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Partitioning of major and trace inorganic contaminants in fly ash acid mine drainage derived solid residues

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ABSTRACT: Acid mine drainage was reacted with coal fly ash over a 24 h reaction time and species removal trends evaluated. The evolving process water chemistry was modeled by the geochemical code PHREEQC using WATEQ4 database. Mineralogical analysis of the resulting solid residues was done by X-ray diffraction analysis. Selective sequential extraction was used to evaluate the transfer of species from both acid mine drainage and fly ash to less labile mineral phases that precipitated out. The quantity of fly ash, volume of acid mine drainage in the reaction mixture and reaction time dictated whether the final solution at a given contact time will have a dominant acidic or basic character. Inorganic species removal was dependent on the pH regime generated at a specific reaction time. Sulphate concentration was controlled by precipitation of gypsum, barite, celestite and adsorption on iron-oxy-hydroxides at pH > 5.5. Increase of pH in solution with contact time caused the removal of the metal ions mainly by precipitation, co-precipitation and adsorption. PHREEQC predicted precipitation of iron, aluminium, manganese-bearing phases at pH 5.53-9.12. An amorphous fraction was observed to be the most important in retention of the major and minor species at pH > 6.32. The carbonate fraction was observed to be an important retention pathway at pH 4-5 mainly due to initial local pockets of high alkalinity on surfaces of fly ash particles. Boron was observed to have a strong retention in the carbonate fraction.

Keywords: *Acid mine drainage; Fly ash; Neutralization; Residue; Sequential extraction*

INTRODUCTION

Fly ash (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 fly ash per year. This is set to increase until alternative sources of energy are fully developed and commercially exploited. Currently only 5 % of the annual production is beneficially utilized as a cement extender (Krüger, 2003) as a soil ameliorant . The rest is stockpiled or slurried to ash dams (Mattigod *et al.*, 1990; Abbott *et al.*, 2001). Globally, about 88 million tons of fly ash, bottom ash, boiler slag and flue gas desulfurization (FGD) residues are generated in the United States annually and 22 % of these solid wastes are used for beneficial purposes. In China, thermal power plants produce nearly 160 million tons and over 50 % of the fly ash is used in different applications such as bricks manufacture, construction of dams and in the cement industry (Okafor and Opuene, 2007). FA tends to accumulate toxic elements such as heavy metals at the high temperatures involved during its generation (Eary *et al.*, 1990; Spears and Lee, 2004) and is considered an environmental hazard in South Africa and other parts of the world. Anions (Cl^-, SO_4^{2-}), oxy-anions of Se, As, Mo, B and Cr and cations (Al, Fe, Na, K, Ca, Sr, Ba, Zn, Cu, Cd and Mg) are leached from the ash heaps by the wastewater derived from the ash slurry or by subsequent infiltration by rain upon disposal (Adriano *et al.*, 1980; Eary *et al.*, 1990; Mattigod *et al.*, 1990; Reardon *et al.*, 1995; Nameni *et al.*, 2008). Of main environmental concern are the toxic trace elements, Pb, Cr, B, Mo, As and Se (Adriano *et al.*, 1980; Carlson and Adriano, 1993; Abbott *et al.*,

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2001; Spears and Lee, 2004) that are likely to leach upon disposal. The pH of a fly ash suspension for example in water can vary depending on the S content of the parent coal (Plank and Martens, 1974). Fly ash derived from anthracite coals are generally high in S and produce acidic fly ashes while fly ashes derived from lignite coals are low in S but high in Ca and produce alkaline ashes (Furr *et al.*, 1977; Page *et al.*, 1979). South African coal is sub-bituminous and generates fly ash that is characterized by low Fe content. The aqueous extracts of this fly ash are strongly alkaline (pH 12-12.5) due to the free lime content (Foner *et al.*, 1999; Gitari *et al.*, 2006; Gitari *et al.*, 2008).

Acid mine drainage (AMD) often contains high concentrations of heavy metals such as Fe, Mn, Al and anions like SO_4 in addition to elements like Zn, Co, Pb, Cr, Cu, in trace concentrations which necessitate these waters to be treated before release. Acid mine drainage (AMD) is produced when sulphide minerals, such as pyrite, found in association with the coal or overburden come into contact with oxygen and water during mining. Sulphide minerals undergo bacterially-catalysed oxidation reactions which generate acidity and increases Fe, sulphate and other toxic elements concentrations in recipient water bodies (Eq. 1).

$$FeS_{2(s)} + 3.5O_2 + H_2O \Rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

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 (Younger *et al.*, 2002).

The neutralization of AMD with various liming agents such as limestone (Cravotta and Mary, 1999; Maree *et al.*, 1992) and lime (Jenke and Gordon, 1983) have been studied extensively. These are the main techniques applied in remediation of acidic mine waters. Some of the limitations of these treatment processes include armoring of limestone particles by the precipitating amorphous ferric hydroxides which reduce efficiency of neutralization and the maximum pH of 7 attained which leaves contaminants such as Mg largely in solution (Maree *et al.*, 1996). A limitation of lime is the high cost involved (Maree *et al.*, 1996). Fly ash has been evaluated by several researchers for its ability to control acid generation in sulphidic mine tailings and mine spoils (Abbott *et al.*, 2001; Xenidis *et al.*, 2002; Pérez-López *et al.*, 2007a-c) and removal of contaminants from aqueous solution (Agyei *et al.*, 2002; Erol *et al.*, 2005; Gitari *et al.*, 2006; Abdel-Ghani *et al.*, 2009). In all these applications the alkaline property of the fly ash was utilized to increase the pH of the solutions and consequently induce contaminants attenuation mechanisms such as precipitation, co-precipitation and adsorption. These authors also observed that the contaminant removal capacity of the fly ash depended strongly on their CaO content.

The highly soluble CaO occurring as sub-micron fragments on the fly ash particles makes it attractive as a liming agent for acidic mine water. In South Africa most power stations producing fly ash are located near the coal mining sites which adds on to the economic viability of the process in addition to being available in large quantities. This survey is a follow up of an article published earlier by the present article author and reported the application of fly ash to neutralize and remove major contaminants in AMD (Gitari *et al.*, 2008). The temporal evolution of the leachate chemistry with time was evaluated. However this treatment option will lead to generation of solid residues that require disposal and one proposed disposal technique is backfill in mine voids. A limitation of the backfill application would be the possible leaching of trace elements with possible contamination of groundwater. In trying to address the suitability of the solid residues as possible backfill material, the present survey presents an assessment of the metal mobility in the solid residues from the AMD treatment. The survey traces the transformation of the contaminants both from AMD and fly ash as they interact and form secondary mineral phases and as the trace elements get adsorbed in the amorphous secondary phases formed. Understanding the physico-chemical phases that these elements partition on will greatly aid in predicting their possible leaching behaviour on disposal.

