Chapter 5

Treatment of Acid Mine Drainage with Coal Fly Ash: Exploring the Solution Chemistry and Product Water Quality

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Additional information is available at the end of the chapter

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Abstract

A treatment process for Acid mine drainage (AMD) using coal fly ash (CFA) was developed. AMD was treated with CFA as the alkaline agent at different CFA: AMD ratios and pH, electrical conductivity (EC) evolution monitored over time. In a separate experiment two AMD sources with differing chemistry were treated with the same CFA to evaluate the impact of AMD chemistry on the treatment process and product water quality. Various CFA: AMD ratios were stirred in a beaker for a pre-set time and the process water chemistry determined. pH was observed to increase in a stepwise manner with buffer zones observed at 4-4.5, 4.5-7 and 6-8. AMD with low concentration of Al^{3+}, Fe^{2+}, Fe^{3+} and Mn^{2+} didn't exhibit these buffer zones. Two competing processes were observed to control the evolving pH of process water: dissolution of basic oxides (CaO, MgO) from CFA led to pH increase and hydrolysis of AMD species such as Al^{3+}, Fe^{2+}, Fe^{3+} and Mn^{2+} led to pH decrease. These processes initiated mechanisms such as precipitation, adsorption and ion exchange that led to decrease in inorganic contaminants as the treatment progressed. Inorganic contaminants removal was directly related to amount of CFA in reaction media. Precipitation of insoluble hydroxides and Al, Fe-oxyhydroxysulphates contributed to removal of major and minor chemical species. Precipitation of gypsum contributed to removal of sulphate. Na, K and Mg remained largely in solution after initial decrease. Significant leaching of B, Sr, Ba, and Mo from CFA was observed and was directly linked to amount of CFA in the reaction media. This will be a shortcoming of the treatment process since other processes may be required to polish up the product water. The treatment of AMD with CFA was observed to depend on CFA, AMD chemistry, treatment time and might therefore be site specific.

Keywords: acid mine drainage, coal fly ash, sulfate, neutralization, inorganic contaminants, pH, coal fly ash: acid mine drainage ratios

1. Introduction

The mining industry in South Africa has a huge potential to impact negatively on the environment. Negative impacts include generation of reactive tailings and acid mine drainage (AMD). In South Africa, the Witwatersrand basin alone decants approximately 10–60 mL/day into nearby rivers [1]. AMD is highly acidic (pH 2–4), sulfate-rich and frequently carries a high concentration of inorganic contaminants. AMD is extremely acidic (as low as pH 2.0) and enriched with iron, manganese, aluminum, sulfate, and metal species such as lead, mercury, cadmium, zinc [2–6]. When sulfide minerals such as pyrite (FeS_2), its dimorph marcasite and pyrrhotite ($Fe_{1-x}S$) are exposed to oxygen and water, they undergo a bacterially catalyzed oxidation reaction which lead to generation of acidity and increased Fe and sulfate concentrations in recipient water bodies (Eq. (1)). The overall reaction is often written as [7]:

$$FeS_2(s) + 3.75O_2 + 3.5H_2O \rightarrow Fe(OH)_3(s) + 2SO_4^{2-} + 4H^+ \quad (1)$$

On interacting with the mine bedrock, the acidic water leaches more chemical species leading to high concentrations of Fe, Mn, Al, Cu, Zn, Mg, Na and Ni in the AMD streams [2, 3].

South Africa environmental regulations require these AMD streams to be treated to acceptable levels before discharging into surface water bodies. A range of active and passive remediation technologies have been adopted by various mining companies to reduce impact of AMD on ground and surface water resources. These technologies include active neutralization by lime, limestone, biological sulfate removal [8–10], eutectic freeze crystallization [11] and the alkaline barium calcium desalination process (ABC) [12]. Passive AMD remediation technologies include alkalinity generating artificially constructed wetlands [13]. Other innovative AMD management and remediation technologies have been developed which involve treatment and recovery of beneficial products such as gypsum and sulfur [12]. Recently, innovative and sustainable management technologies for AMD have been developed which involve treatment and recovery of drinking water that is supplied to communities near the mines while the gypsum recovered is used in construction of gypsum boards and houses. This is to reduce the cost of treatment and make the process sustainable [14]. Bhattacharyya and Gupta [15] observe that these AMD management technologies are still expensive and mining companies are still searching for cheaper treatment and management technologies.

