study shows that the Na and Cl-rich solid phase(s) formed during the fly ash/brine interaction are highly soluble and could easily dissolve when in contact with solution, irrespective of the pH of the solution.

Introduction

Fly ash, a coal combustion by-product has been considered to be a significant source of potential toxic elements released to the environment.¹ The release of the species contained in fly ash is dependent on the characteristic of the types of coal burnt, the combustion conditions and the handling of the residue. Fly ash is being disposed of in landfills, and used in some beneficial ways which include additives to cement and soil amendment. In South Africa, according to the ESKOM report,² ESKOM generates approximately 40 Mt of fly ash annually of which only 5 % is currently beneficially utilized, the rest being disposed of in ash dams, landfills or ponds while SASOL Synfuels at Secunda produces 3 Mt fly ash and 7 Mt gasification ash annually.³ Brine is another waste generated in power utilities as a result of water re-use. Brine contains

major and minor species in significant quantities which makes its disposal problematic.⁴
⁵ In the search for ways to reduce the disposal problems of brine and fly ash, some coal-fired power generating utilities in South Africa use brine streams to hydraulically transport fly ash to ash dumps while others use brine for dust suppression in ash dumps. Despite the co-disposal of fly ash with brine, the interaction chemistry of the species in the system has not been fully investigated. The interactions of some species in the fly ash and brine could result in precipitation of salts due to super-saturation or adsorption. Therefore, it is necessary to study the chemical interactions in fly ash/brine systems to determine the sustainability of fly ash and brine co-disposal scenario over time.

This study aims at determining the effect of the long-term fly ash/brine interactions on the removal of major and minor elements from brine solution, and to determine the stability of the elements captured in the fly ash/brine residue when in contact with solutions of different pH values.

Methods

Long-term fly ash-brine interactions experiment

The fly ash-brine interaction experiment was carried out by weighing 600 g of each of the fresh fly ash into 1L plastic container. 600 mL of the brine solution was accurately measured and mixed with the fly ash in the plastic container. After the mixing of the fly ash and the brine solution in the plastic container, the container was closed. The mixture of fly ash and brine (1:1 wt/v) in the container was allowed to stand for a period of 12 months. The fly ash/brine residue was oven-dried at 50 °C, crushed, milled, homogenized and stored in tightly-closed plastic containers at room temperature for further experiments and analysis. Elemental analysis of fresh fly ash and fly ash/brine residue was done by XRF using a Philips PW 1480 X-ray spectrometer fitted with a Cr tube and five analyzing crystals namely LIF 200, LIF 220, GE, PE and PX at 40 kV and 50 mA tube operating conditions.

Acid Neutralization Capacity experiment (ANC)

The acid neutralization capacity (ANC) test was carried out on the fly ash/brine residue based on the methodology of the European standard prEN14429.⁶ The method is divided into two stages which are; the preliminary test to determine the acid consumption of the fly ash/brine residue; followed by the determination of acid neutralization capacity of the fly ash/brine residue.

Results and discussion

Chemical composition of fresh fly ash and fly ash/brine residue

The results of the XRF analysis showed that the total concentrations of some of the elements such as Ca, Mg, Ba, Cl, K, Na, S and Sr in the fresh fly ash are very high

(Figure 1). The concentration of Na, K, Cl and S (SO₄) increased after interaction with brine for 12 months. In comparison with their concentrations in the fresh fly ash, the concentration of minor elements such as Co, Mo, Ni, Pb and Zn increased significantly upon long-term contact with the brine solution (Figure 2).