Phase-selective chemical extractions involving multiple extracting agents is one of the approachs utilized to understand the distribution of metals in a sediment (Tessier *et al.*, 1979; Shuman, 1985; Ure *et al.*, 1993). Metals in sediments or precipitates may be present in several different physicochemical phases that act as reservoirs or sinks of trace elements in the environments (Jenne, 1977; Beckett, 1988; Sposito, 1983; Mahvi, 2008). These phases include broad categories such as: water soluble, exchangeable; specifically adsorbed; carbonate; secondary Fe and Mn oxides; organic matter; sulphides and silicates. All of these may occur in a variety of structural forms. The sequential extraction schemes can be a very useful method, for characterizing solid phases associated trace elements in soils, sediments or particulates (Adamo *et al.*, 1996; Ma and Rao, 1997; Mohsenzadeh *et al.*, 2006; Karbassi *et al.*, 2008; Feng *et al.*, 2009). In this study, the sequential extraction procedure is intended to semi-quantitatively evaluate the trends of mass transfer of major and selected trace elements from AMD and FA to the resulting precipitates admixed with residue matrix of the fly ash as the pH of the system evolves and also confirm to some extent the contaminants removal mechanisms observed in the treatment process.

MATERIALS AND METHODS

Sample description

The fly ash used was obtained directly from a coal combustion power generating station in South Africa and kept in tightly locked PVC buckets to prevent ingress of CO_2 which leads to loss of alkalinity (Campbell, 1999). AMD samples were obtained from a coal washing plant in Mpumalanga, South Africa. The samples were scoped from a holding dam by use of 5 L high density polyethylene containers which were initially rinsed with 2 % ultra-pure nitric acid solution. The containers were rinsed thoroughly with the AMD before sampling. Samples were preserved with ice in cool boxes until refrigeration in the laboratory. Total elemental analysis of FA and solid residues (SR) was done on powder briquettes by X-ray fluorescence (XRF) and reported in % w/w for major and ppm for trace elements. Samples of raw AMD and reaction mixture were filtered through a 0.45 µm nucleopore membrane and the filtrate analysed for the major elements, trace elements and SO_4^{2-}. Cation analysis of the aqueous samples was done by inductively coupled plasma-mass spectrometer (ICP-MS: ELAN 6000). The accuracy of the analysis was monitored by use of NIST water reference material. Fe^{2+}/Fe^{3+} analysis was done by the colorimetric method using 2,2-bipyridal as the complexing reagent. SO_4^{2-} analysis was done by Ion Chromatography (Dionex DX-120). The results of the chemical characterization of the samples used are presented in Tables 1 and 2.

Neutralization reactions

The fly ash/AMD neutralization experiments were conducted by stirring a mixture of fly ash and AMD in which the fly ash and AMD were weighed to give a specific FA: AMD ratio. Two FA: AMD ratios 1:3 and 1:1.5 were investigated. The AMD was stirred for 30 min for equilibration before the fly ash was added. An overhead stirrer was used for all the experiments. The progress of the reaction was monitored by measuring the pH and electrical conductivity (EC) with a Hanna HI 991301 portable pH/EC/TDS/temperature probe. The probe was calibrated for pH by use of buffer 4.01 and 7.01 and the accuracy ascertained with a buffer 10.01 solution. Conductivity calibration was ascertained by use of 12.88 mS/cm conductivity standard solution. The reactions were stopped at designated reaction times and pH. The mixture was filtered through 0.45µm nucleopore membrane and the filtrate analyzed for the major elements, trace elements and SO_4^{2-}. Cation analysis of the water samples was done by ICP-MS (ELAN 6000). SO_4^{2-} analysis was done by Ion Chromatography (Dionex DX-120).

X-ray diffraction (XRD) analysis and calculation of saturation states

XRD spectra of the powder mounts of the solid residues were obtained by step-scanning at intervals of 0.02^0 2θ from 5^0 to 85^0 and counted for 0.5 s per step. A Phillips PANalytical instrument was used with a pw3830 x-ray generator operated at 40 kV and 25 mA. The X'pert graphics and identify program was used to identify the mineral phases using the JCPDF database. Activities of aqueous species and mineral saturation indices of selected mineral phases were calculated using PHREEQC code (Parkhurst, 1995) and the WATEQ4F database (Ball and Nordstrom, 1991).

Selective sequential extractions

The extraction scheme adopted is a combination of the methods developed by Chao, (1972); Tessier *et al.* (1979) and Muller and Seiller (1999) with addition of the amorphous Fe, Mn and Al oxyhydroxide fraction. Six operational fractions were selected. One of the approachs to understand the distribution of metals in sediment is done by phase-selective chemical extractions involving multiple extracting agents (Tessier *et al.*, 1979; Shuman 1985; Ure *et al.*, 1993). The reagents utilized in sequential extraction are chosen such that they are selective and specific towards a particular physico-chemical form. The reagents destroy the binding agents between the metals and the sediments allowing them to be released into solution. Sequential extractions were performed on the equivalent masses ranging from 1-10 g dry matter for the solid residues recovered from the 1:3 FA: AMD reactions. The % moisture content of the solid residues were determined on separate portion of the wet solid residues by drying at 105 °C for 12 h for each extraction and this value was used to calculate the mass of dry solid residues used in each experiment. The extraction was carried out by agitating the samples in a table shaker.

After each extraction, samples were centrifuged at 1000 rpm for 10 min and the supernatant filtered through a 0.45 µm nucleopore membrane. The extracted solid residue sample was then washed with milliQ water, centrifuged, the supernatant decanted and discarded. The extraction was done in triplicate. For each extraction a blank sample was prepared using the extraction reagents and analyzed to account for any background contribution. In addition NIST-1640 water standard reference material was analyzed for every batch of 20 samples for quality control. The extraction was done for both the fresh FA and solid residues (SR) recovered at pH 4, 4.92, 6.32 and 9.12 for FA: AMD ratio of 1:3.The extraction sequence consisted of six stages.

The procedure for extraction was as follows:

- Water soluble fraction- 10 g of the wet solid residues in 100 mL MilliQ water were agitated for 1 h. This sample was initially washed by shaking with 10 mL MilliQ water for 5 min and the liquid extract discarded. This was done to remove the dissolved components from the batch experiments.
- Exchangeable fraction-7 g of wet solid residues recovered from the water soluble fraction was extracted with 70 mL of $MgCl_2$ solution (1 M $MgCl_2$ solution) at pH 7, by continuous agitation for 1 h at room temperature (Tessier *et al.*, 1979).
- Carbonate fraction-6 g of the wet solid residues recovered from the exchangeable fraction were extracted with 60 mL of 1 M sodium acetate/acetic acid buffer solution at pH 5 by agitating continuously for 5 h (Tessier *et al.*, 1979).
- Crystalline Mn-oxides -5 g of the wet solid residues recovered from the carbonate fraction were extracted with 125 mL of 0.1 M hydroxylamine hydrochloride prepared in 0.01 M HNO_3 at pH 2 for 30 min by continuous agitation (Chao, 1972; Shuman, 1985).
- Amorphous Fe, Mn, Al- oxides, (oxy) hydroxides-4 g of the wet solid residues recovered from the crystalline Mn-oxide fraction was extracted with 800 mL of the 0.2 M ammonium oxalate/oxalic acid buffer at pH 3 for 4 h in the dark (Cornell and Schwertmann, 1996).
- Crystalline Fe oxides-2- 2.5 g of the wet solid residues recovered from the amorphous Fe, Mn, Al- oxides, (oxy) hydroxides fraction were extracted with 60-75 mL of ammonium oxalate monohydrate 0.2 M + oxalic acid 0.2 M + 0.1 M ascorbic acid mixture at pH 3.25 by agitating for 30 min in a water bath maintained at 95 ± 5 °C (Muller and Seiller, 1999).