South Africa uses more than 100 MT of low grade bituminous coal annually to produce electricity in coal powered utilities. These coal power utilities in turn produce 28 MT of coal fly ash annually that is disposed of on land as ash dumps or slurried to ash dams due to lack of alternative application of this coal combustion by-product [16]. Fly ash is a powdery substance which consists of fine spherical particles which are either solid or hollow. It is a ferro-aluminosilicate material with particles ranging in size from 20 to 80 μm, its surface is enriched with trace elements of Si, Al, Fe, Ca, K and Na [17, 18]. Several authors have reported that South African coal fly ash consists mainly of aluminosilicate glass matrix in addition to crystalline mullite and quartz. This glass phase was observed to be associated with elements such as As, Na, Mg, K, Sr, B and Mo as soluble salts on the surface of the spheres [3, 19, 20].

The South African coal is sub-bituminous and generates coal fly ash that has low Fe content and the aqueous extracts of this coal fly ash are strongly alkaline (pH 12–12.5) due to the free lime content [16, 21–24]. The highly soluble CaO occurring as sub-micron fragments on the fly ash particles accounts for the alkaline properties of the coal fly ash [3].

Traditionally, AMD neutralization and remediation has been carried out using liming agents such as limestone, lime and sodium hydroxide [9, 10, 13, 25, 26]. An important disadvantage of these liming agents is cost and generation of large volumes of sludge that requires disposal. Due to those limitations, mining companies are always on the lookout for cheaper and effective liming agents.

Several research reports have highlighted the application of fly ash for the control of acid generation from sulphidic rich wastes [27, 28] and for amendment of acidic soils [29]. The studies involved blending the mine spoils, tailings and acidic soils with varying amounts of fly ash. These authors observed that the coal fly ash controlled the acid generation from the wastes by release of alkalinity over time to the system which neutralized the acidity produced. Several authors have reported on the successful application of coal fly ash for inorganic contaminants removal from AMD and acidic leachates [8, 19, 30, 31]. They observed that contaminants removal was directly proportional to CaO content of the fly ash. The authors concluded that coal fly ash due to its free lime content can be used as a neutralization and inorganic contaminants removal for AMD remediation.

Most of the power utilities generating coal fly ash in South Africa are located near coal mines supplying them with coal [6]. These coal mines are also the sources of AMD that requires remediation. This chapter reports on work done to explore the possibility of utilizing coal fly ash for treatment and remediation of AMD. The fact that most of the coal-powered utilities are near the coal mines that supply them with coal and produce AMD, makes the proposed treatment process economically viable. A fundamental understanding of the solution chemistry and product water quality after neutralization of AMD with coal fly ash is a prerequisite for this treatment process.

2. Collection of samples, physicochemical analysis and experimental methods

2.1. Collection and preparation of samples

Coal fly ash (CFA) samples were collected from two coal-powered utilities in Mpumalanga, South Africa and stored in tightly lockable plastic containers. The AMD samples used were collected from two collieries and a government AMD treatment plant that remediates AMD seepage from an old abandoned mine in Witbank, South Africa. The AMD samples from the government AMD treatment plant were scooped from the seepage point while samples for the two collieries consisted of AMD pumped from underground old mine workings to a collection dam and underground mine voids, respectively.

Raw AMD samples were filtered by using 0.45 μm pore cellulose nitrate membrane filters and diluted with MilliQ (ultrapure) water to EC < 1.5 mS/cm and 3 drops of dilute HNO_3 added and kept refrigerated at 4°C until analysis for cationic species. Samples for anion analysis were diluted with MilliQ water and refrigerated at 4°C until analysis.