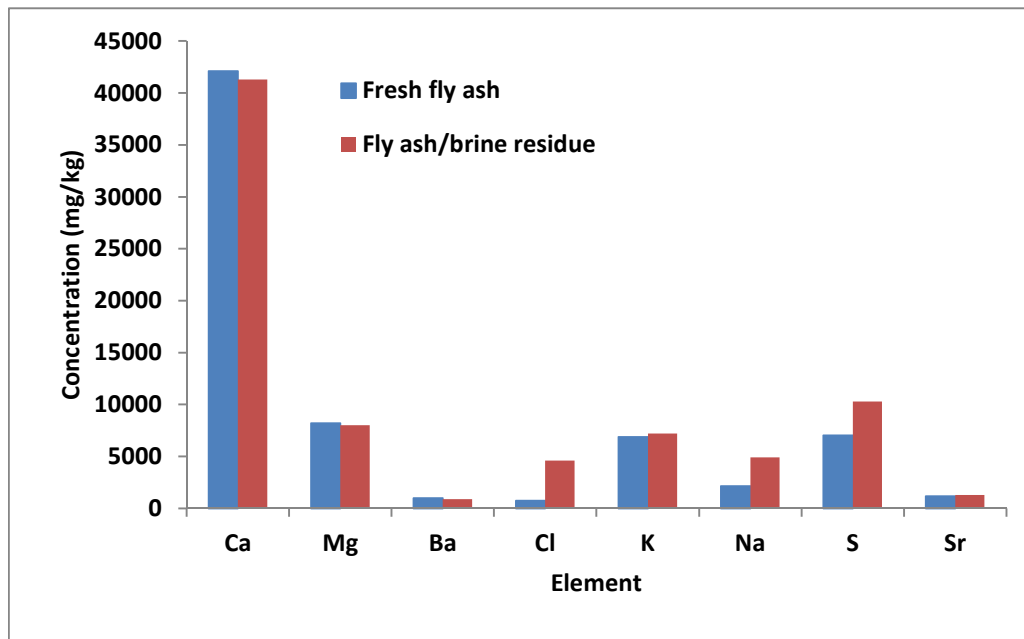


Figure 1: Concentrations of Ca, Mg, Ba, Cl, K, Na, S and Sr (mg/kg) in fresh fly ash and solid residues recovered from fly ash-brine for 12 months

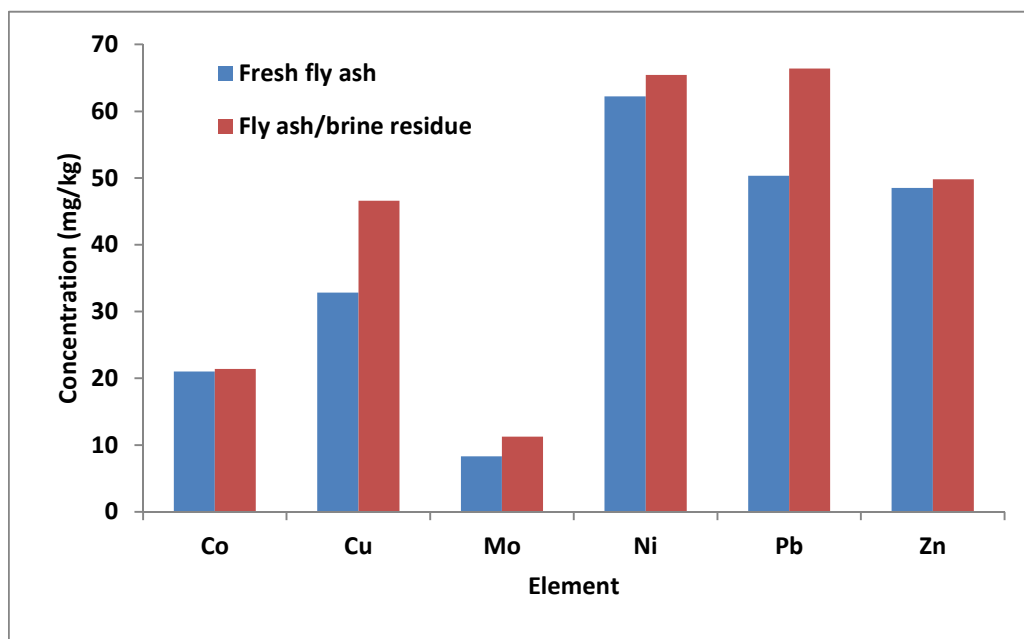


Figure 2: Concentrations of Co, Cu, Mo, Ni, Pb and Zn (mg/kg) in fresh fly ash and solid residues recovered from fly ash-brine for 12 months