Between each extraction step a sub-sample was kept aside for moisture content determination.

RESULTS AND DISCUSSION

Chemical characterization of fly ash and acid mine water

The XRF results (Table 1) show that the fly ash consists of three main components: Al_2O_3, Fe_2O_3 and SiO_2 confirming that it's an alumino-silicate material. Major phases detected by XRD were mullite and quartz (data not shown). Among the minor elements, Sr, Ba, Cr, Zr and Ni occur in high concentration. Traces of Mo are also present. These concentrations are within the ranges reported by Eary *et al.* (1990). The AMD is strongly acidic (pH 2.19). Major elements include Al, Mn, Fe^{3+}, Fe^{2+} and SO_4^{2-}. The AMD has high SO_4^{2-} content (Table 2) typical of leachate from sulphide rich coal mine tailings and underground mine water (Uhlmann *et al.*, 2004).

Composition of solid residues

The results of XRF analysis of the SR samples collected at pH 9.0 for 1:3, FA: AMD ratio are shown in Table 1. A comparison of the composition of FA and the SR indicates a decrease in SiO_2, CaO and MgO. The decrease in SiO_2 reflects the dissolution of amorphous SiO_2 at low pH while the decrease in CaO and MgO content in the solid residues reflects the dissolution of free lime and MgO which is responsible for the neutralizing capacity of the fly ash. An increase in Fe_2O_3, Al_2O_3 and MnO in the solid residues indicates the removal of these elements from AMD as insoluble precipitates.

Reaction of acid mine drainage with fly ash: pH profiles.

The evolution of pH values with time for the 1:3 and 1:1.5 FA: AMD ratios are presented in Fig. 1a. The pH values for the 1:3 ratio are characterized by

Table 1: Composition of fly ash and solid residues collected at pH 9.2 for 1:3: fly ash: acid mine drainage ratio

Fly ash				Solid residues (SR)	
Elements	Concentration (% w/w)	Elements	Concentration (mg/kg)	Elements	Concentration (% w/w)
SiO_2	52.4 ± 2.360	Cu	45.3 ± 6.600	SiO_2	45.81 ± 3.600
TiO_2	1.34 ± 0.050	Mo	5.5 ± 1.230	TiO_2	1.29 ± 0.060
Al_2O_3	23.4 ± 1.080	Ni	92.4 ± 6.500	Al_2O_3	22.57 ± 2.100
Fe_2O_3	4.72 ± 0.960	Pb	57.4 ± 13.60	Fe_2O_3	6.31 ± 1.290
MnO	0.06 ± 0.001	Sr	1465.9 ± 113.8	MnO	0.1 ± 0.010
MgO	2.67 ± 0.035	Zn	54.3 ± 4.710	MgO	2.33 ± 0.650
CaO	8.41 ± 0.574	Zr	478.1 ± 125.7	CaO	7.18 ± 2.620
Na_2O	0.35 ± 0.253	Co	16.2 ± 13.08	Na_2O	0.4 ± 0.014
K_2O	0.48 ± 0.032	Cr	181.2 ± 1.140	K_2O	0.53 ± 0.130
P_2O_5	0.34 ± 0.212	V	147.4 ± 39.00	P_2O_5	0.63 ± 0.040
Cr_2O_3	0.03 ± 0.009	Ba	931 ± 95.20	Cr_2O_3	NA
SO_3	NA			SO_3	3.52 ± 0.210

Results presented as mean ± SD for N = 3

Table 2: Chemical and physical characteristics of acid mine drainage (concentration in mg/L except for pH, EC and acidity)

Parameter	Concentration	Parameter	Concentration
pH	2.19 ± 0.02	Ni	6.16 ± 1.230
EC (mS/cm)	15.77 ± 0.01	Cu	7.10± 2.140
Acidity (mmol H^+/L)	289 ± 1.01	Zn	15.71 ± 3.460
B	10.3 ± 1.26	Se	10.39 ± 0.023
Na	102.9 ± 10.6	Sr	1.95 ± 0.021
Mg	399.4 ± 30.7	Mo	0.014 ± 0.002
Al	453.4 ± 17.9	Ba	0.108 ± 0.003
Si	99.2 ± 9.43	Pb	0.455 ± 0.022
Ca	146.9 ± 12.5	SO_4^{2-}	24880 ± 96.70
Mn	95.8 ± 7.89	Cl^-	370 ± 55.60
Fe^{2+}	4444.9 ± 59.8	NO^{3-}	90 ± 20.30
Fe^{3+}	2065.6 ± 10.3		

Results presented as mean ± SD for N = 3

two buffer regions, at pH 4 - 4.5 and pH 6.0. The 1:1.5 ratio shows two buffer regions, at pH 4.5 - 5.0 and at pH 9.0. However, the buffering exhibited by the AMD at the 1:1.5 ratio is stronger. This is evident from the lower gradient of the curves at this buffer region for this ratio. The dissolution of oxide components such as CaO and MgO (Table 1) from fly ash contributes to an increase in solution pH.

Offsetting the pH increase is the hydrolysis of AMD constituents such as Fe^{3+}, Al^{3+}, oxidation of Fe^{2+} to Fe^{3+} and subsequent hydrolysis to ferric hydroxides, this would explain the strong buffering plateaus observed at pH 4-6.5.

Profiles of the major and minor inorganic contaminants with reaction time

The trends of the major inorganic species are shown in Figs. 1 b- j while the minor and trace inorganic species in the process waters with reaction time and pH for both ratios are shown in Table 3.

Sulphate

The AMD samples were characterized by high SO_4^{2-} levels (24880 mg/L) (Fig. 1 b). A decreasing SO_4^{2-} concentration to a minimum was observed with time for both FA: AMD ratios. The 1:1.5 ratio registered a large decrease at pH > 7 than the 1:3 ratio. The fact that SO_4^{2-} concentration did not double on increasing the amount of fly ash in the mixture (i.e, 1:1.5 FA: AMD ratio) means that a solubility control for SO_4^{2-} exists. The increase in pH of the reaction mixture is attributed to the dissolution of CaO in the fly ash releasing Ca^{2+} ions which interacts with SO_4^{2-} to form gypsum. Geochemical calculations with PHREEQC predicted saturation of the solution with gypsum for the entire reaction time for both ratios (Figs. 2 a and b). In addition

Al-(oxy)hydroxysulphates such as alunite, basaluminite and jurbanite could also have contributed to low SO_4^{2-} levels at pH < 7. PHREEQC predicted saturation of the process waters with these oxy hydroxysulphates at pH < 7 (Fig. 2 c and d). Fe-(oxy) hydroxides precipitating at pH > 7 are also known to