2.2. Coal fly ash/acid mine drainage treatment experiments

The AMD/coal fly ash treatment experiments were designed to develop neutralization patterns that would indicate buffering properties of the AMD and also show the contact time required for the breakthrough to circum-neutral-alkaline pH in the product. Department of Water Affairs and Forestry [32] South Africa requires pH for treated water for release into surface water bodies to be in the range of 6–9. The batch treatment experiments were conducted by stirring a mixture of coal fly ash and AMD which was pre-determined to give a specific coal fly ash/AMD ratio (FA:AMD). An overhead stirring system was used to agitate the mixture for all experiments. The progress of the reaction was monitored by measuring the pH and EC with a Hanna HI 991301 portable pH/EC/TDS/Temperature metre.

A second set of treatment experiments were repeated at selected FA:AMD ratios to explore the product water chemistry and inorganic contaminants removal efficiency of the coal fly ash with increasing pH of the process water. The solid residues were separated by filtration and the process water samples were prepared for cationic and anionic species analysis. Cationic species were analyzed using ICP-MS (ELAN 6000) and the accuracy of the analysis monitored by the use of NIST water standards. Fe^{2+}/Fe^{3+} analysis was done by the colorimetric method using 2, 2-bipyridal as the complexing reagent. Sulfate analysis was done turbidimetrically by a portable data logging spectrophotometer (Hach DR/2010) and ion chromatography (Dionex DX-120).

Chemical characteristics of the coal fly ash samples were ascertained by X-ray fluorescence spectroscopy (XRF) by fusing with lithium metaborate. The solid residues collected after reacting coal fly ash with AMD were analysed by Phillips PANalytical X-ray diffractometer (XRD) using Cu Kα radiation generated at 20 mA and 40 KV. Specimens were step scanned as random powder mounts from 5 to 85° 2θ integrated at 0.02° 2θ per second. Powder samples of the solid residues were also observed under a scanning electron microscope (SEM-EDX) equipped with an energy dispersive X-ray analysis system (Hitachi X-650 microanalyzer).

3. Results and discussion

3.1. Chemical composition of coal fly ash

The chemical composition of the coal fly ashes used in the AMD treatment experiments are presented in **Table 1**.

The three major oxides identified in the two coal fly ashes were Al_2O_3, Fe_2O_3 and SiO_2. Coal fly ash B had higher Al_2O_3 content while coal fly ash A showed higher Fe_2O_3 content. These

Coal fly ash A				Coal fly ash B			
Species	**% (w/w)**	**Species**	**ppm**	**Species**	**% (w/w)**	**Species**	**ppm**
SiO_2	53.4 ± 2.4	Cu	47.3 ± 6.6	SiO_2	53.8 ± 0.29	Cu	57.9 ± 9.9
TiO_2	1.34 ± 0.05	Mo	5.22 ± 0.14	TiO_2	1.44 ± 0.11	Mo	6.56 ± 0.15
Al_2O_3	23.4 ± 1.1	Ni	93.4 ± 6.5	Al_2O_3	26.2 ± 2.52	Ni	58.2 ± 1.2
Fe_2O_3	4.72 ± 0.96	Pb	56.4 ± 13.6	Fe_2O_3	3.40 ± 0.24	Pb	29.1 ± 7.18
MnO	0.06 ± 0.002	Sr	1463.9 ± 111.8	MnO	0.05 ± 0.02	Sr	2056.0 ± 205
MgO	2.69 ± 0.05	Zn	57.3 ± 4.71	MgO	2.48 ± 0.58	Zn	25.4 ± 1.35
CaO	8.43 ± 0.57	Zr	488.1 ± 125.7	CaO	8.50 ± 1.75	Zr	536.1 ± 131.3
Na_2O	0.35 ± 0.25	Co	18.3 ± 13.08	Na_2O	0.49 ± 0.05	Co	10.4 ± 3.3
K_2O	0.49 ± 0.03	Cr	179.2 ± 1.14	K_2O	0.86 ± 0.07	Cr	122.7 ± 27.8
P_2O_5	0.35 ± 0.22	V	147.4 ± 38.9	P_2O_5	0.60 ± 0.22	V	145.8 ± 32.8
Cr_2O_3	0.03 ± 0.009	Ba	928.0 ± 91.9	Cr_2O_3	0.03 ± 0.006	Ba	1559.2 ± 346.7
NiO	0.011 ± 0.001			NiO	0.009 ± 0.002		
$V2O_5$	0.019 ± 0.002			V_2O_5	0.02 ± 0.003		
ZrO_2	0.052 ± 0.012			ZrO_2	0.055± 0.003		
LOI	2.36 ± 0.19			LOI	1.33 ± 0.36		