The increase in the concentrations of most of the species such as Na, S, K, Cl, Cu, Mo, Ni and Pb in the fly ash/brine residue could be attributed to their removal from the brine solution and subsequently taken up by the fly ash either by adsorption or precipitation processes. Although, the concentrations of elements such as Ca, Ba, Mg and Sr in the fly ash residue were expected to decrease significantly due to their high solubility when in contact with water, the slight change observed in their concentrations in the fly ash/brine residue compared with their concentrations in the fresh fly ash could indicate that these elements formed new phases under static conditions after being leached from the fly ash. The formation of new mineral phases is possible due to the interactions of these species with other species such as SO_4 contained in the brine solution.

Influence of pH on the release of major elements

As shown in Figure 1, Na and Cl were removed from the brine solution by the fly ash during fly ash/brine interaction experiment. The release of Na and Cl into solution during the ANC tests carried out on the fly ash/brine residue exhibits leaching behaviour that was independent of pH (Figure 3). The concentration of Na and Cl in leachate was high at the natural high pH of the ANC systems, and this high concentration was maintained irrespective of the pH of the systems. The trends of release of Na and Cl in the ANC systems suggest the rapid dissolution of the transient Na-rich soluble salts such as halite (NaCl) or Na_2SO_4 that may have formed in the fly ash residues during the fly ash/brine interaction experiment for 12 months.^{7, 8}

The release of K was found to be slightly different from that of Na as a gradual increase was observed with decrease in the pH values upon acidification (Figure 3). The leaching pattern of K suggests that, apart from the soluble salts of K in the fly ash, K could also be present in the matrix of the fresh fly ash and fly ash/brine residue. The slow release of K observed in the fly ash/brine residue as the pH decreased could be attributed to the dissolution of less soluble phases in the fly ash and the fly ash/brine residue.

The concentration of SO_4 in the leachate of the ANC test from the fly ash/brine residue was high at natural pH of the ANC systems (Figure 3). The concentration of SO_4 significantly increased with decrease in the pH of the ANC systems. The results in Figure 1 showed that SO_4 was significantly removed from the brine solution by the fly ash during the fly ash/brine interaction experiment for 12 months. Therefore, the increase observed in the concentration of SO_4 when the fly ash/brine residue contacted water (natural pH) at the start of the ANC tests could indicate the release of soluble SO_4 species that was removed from the brine during the fly ash/brine interaction experiment while the continuous increase could be attributed to the dissolution of the SO_4 -rich phases in the fly ash/brine residue as the pH decreased. This shows the instability of the mineral phases that captured SO_4 from the brine solution.

The trend of release of SO_4 from the fly ash/brine residue indicates that the SO_4 removed from the brine solution by the fly ash is mobile even at high pH upon contact with water.