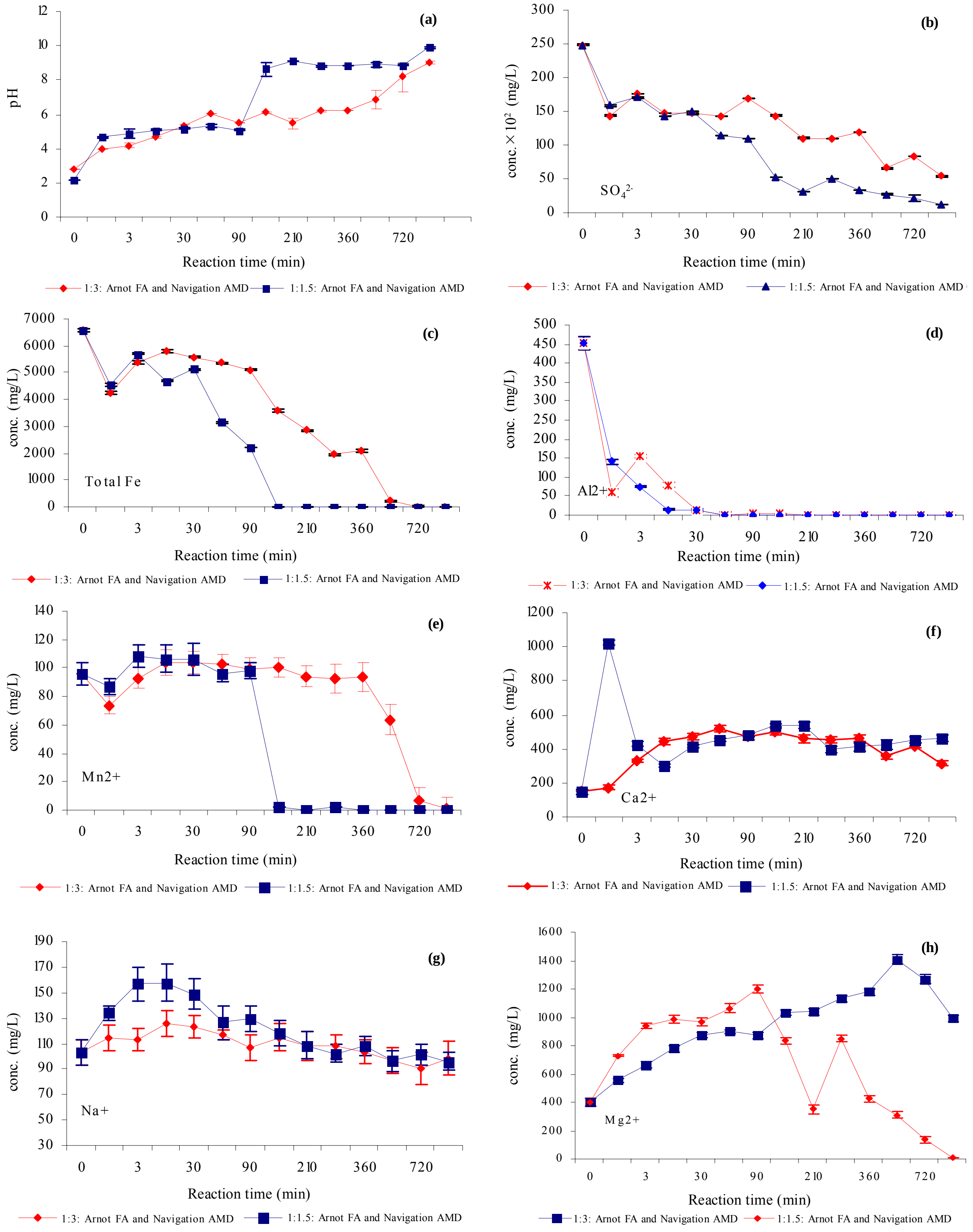

Fig. 1: Variation of pH, SO4^{2-}, Al^{3+}, Total Fe, Ca^{2+}, B, Mn^{2+}, Mg^{2+}, Sr and Na^{+} with reaction time (min) in process waters for 1:3 and 1:1.5 FA: AMD ratio. Error bar represents 1 SD above and below the mean (N = 3) (Gitari *et al.*, 2008). Reproduced with permission from Elsevier publishers.

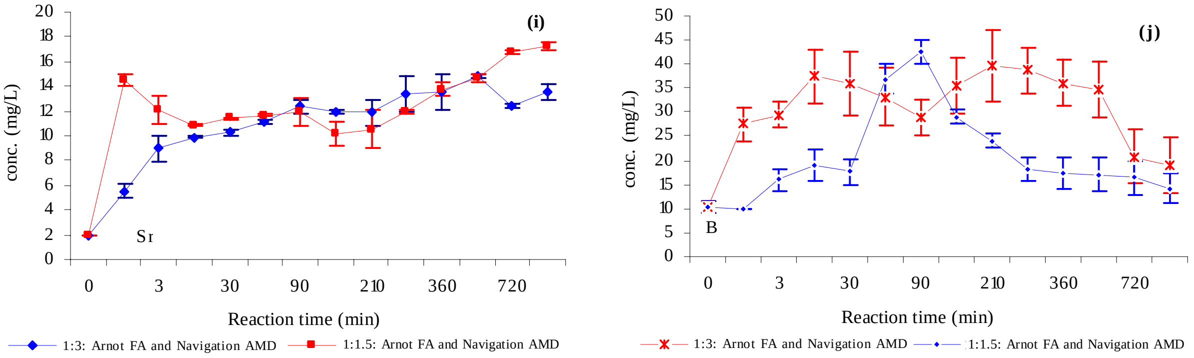

Fig. 1 (Continued): Variation of pH, SO4^{2-}, Al^{3+}, Total Fe, Ca^{2+}, B, Mn^{2+}, Mg^{2+}, Sr and Na^{+} with reaction time (min) in process waters for 1:3 and 1:1.5 FA: AMD ratio. Error bar represents 1 SD above and below the mean (N = 3) (Gitari *et al.*, 2008) Reproduced with permission from Elsevier publishers.

Table 3: Minor and trace contaminants removal as a function of pH and reaction time (min) for FA: AMD ratios of 1: 3 and 1:1.5

1:3 FA: AMD ratio					
Reaction time (min)	AMD	3	15	270	1440
Elements	Concentration in mg/L except pH				
Si	99.16 ± 9.430	74.64 ± 6.400	65.26 ± 4.580	6.71 ± 0.980	0.853 ± 0.003
Cu	7.10 ± 2.140	2.24 ± 0.004	2.09 ± 0.034	0.023 ± 0.013	0.008 ± 0.002
Zn	15.71 ± 3.460	14.18 ± 2.350	13.37 ± 1.070	0.783 ± 0.023	0.192 ± 0.001
Se	0.390 ± 0.023	0.119 ± 0.004	0.027 ± 0.002	0.032 ± 0.002	0.146 ± 0.003
Mo	0.014 ± 0.002	0.027 ± 0.030	0.057 ± 0.003	0.163 ± 0.001	0.834 ± 0.003
Pb	0.455 ± 0.022	0.014 ± 0.002	0.059 ± 0.005	0.002 ± 0.001	0.002 ± 0.001
pH	2.78 ± 0.010	4.17 ± 0.010	4.92 ± 0.100	6.32 ± 0.030	9.12 ± 0.005
1:1.5 FA: AMD ratio					
Reaction time (min)	AMD	3	30	90	480
Elements	Concentration in mg/L except pH				
Si	99.16 ± 9.430	95.6 ± 6.54-	77.64 ± 3.980	14.5 ± 3.410	1.19 ± 0.011
Cu	7.1 ± 2.140	7.79 ± 1.302	7.55 ± 0.431	0.782 ± 0.017	0.009 ± 0.003
Zn	15.71 ± 3.460	15.63 ± 2.103	10.05 ± 1.460	1.61 ± 0.014	0.131 ± 0.001
Se	0.39 ± 0.023	ND	0.694 ± 0.003	0.162 ± 0.002	0.25 ± 0.006
Mo	0.014 ± 0.002	0.107 ± 0.002	0.118 ± 0.001	0.307 ± 0.003	0.8 ± 0.035
Pb	0.455 ± 0.022	0.255 ± 0.002	0.164 ± 0.002	0.013 ± 0.001	0.005 ± 0.002

adsorb large quantities of SO_4^{2} and could also have contributed to the low levels observed (Seth and Elliot, 2000).