Table 1. Chemical composition of coal fly ashes A and B used in AMD treatment experiments.

coal fly ashes can be classified as class F according to the American Society for Testing and Materials [33] since ($SiO_2 + Al_2O_3 + Fe_2O_3 \geq 70\%$). The CaO content shows slight variation with coal fly ash B showing a slightly higher value. The total CaO content detected by XRF includes total CaO including that locked up in the aluminosilicate matrix. XRF does not distinguish the free lime from that trapped within the glass matrix. The free CaO content of CFA is important because of its availability for rapid dissolution, which has implications on its neutralization potential during AMD treatment. Substantial MgO was observed in both coal fly ashes and could contribute significantly in the neutralization of AMD. Both coal fly ashes showed high concentrations of Sr, Ba, Cr, Zr and Ni (**Table 1**). Trace elements of Mo are also present. These species are likely to be released into solution during the AMD treatment process.

3.2. Physicochemical properties of acid mine drainage samples

The physicochemical properties of the AMD samples used in the treatment experiments are presented in **Table 2**.

The AMD samples are highly acidic with the pH ranging from 2.39 for Navigation samples to 2.92 for Brugspruit samples (**Table 2**). All the samples exhibit high electrical conductivity

Parameter	Navigation	Bank	Brugspruit
pH	2.39 ± 0.05	2.46 ± 0.03	2.91 ± 0.02
EC (mS/cm)	10.83 ± 0.13	10.78 ± 0.15	10.02 ± 0.06
Acidity (mg/l $CaCO_3$)	6950 ± 70.7	7000 ± 70.7	500 ± 0.0
TDS (mg/L)	16765 ± 50.5	19410 ± 76.8	8975 ± 60.5
B	1.37 ± 0.163	1.51 ± 0.08	2.29 ± 0.221
Na	358.7 ± 2.95	399.9 ± 21.3	4137.9 ± 233.0
Mg	2661.7 ± 35.0	2844.2 ± 148.1	388.7 ± 19.7
Al	1068.1 ± 11.28	1140.1 ± 61.58	60.0 ± 2.9
Si	82.01 ± 1.24	87.8 ± 5.87	69.7 ± 3.5
K	23.03 ± 2.86	19.3 ± 4.21	52.6 ± 3.6
Ca	653.3 ± 10.6	1012.3 ± 75.9	842.1 ± 117.4
Mn	226.3 ± 4.7	242.3 ± 12.9	31.6 ± 1.50
Fe	5599.9 ± 80.9	6115.9 ± 327.5	250.8 ± 11.2
Fe^{2+}	3725.1 ± 30.5	2886.3 ± 20.7	153.1 ± 9.5
Fe^{3+}	1451.9 ± 45.2	3344.6 ± 50.5	126.1 ± 6.5
Ni	6.95 ± 0.02	7.96 ± 1.16	2.35 ± 0.13
Cu	0.355 ± 0.007	0.345 ± 0.018	0.116 ± 0.012
Co	4.3 ± 0.11	4.57 ± 0.32	1.15 ± 0.063
Zn	48.99 ± 30.63	17.7 ± 0.65	9.52 ± 0.49
Sr	7.69 ± 0.226	8.39 ± 0.45	1.05 ± 0.058
Mo	0.04 ± 0.002	0.044 ± 0.003	0.036 ± 0.004
Ba	0.209 ± 0.002	0.189 ± 0.01	0.148 ± 0.018
SO_4^{2-}	11888.1 ± 20.6	14949.7 ± 28.3	6155 ± 54.3
Cl^-	729.3 ± 15.3	265.9 ± 10.6	720 ± 11.5
NO_3^-	163.2 ± 21.6	41.6 ± 5.7	BDL

Table 2. Physicochemical properties of AMD samples used in the treatment experiments.