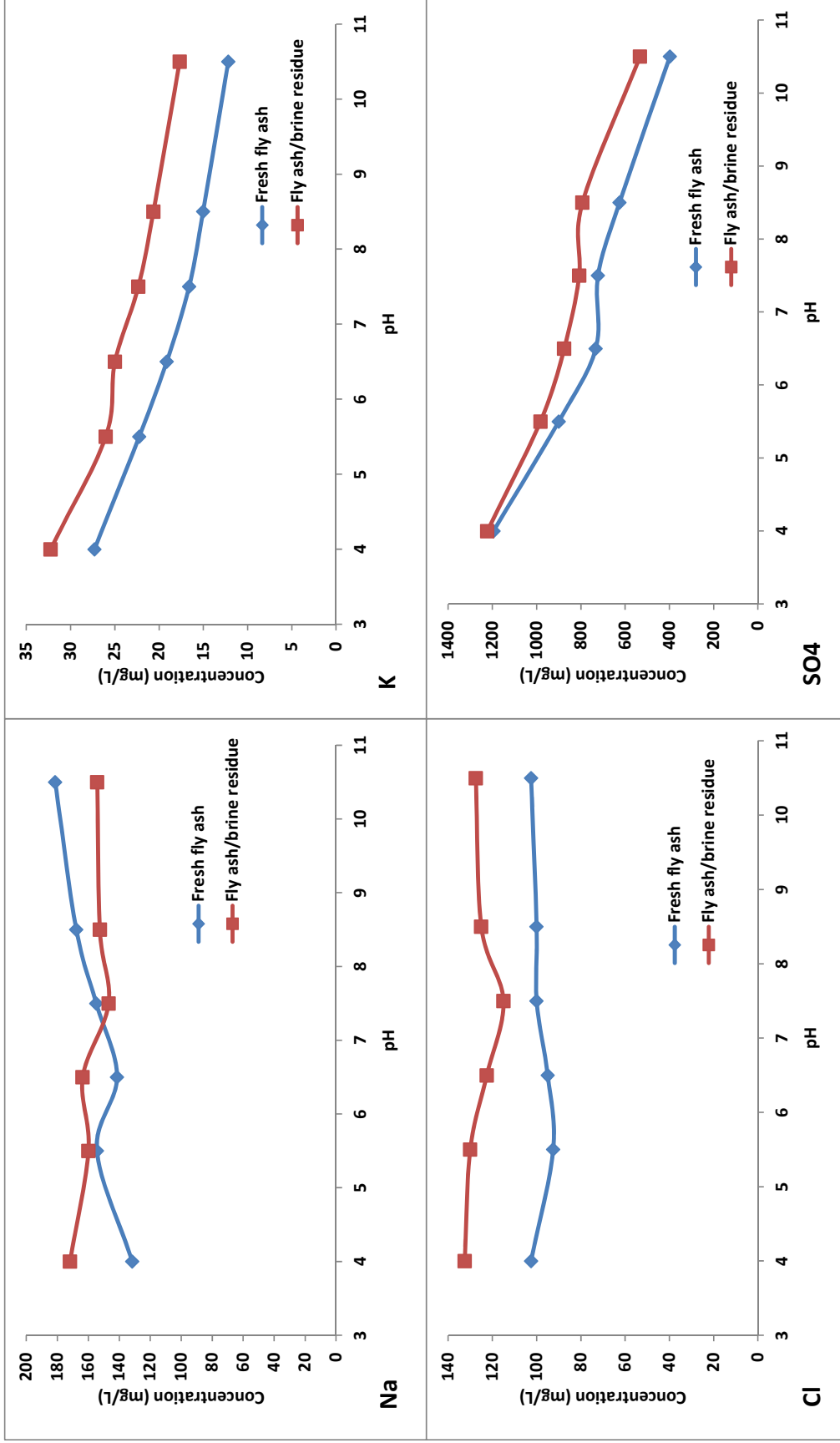


Figure 3: Concentration of Na, K, Cl and SO₄ leached from fresh fly ash and fly ash/brine residue as a function of pH.

Influence of pH on the release of minor elements

The concentrations of Co, Ni and Pb were low in the leachate solutions of the ANC tests at alkaline pH. Co concentration was observed to be low between pH \approx 8 and the natural high pH in the leachates of the fresh fly ash and fly ash/brine residue; Ni was at its lowest concentration between pH 7.5 and the natural high pH while the concentration of Pb was low between pH 6 and the natural high pH (Figure 4). These elements were removed from the brine solution (Figure 2) which indicates that they are enriched in the fly ash/brine residue. Heavy metals (such as Co, Ni, Cu, Zn, Pb and Cd) are strongly adsorbed to the surface of the oxy-hydroxides thereby decreasing the availability of these elements in solution at high pH.⁹ The release of Co, Ni and Pb in the ANC systems as the pH decreased could be controlled by the dissolution of Fe and Mn oxy-hydroxides. At low pH, it was suggested that the increase in concentration of Co, Ni and Pb could be attributed to gradual desorption from the oxy-hydroxides.¹⁰ The release of Pb could also be controlled by the precipitation of $\text{Pb}(\text{OH})_2$ at alkaline pH (>9).¹¹