Total Iron

Both ratios registered greater than 90 % removal on the reaction mixture attaining pH greater than 7 (Fig. 1c). The initial decrease in concentration for both ratios at pH 4-4.5 indicates removal of Fe^{3+} inform of hydroxides or oxyhydroxysulphates. The significant drop observed at pH greater than 7 is attributed to the rapid oxidation of $Fe^{2+}$and subsequent hydrolysis of Fe^{3+} to form insoluble hydroxides. Optimum oxidation of Fe^{2+} occurs at pH ≈ 7 (Stumm and Lee, 1961). The AMD samples were characterized by high concentrations of Fe^{2+} as compared to Fe^{3+} (Table 2). Geochemical calculations indicated that the solution was over-saturated with $Fe(OH)_{3(a)}$, goethite, ferrihydrite and hematite for both ratios (Figs. 2 e and f). In our previous reported findings (Gitari *et al.*, 2008) although schwertmannite was predicted to be precipitating, activity plots revealed that the ferric hydroxides were controlling the Fe^{3+} activity in the process waters. Substitution or adsorption of SO_4^{2-} for hydroxide ions on ferrihydrite and formation of schwertmannite-like phase has been proposed and could also have contributed to low levels of SO_4^{2-} (Nordstrom and Alpers, 1999). XRD analysis however did not reveal any Fe-bearing mineral phases probably due to their amorphous nature.

Aluminium

For both ratios Al concentration was observed to

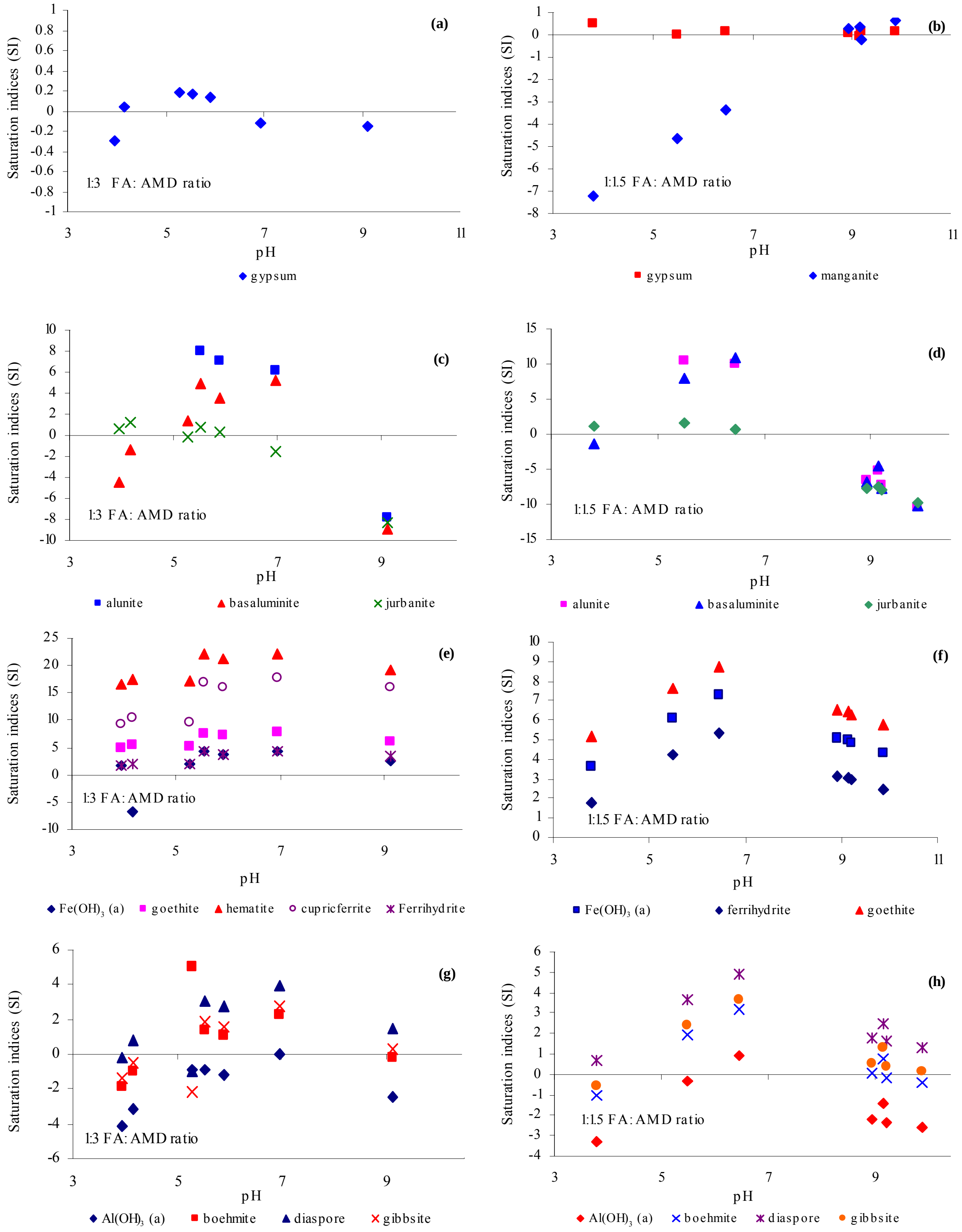

Fig. 2: Saturation indices of selected mineral phases for 1:3 and 1:1.5 FA: AMD ratios as a function of pH

decrease steadily with increasing pH (Fig. 1d). At pH greater than 5, 95 % of the Al was removed from solution. Geochemical calculations with PHREEQC indicated that the solutions were over-saturated with jurbanite at pH 3.96-5.9, basaluminite, boehmite and alunite at pH 5.28-6.95, gibbsite and diaspore at pH 5.53-9.12 (Figs. 2g and h).

Silicon

A steady decline in Si concentration was observed for both ratios as the pH increased (Table 3). The decrease in Si was attributed to formation of Ca-Si-O, Ca-Mg-Si-O rich gels as the pH increased. Previous SEM-EDX analysis of the solid residues from neutralization of AMD by fly ash indicated presence of Ca-Mg-Si rich gels (Gitari *et al*., 2008).

Manganese

Both ratios exhibited a similar trend in the removal of Mn^{2+}. Concentrations were observed to increase to a maxima at pH 4.5-4.9 for both ratios. Near complete removal of Mn^{2+} was observed as the reaction mixture attained pH 7-9 (Fig. 1e). PHREEQC geochemical calculations indicated the solution to be at saturation or over-saturation with manganite at pH greater than 8.5 for ratio 1:1.5 (Fig. 2b).