(10.02–11.36 mS/cm), typical of most AMD impacted mine waters. This is attributed to high sulfate content which contributes to the high conductivity values of the samples. The sulfate correlated positively with the EC measurements for most of the acidic coal mine waters investigated in this study. The sulfate recorded in these samples ranged from 6155 to 14950 mg/L making this anion dominant in the AMD samples while major cationic species included Na, Ca, Mg, Al, Mn and Fe. It is worth noting that Navigation and Bank AMDs had significantly higher total Fe iron content than Brugspruit AMD.

3.3. Treatment of Fe-rich acid mine drainage samples using different coal fly ashes: the role of coal fly ash chemistry

The pH and electrical conductivity (EC) trends of the treatment reactions at a FA to AMD ratio of 1:3 are shown in **Figure 1**.

The EC for treatment processes followed the same trend with continuous decrease as the agitation progressed. A zone was observed for the three treatment processes where the EC remained constant (**Figure 1**). In terms of contact time, it coincided with the pH buffer zones.

Both coal fly ashes A and B showed potential capacity to neutralize AMD at CFA:AMD ratios of 1:3. The pH-neutralization trends for all reactions showed a strong pH buffering zone at pH 6.2–6.8 which was observed to last for different reactions times depending on the coal fly ash or AMD type used. This pH buffer zone is associated with the oxidation and hydrolysis of Fe^{2+} which releases H^+ ions and delays the rise in pH [6] (Eq. (3)). Al^{3+} undergoes hydrolysis at pH ≈ 4.5 and will also contribute to pH buffer in this zone (Eq. (2)).

$$Al(H_2O)_6^{3+} \Rightarrow Al(OH)_3 + 3H^+ \quad \text{Acidity release : pH decrease} \tag{2}$$