The concentrations of Cu and Zn released from the fly ash/brine residue were very low between pH 6 and the natural high pH at the start of the ANC tests, which increased significantly at pH below 6 (Figure 5). The trends of Cu and Zn (Figure 5) released from the fly ash/brine residue were similar to what was observed for Co, Ni and Pb (Figure 4) in the ANC systems. This is an indication that the release of Cu and Zn could also be controlled by sorption on the reactive surfaces of hydrous Fe or Al oxy-hydroxides.¹² Apart from adsorption on Fe oxy-hydroxides, the release of Zn and Cu has been observed to be controlled by the formation of hydroxide complexes at alkaline pH.^{13, 14} Surface complexation to Fe- and Al (hydr)oxides or formation of hydroxide complexes could account for the initially low concentration of Cu and Zn at high pH in the ANC leachates while their increase in the leachates at low pH could be as a result of the dissolution or desorption of the complexes.

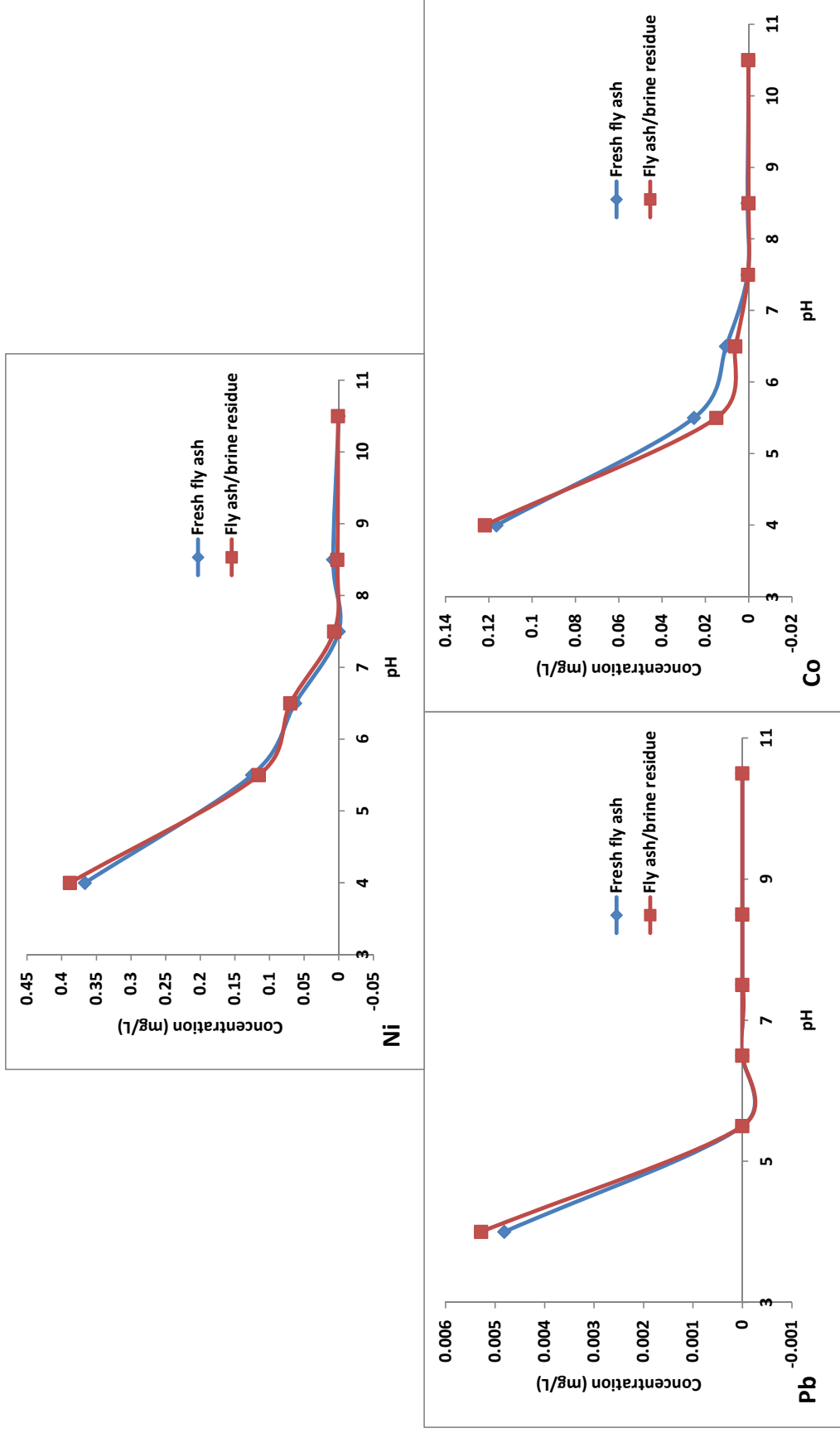