Zinc, Copper and Lead

Cu exhibited different removal trends for the two FA: AMD ratios. For 1:3 FA: AMD ratio a significant drop was observed at pH e” 4 while for 1:1.5 FA: AMD ratio a significant drop was observed at pH > 5.7 (Table 3). In the 1:3 FA: AMD ratio removal of Cu could be mainly through adsorption on the iron (oxy) hydroxides that formed during the neutralization process while in 1:1.5 ratio it could be attributed to precipitation reactions. According to Brittons (1956) Cu hydroxide precipitates at pH ≈ 5.3 while Zn hydroxide precipitates at pH 7. Zn removal followed a similar pattern for both ratios with concentration significantly reducing at pH e” 6 suggesting precipitation as the main mechanism. PHREEQC simulation predicted the solution to be super-saturated with CupricFerrite ($CuFe_2O_4$) suggesting co-precipitation as the main mechanism responsible for Cu removal (Fig. 2 e). Pb removal in the process water followed the same trend in both ratios (Table 3). Concentration decreased steadily with increasing pH to near detection limits at pH ≈ 9. The removal trends suggest precipitation as the main mechanism responsible for Pb removal.

Sodium, magnessium, calcium and strontium

These species in addition to their presence in AMD are also released in significant quantities in the reaction mixture. Their release results from dissolution of their soluble salts on the surface of the fly ash particles. The concentration profile reveals a peak at between 15-270 min of reaction time for 1:3 ratio and between 30-90 min of reaction time for 1:1.5 ratio, the concentration was observed to decrease as the pH increased. A substantial concentration of these species remains largely in solution compared to the initial concentration in the AMD (Figs. 1 f- i). PHREEQC modeling predicted formation of Na-jarosite at pH (3.8-6.95) and celestite at pH (3.8-9.88) for both ratios. Ca plays a significant role in the removal of SO_4^{2-} as gypsum (Figs. 2 a and b).

Boron, molybdenum and selenium

Boron is one of the highly mobile elements associated with fly ash. A steady increase in concentration to a maxima for B was observed for both ratios with a significant decrease at pH ≥ 9 (Fig. 1 j). The decrease in B at alkaline pH has been attributed to its interaction with Ca-bearing mineral phases such as calcite and ettringite (Kitano *et al.*, 1978; Akira *et al.*, 2005). SEM analysis revealed presence of ettringite for solid residues collected at pH e” 9 in previous AMD neutralization experiments with fly ash (Gitari *et al.*, 2008). Mo remained below 0.3 mg/l at pH< 6.32 for both ratios (Table 3). The concentration significantly increased for both ratios at pH e” 9. Mo exists as the MoO_4^{2-} ion at pH > 3 (Eary *et al.*, 1990) and it is likely that it was removed as metal molybdates at pH< 6.32. This becomes evident at pH > 8 when Fe and Al are out of solution for both ratios. Mo concentration thereafter increases to 0.08 mg/L or greater. Se is observed to follow the same trend as Mo remaining at lower concentration at pH < 6.32 increasing as the pH approaches 8 (Table 3). This is more evident for the 1:3 FA: AMD ratio. Se also exists as oxyanion at neutral to alkaline pH and its removal could be through formation of metal selenites and selenates or adsorption on Fe, Al-oxides, oxy-hydroxides.

Selective sequential extractions (SSE)

The hypothesis that major and trace elements from both fly ash and AMD are transformed into non-labile mineral phases was tested.

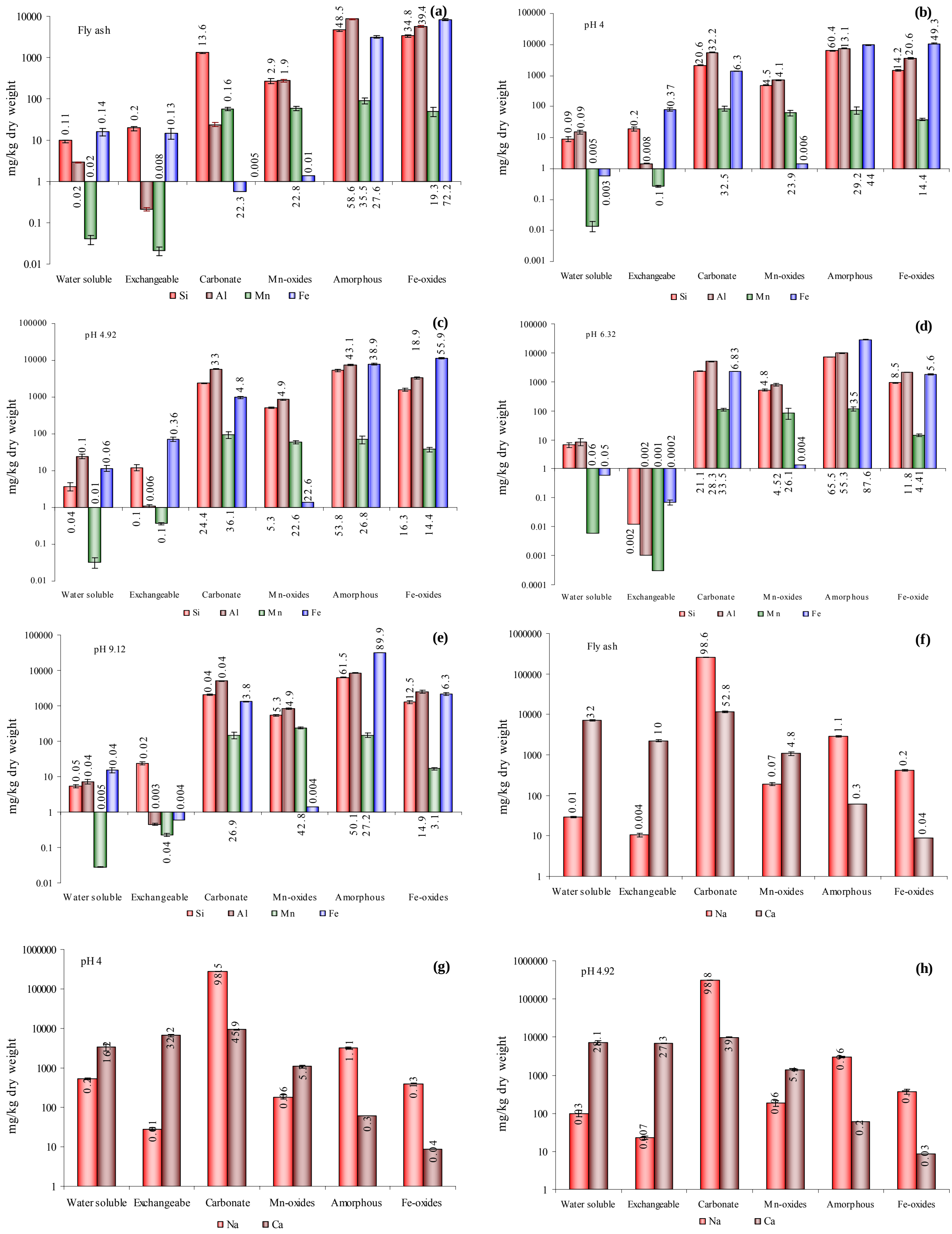

Fig. 3: Extractable concentrations (mg/kg dry weight) for various fractions as a function of pH (numbers on the bars represent % contribution of each element for each extracted fraction for fly ash and solid residues)