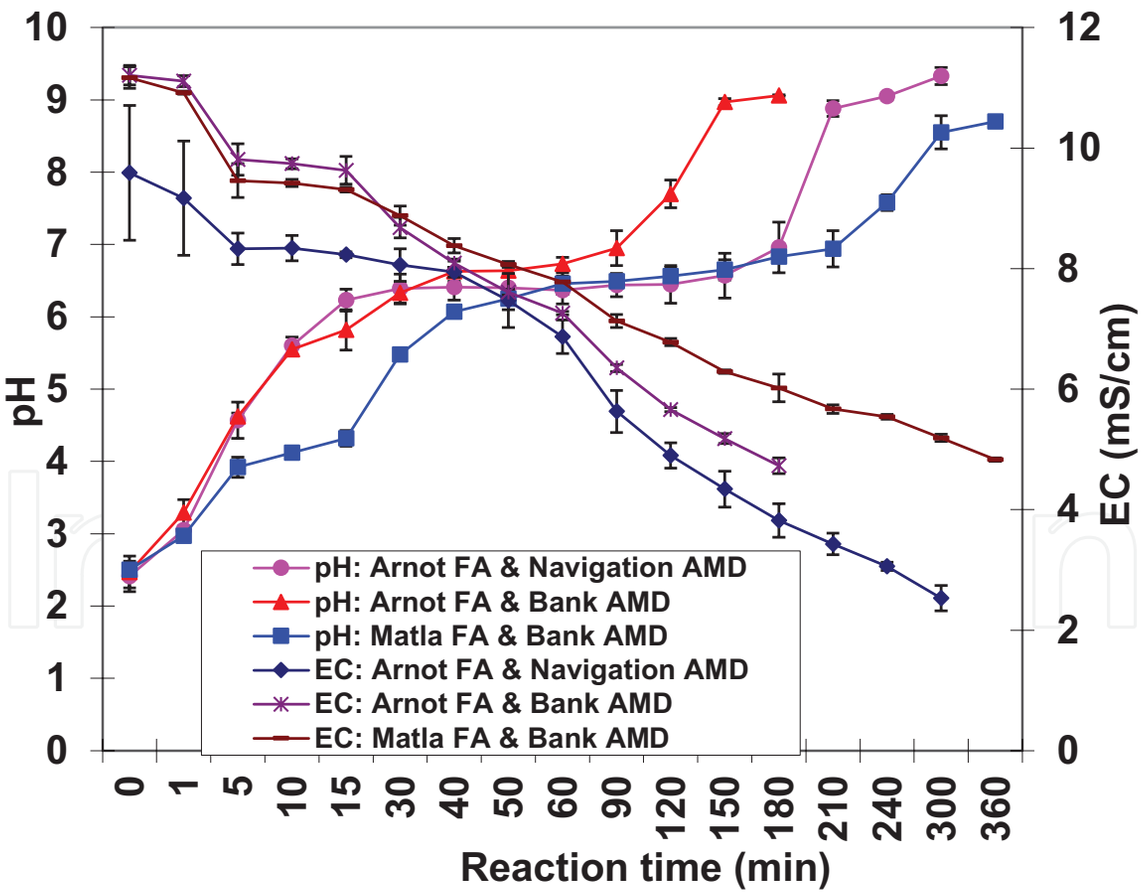

Figure 1. pH and EC for the treatment reactions at a FA:AMD ratio of 1:3 between, CFA-A and B with Bank AMD; and CFA-A with Navigation AMD. Values reported as mean ± SD (n = 4), error bars reflect 1 SD above and below the mean.

$$\begin{aligned} &Fe^{2+} + 0.25O_2 + H^+ \Rightarrow Fe^{3+} + 0.5H_2O \\ &Fe^{3+} + 3\,H_2O \Rightarrow Fe(OH)_3 + 3H^+ \text{ net acidity release: pH decrease} \end{aligned} \tag{3}$$

This pH buffering zone is a result of high concentrations of Fe^{2+} and Al^{3+} in the AMD (≈3000–4000 mg/L for Fe^{2+} and ≈1150 mg/L for Al^{3+}) (**Table 2**). It should be noted in **Figure 1** that it took longer time for CFA-A to overstep the acidic buffer zone with Navigation AMD as compared to Bank AMD. This is attributed to the high concentrations of Fe^{2+} in Navigation AMD than Bank AMD (**Table 3**) that could sustain the buffering capacity. It is observed that both solutions broke through to a pH of ≈9, with Navigation AMD taking 200 min and only 150 min for Bank AMD to break through. This indicates that the chemistry of the AMD is crucial in this treatment process. A small buffer zone was also observed at pH 4–4.5 for treatment reaction between CFA-B and Bank AMD. This buffer zone is attributed to the hydrolysis and precipitation of Fe^{3+} with subsequent consumption of H^+ (Eq. (3)). It should be observed that Bank AMD had twice the concentration of Fe^{3+} as Navigation AMD. This aspect is also confirmed in the pH trend for the CFA-A and Bank AMD with a slight buffering at pH ≈5.5 (**Figure 1**). Coal fly ash B appeared to have less free alkalinity than CFA-A. This is evident from the pH trends during the treatment process between both CFAs and Bank AMD. To break through to pH ≥ 8.7 (**Figure 1**), contact time required was greater with CFA-B than CFA-A for the treatment of Bank AMD. The neutralization potential of CFA depends on free CaO available and in this case, CFA-A seems to have more free CaO than CFA-B. It should be noted that XRF gives the total CaO content of the coal fly ash and therefore results in **Table 1** which do not reflect free CaO. This aspect confirms that the chemistry of the coal fly ash will also be an important factor in this treatment process.

3.4. Treatment of iron-rich and iron-poor acid mine drainage with coal fly ash: the role of CFA/AMD ratios and acid mine drainage chemistry

To evaluate the effect of AMD chemistry and CFA/AMD ratios on the treatment process and product water quality, CFA-B was reacted with Brugspruit and Navigation AMD. Brugspruit AMD had low total Fe, Al and Mn content while Navigation AMD had high concentration of total Fe, Al and Mn in addition to high SO_4^{2-} content (**Table 2**). **Figure 2** shows the trends of pH and electrical conductivity (EC) for the treatment process between CFA-B and Brugspruit AMD at various CFA:AMD ratios.