Figure 4: Concentration of Ni, Pb and Co leached from fresh fly ash and fly ash/brine residue as a function of pH.

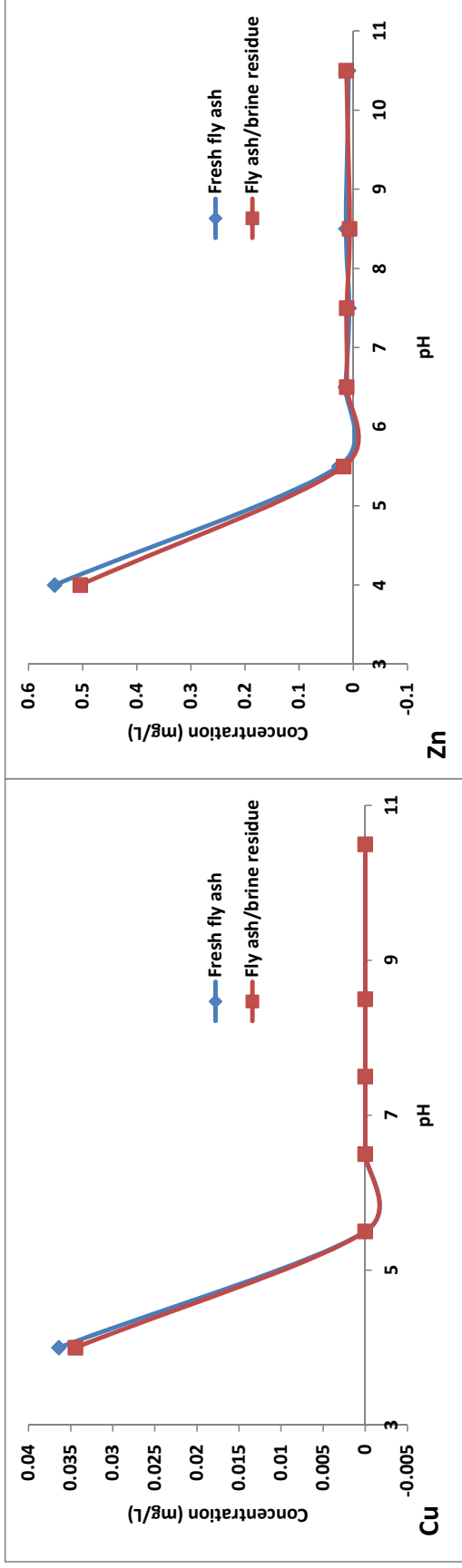


Figure 5: Concentration of Cu and Zn leached from fresh fly ash and fly ash/brine residue as a function of pH.

Conclusion

The release of significant amounts of the major species such as Na, Cl and SO₄ at natural high pH of the ANC systems is an indication that most of the species removed from the brine solution by the fly ash during the fly ash/brine interaction are highly mobile. However, Cu and Zn in the fly ash/brine residue are not mobile under alkaline condition but are mobilized when the pH is reduced below 6.

The rapid release of major species from the fly ash/brine residue shows that the species removed can easily leach upon water ingress or change in pH thereby leading to increase in the concentration of these species in the water bodies in the catchment area where ash dump is located.

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