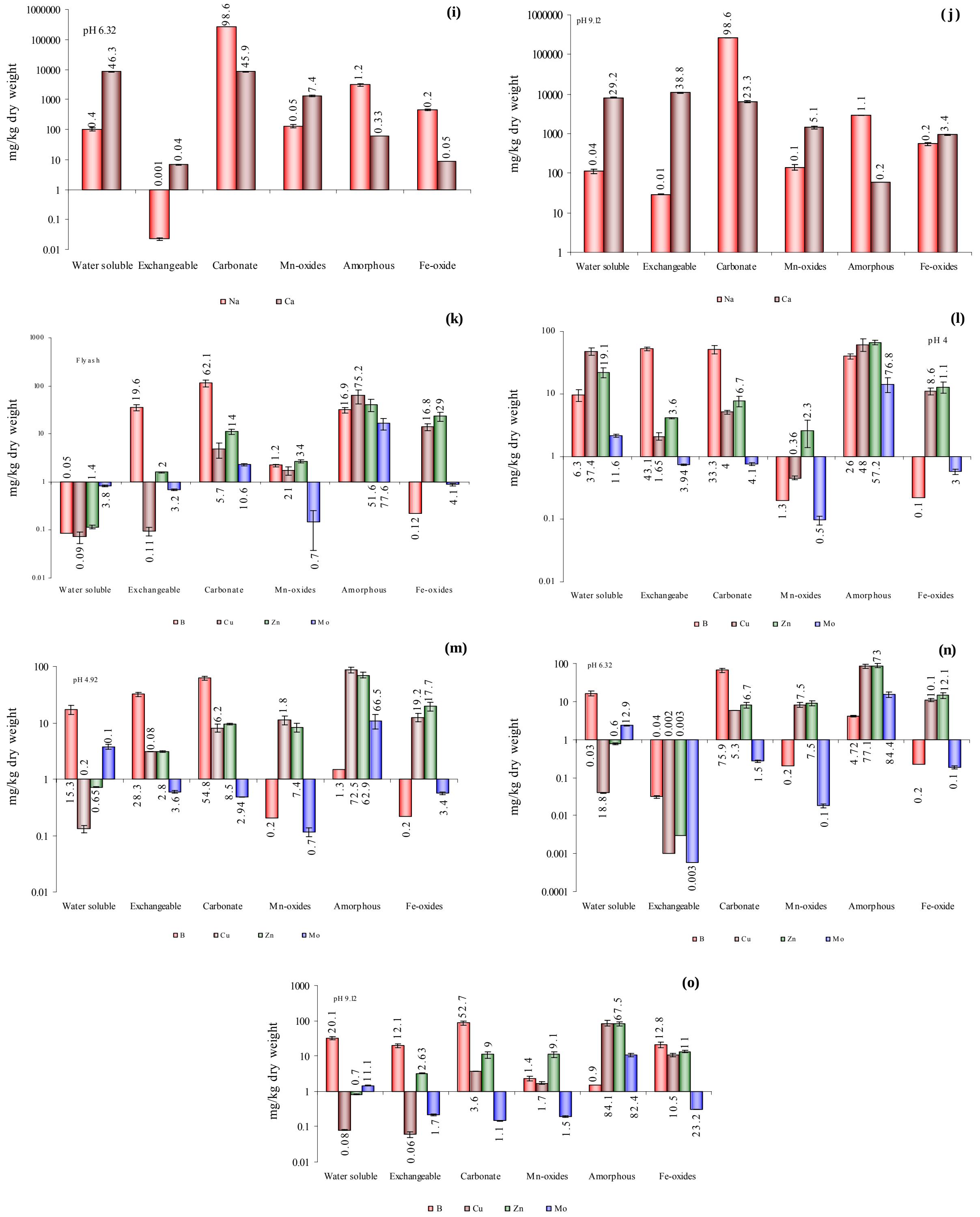

Fig. 3 (Continued): Extractable concentrations (mg/kg dry weight) for various fractions as a function of pH (numbers on the bars represent % contribution of each element for each extracted fraction for fly ash and solid residues)

The residue fraction after sequential extraction was ignored since it contains non-labile elements locked up in the residue aluminosilicate matrix of the fly ash and was assumed to be of less significance in dictating the redistribution of the elements in the resulting mineral phases. The results are discussed with respect to the increase in pH and precipitation of Fe, Mn and Al, the major species in AMD. The total extracted amounts in mg/kg dry weight for the six fractions is used to derive the % contribution of each element for each extracted fraction for fly ash and solid residues collected at pH 4, 4.92, 6.32 and 9.12. The results of the sequential extraction are presented in Fig. 3.

Al, Fe, Mn and Si concentration profiles

The distribution of Al, Fe and Mn in the fly ash indicates their occurrence in the amorphous and in crystalline Fe and Mn-bearing phases (Fig. 3 a). On contact with AMD these solid phases release Fe, Mn and Al into solution which on elevation of pH re-precipitates to form amorphous (oxy) hydroxides. The trends for the three elements represents a relocation to the amorphous fraction as the pH of the reaction mixture increases (Figs. 3 b - e).The high proportion of Al (39.4 %) in Fe-oxide fraction in fly ash represents its occurrence as $Ca_6Al_4Fe_2O_{15}$ crystalline phases (Mattigod *et al.*, 1990) and the decrease in content in this fraction as the pH increases probably represents its dissolution and relocation to the carbonate and amorphous phases (Figs. 3 b - e). At pH 4 a significant portion (32.2 %) is retained in the carbonate fraction. The solid residues at pH 4 were collected after only 3 min of reaction time which means pockets of high alkalinity accompanied by ingress of CO_2 existed especially at the surface of fly ash particles that could have led to local precipitation of metal carbonates (Fig. 3 b). At pH > 6.32 the amorphous fraction became the dominant phase retaining Al, indicating a significant proportion of Al from AMD was hydrolyzing to form amorphous (oxy) hydroxides. However the carbonate fraction still retains a significant proportion at this pH range (28.3-30 %) (Figs. 3 d and e).

The high % (22.3) of Mn in the carbonate and Mn-oxide fraction (22.8 %) (Fig. 3 a) indicates the presence of Mn in the fly ash as $MnCO_3$, MnO or Mn_3O_4 respectively (Eary *et al.*, 1990). The 19.3 % present in Fe-oxide fraction represents Mn present in the spinel type solids which include magnetite, ferrite and hematite (Eary *et al.*, 1990). A significant portion (35.5 %) is locked up in the amorphous phase (Fig. 3a). At pH 4-5 there is increased content in the carbonate fraction due to local pockets of high alkalinity and ingress of CO_2 leading to formation of carbonates. At pH 6.32 the amorphous and carbonate fractions (Fig. 3d) become significant in the retention of Mn. However as the solution attains pH 9.12 the Mn-oxide and amorphous fractions become important (Fig. 3 e). At pH > 7 Mn^{2+} oxidation is fast (Eary *et al.*, 1990) and PHREEQC modeling predicted precipitation of manganite.

Fe is present in fly ash mainly as crystalline Fe-oxides (72.2 %) and in amorphous form probably as Ca, Al ferric phases (Mattigod *et al.*, 1990). These phases on contact with highly acidic AMD undergo dissolution releasing Fe^{3+} into the reaction mixture. This is observed in the decreased content in the Fe-oxide and amorphous fraction at pH 4 (Fig. 3 b). However a significant proportion is relocated to the carbonate fraction at this pH re-affirming the existence of local pockets of high alkalinity and ingress of CO_2 leading to the precipitation of metal carbonates. As the solution attains pH 6.32 the amorphous fraction becomes significant in retention of Fe (87.6-89.9 %) (Figs. 3 d and e). This coincides with the pH of optimum oxidation Fe^{2+} and hydrolysis of Fe^{3+} which indicates that it is hydrolyzing mainly to amorphous Fe (oxy) hydroxides.