The treatment of Brugspruit AMD with low ratios of CFA-B led to alkaline pH (pH ≈ 10) within 5 min of reaction time (**Figure 2**). This indicates that even low amounts of FA could be used to achieve neutralization in some cases depending on the chemistry of AMD being treated. Treatment of Brugspruit AMD with CFA-B:AMD ratios of between 1:3.5 and 1:8 led to highly alkaline pH (pH > 12) in product water. The ratio of CFA used was directly proportional to the decrease of EC. The EC seemed to decrease within the initial 5 min of treatment and then stabilized at a minimum of 8.5–9 mS/cm. It should be observed all the CFA-B:AMD treatment ratios used led to a final pH ≥ 12 after 360 min of reaction. It should be noted that the buffer zones observed with CFA-A:Navigation AMD and CFA-B:Bank AMD treatment are not observed with Brugspruit AMD in all the CFA:AMD ratios employed (**Figures 1** and **2**). This

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													DWAF limits	
FA:AMD	**AMD**		**1:3.5**		**1:5**		**1:8**		**1:2**		**1:3**		**Irrigation**	**Domestic use**
Species	ave	SD	ave	SD	ave	SD	ave	SD	ave	SD	ave	SD		
B	2.29	0.221	1.92	0.123	2.79	0.004	5.93	0.57	6.12	0.59	4.42	1.35	0.5	0.05
Na	4137.99	233.007	1482.34	50.64	1561.34	55.04	1580.24	45.5	3034.67	80.84	2394.18	100.4	70	100
Mg	388.65	19.707	0.24	0.021	1.46	0.21	0.833	0.021	297.04	21.4	236.86	25.3		30
Al	60.04	2.886	0.15	0.003	0.99	0.06	2.44	0.25	0.153	0.011	0.32	0.015		
Si	69.73	3.495	0.82	0.013	2.65	0.28	3.29	0.201	13.99	2.91	16.72	1.25		
K	52.59	3.634	20.21	3.74	21.26	1.34	15.54	2.5	45.33	5.69	37.53	5.43		50
Ca	842.11	117.44	546.89	60.34	478.65	20.56	793.38	30.58	877.22	20.56	635.68	30.98		32
Cr	0.77	0.067	0.5	0.034	0.526	0.023	0.375	0.028	0.525	0.021	0.176	0.022		
Mn	31.58	1.481	0.028	0.002	0.066	0.013	0.026	0.002	0.339	0.004	6.24	0.68		
Fe	250.84	11.203	2.62	0.421	3.497	0.251	0.853	0.037	4.23	0.15	3.52	0.15		
Ni	2.35	0.127	0.031	0.002	0.051	0.002	0.194	0.022	0.332	0.002	0.602	0.021	0.2	0–0.02
Co	1.15	0.063	0.001	0.0005	0.002	0.0005	0.004	0.00057	0.017	0.001	0.115	0.002	0.05	0–0.05
Cu	0.11	0.011	0.031	0.001	0.04	0.002	0.049	0.003	0.044	0.002	0.045	0.0015	0.2	1
Zn	9.52	0.491	1.13	0.052	9.19	1.19	16.44	1.48	1.21	0.08	8.047	0.038	1	3
As	0.11	0.491	0.004	0.001	0.006	0.001	HDL		0.014	0.002	0.007	0.002		
Se	0.032	0.006	0.072	0.003	0.054	0.003	0.084	0.018	0.04	0.018	0.017	0.001		
Sr	1.046	0.057	13.86	2.54	9.539	2.31	9.23	2.68	10.23	1.58	5.71	0.32		
Mo	0.036	0.0037	0.219	0.002	0.181	0.011	0.16	0.004	0.134	0.013	0.092	0.003	0.01	0–0.05
Cd	0.012	0.0007	0.002	0.0004	0.002	0.001	0.003	0.00035	0.001	0.0005	0.002	0.0005		
Ba	0.148	0.0147	0.569	0.005	0.684	0.026	0.626	0.058	0.579	0.026	0.432	0.015		

													DWAF limits	
FA:AMD	**AMD**		**1:3.5**		**1:5**		**1:8**		**1:2**		**1:3**		**Irrigation**	**Domestic use**
Pb	0.178	0.02	0.015	0.002	0.017	0.002	0.018	0.003	0.011	0.005	0.013	0.001		
SO_4	6165	10	6137	7	5668.03	47.53	4601.77	3.37	7182.96	7.46	3709.80	58.99		
Cl	720	22.3	385.28	19.5	285.52	6.8	276.15	20.3	449.73	15.8	326.12	19.2		
pH	2.55	0.12	9.16	0.04	9.73	0.13	12.04	0.05	12.64	0.14	12.62	0.12		6–9

ave, average; SD, standard deviation.