The Si trend shows a redistribution amongst three fractions as the fly ash interacts with AMD: amorphous, Fe-oxide and carbonate fractions. At pH > 4 the amorphous fraction becomes most important in retention of Si (Figs 3 c- e).

Ca and Na concentration profile

Ca trends in the extracted fractions represent a redistribution between three phases: water soluble, exchangeable and carbonate (Figs. 3 f- j). In the fly ash Ca is highest in carbonate fraction (52.8 %) indicating its presence as a carbonate phase and water soluble fraction (32 %). As dissolution occurs on contact with AMD redistribution occurs in the three fractions, however water soluble and the carbonate fractions still retain a significant proportion of the total Ca. Retention of Ca in the carbonate fraction despite dissolution at acidic pH indicates that formation of calcite due to ingress of CO_2 was taking place. Formation of soluble anhydrite or gypsum at acidic pH and high SO_4^{2-} content could also account for the increased retention in the water soluble fraction (Fig. 3 g). At pH 9.12 the exchangeable fraction becomes significant in retention of Ca as water soluble and carbonate fractions (Fig. 3 j).

Na shows redistribution amongst three fractions: water soluble, amorphous oxides and crystalline Fe-oxide. In the fly ash Na is mainly present in the carbonate fraction (98. 6 %) which suggests its occurrence as a carbonate. Na remains retained in the carbonate fraction as the pH increases to 9.12, and remains at H” 1.0 % in the amorphous fraction for the entire experiment (Fig. 3 i). However it should be noted that there is release of Na into the reaction mixture judging by the total of the six fractions as the pH increases (Figs. 3 f - j). The high retention of both elements in the carbonate fraction at pH 4 (Fig. 3 f) suggests that at 3 min of reaction time due to inadequate mixing local pockets of high alkalinity existed especially at the particle surfaces and ingress of CO_2 accompanied by the formation of CO_3^{2-} could have led to the precipitation of $CaCO_3$ and Na_2CO_3.

Cu and Zn concentration profile

The Cu profile shows redistribution within three fractions: amorphous, water soluble and Mn-Fe-oxide fractions as the pH increases (Figs. 3 k - o). The high Cu percentage (75.2 %) in the amorphous fraction in fly ash indicates it’s presence in the amorphous aluminosilicate glass matrix (Hullet *et al.*, 1980). The 16.8 % (Fig. 3k) in Fe-oxide fraction shows incorporation in the magnetic fraction consisting of spinel type solids such as magnetite, ferrite and hematite (Hullet *et al.*, 1980). At pH 4 dissolution of the Cu bearing mineral phases is observed to occur with relocation to the carbonate fraction due to the local development of high concentrations of CO_3^{2-} as result of ingress of CO_2 (Fig. 3 l). At pH > 5 the amorphous and Fe-Mn-oxide fraction become significant in retention of Cu indicating the importance of adsorption processes in controlling the attenuation of Cu (Figs. 3 m - o). Zn is observed to be undergoing redistribution in amorphous, Fe, Mn-oxides fractions. The carbonate fraction seems to be important at pH 4 (Fig. 3 f) and as the solution attains pH > 5 (Figs. 3 m - o). The significance of the two fractions: amorphous, Mn Fe-oxide, indicates the importance of the adsorption processes in controlling the attenuation of Zn as the pH increases.

B and Mo concentration profiles

In the fly ash 62.1 % of the B is present in the carbonate fraction and a significant fraction is present in the exchangeable (19.6 %) and amorphous fractions (16.9 %) (Fig. 3k). Several authors have observed association of borate-boron with calcite (Kitano *et al.*, 1978; Akira *et al.*, 2005) and this probably explains the high concentration observed in the carbonate fraction. An observation of Ca trends indicate occurrence of 52.8 % in the carbonate fraction which reinforces the borate-boron-calcite association at alkaline pH. A significant percentage (77.6 %) of Mo is present in the amorphous fraction in the fly ash and also in the carbonate fraction (10.6 %) (Fig. 3 k).

An observation of the sequential extraction results (Figs. 3 k - o) indicates that B is being re-distributed among three fractions: exchangeable, carbonate and amorphous oxides as the pH increases. The increase in B concentration in the exchangeable fraction at pH 4.92 probably reflects the adsorption of released $B(OH)_3$. As the pH increases to > 5 most of the B gets partitioned to the carbonate and water soluble fraction with a substantial portion being retained by the crystalline Fe-oxide fraction. An important feature to note is that amorphous fraction is important in retention of B at pH 4 and 6.32. This corresponds to the pH at which Fe^{3+} and Al are precipitated and pH 6.32 at which hydrolysis and precipitation of Fe^{2+} to amorphous Al and ferric (oxy) hydroxides occur.

Mo seem to be redistributed within two main fractions: water soluble and the amorphous oxide (Figs. 3 k - o). As the pH increases and dissolution of the amorphous glass phase in the fly ash occurs, Mo is translocated to the water soluble fraction. This could be a limitation in the application of the fly ash in this process. However at pH 6.32 a significant portion (84.4 %) of the total Mo is retained in the amorphous precipitates (Fig. 3 l). This indicates that hydrolysis and precipitation of Fe^{2+} has an impact in the removal of Mo.

CONCLUSION

The major inorganic species Fe, Mn, Al and SO_4^{2-} seem to be mainly removed through precipitation of amorphous oxides, (oxy) hydroxides and basic hydroxyl sulphates. Precipitation and adsorption on the precipitated amorphous oxides seems to be the main mechanisms of removal of the minor species such as Cu, Zn, Mo and B.

The sequential extraction results reveals that the carbonate fraction is important in retaining all the contaminants at pH 4. This is postulated to be mainly due to local pockets of high alkalinity that existed on initial contact of fly ash particles with AMD. Dissolution of fly ash components is confirmed through the decrease of Fe in the Fe-oxide fraction at pH 4. The importance of the amorphous fraction is confirmed as an important fraction in the retention of the major species Mn, Fe and Al at pH > 6.32. A substantial proportion of Fe is translocated to the amorphous fraction at pH 6.32 confirming that precipitation of Fe as amorphous oxides is a significant clean-up mechanism in this process. Cu and Zn are also observed to increase in the amorphous fraction at pH > 6.32 emphasizing the importance of adsorption processes in the removal of the minor species. Hydrolysis and precipitation of Fe^{3+} was observed to have an impact in the attenuation of Mo. That B has a strong association with calcite formation is evidenced by the increased content in the carbonate fraction at pH > 5 and that the amorphous fraction also plays an important role at pH 4-6.32.

The alkali metals Na, and Ca after the initial dissolution are mainly retained in the carbonate and amorphous fractions with a substantial fraction also retained in water soluble fraction. Mo was retained in the water soluble fraction at pH > 4. The retention in the water soluble fraction presents a risk in the disposal of these solid residues due to possible re-solubilization on contact with water or acidic leachates.

That the amorphous fraction was observed to be the most important in retention of the major and minor species at pH > 6.32 implies that the concentration of total Fe and Al in the AMD being treated will have a direct effect on the efficiency of the treatment process.

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