Table 3. Concentration of inorganic contaminants at various final pH of solution and CFA:AMD ratios for treatment of Brugspruit AMD with CFA-B (concentrations are in mg/L except for pH).

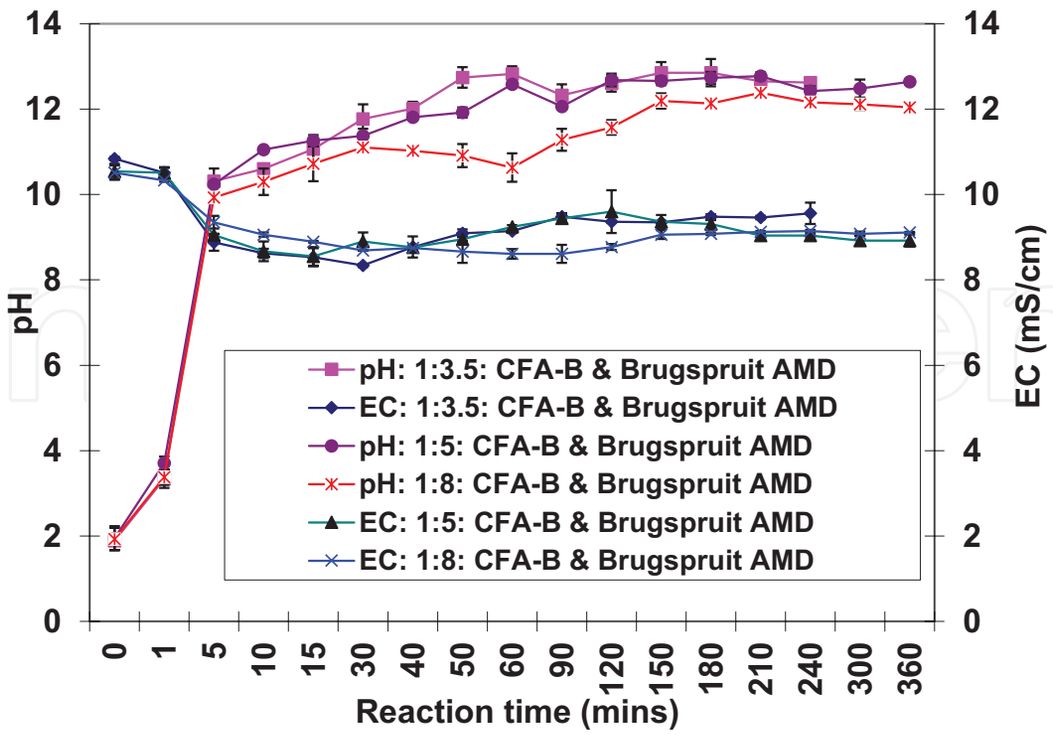

Figure 2. pH and EC trends for the treatment process for various CFA-B:Brugspruit AMD ratios. Values reported as mean ± SD (n = 4), error bars reflect 1 sample SD above and below the mean.

is a strong indication that AMD chemistry has a significant role to play in the final product water chemistry.

Figure 3 shows the trends of pH and electrical conductivity (EC) for the treatment process between CFA-B and Navigation AMD at various CFA:AMD ratios.

The pH and EC trends for the treatment process of Navigation AMD with CFA-B are distinctively different from those of the treatment process for Brugspruit AMD (**Figures 2** and **3**). For the Navigation AMD treatment process, there is a stepwise increase in pH as the treatment progresses. Buffer zones are also observed at pH 3.5–4 and pH 5.5–6.5.

Despite the high CFA:AMD ratios employed in the treatment as compared to Brugspruit treatment, the breakthrough to pH > 10 only occurs after 210 min (**Figure 3**) and for lower CFA:AMD ratio of 1:3, a breakthrough was not achieved after 360 min. It should be noted that the stepwise increase in pH with time is lacking for the Brugspruit AMD. Stepwise and gradual decrease in EC is noted for the Navigation AMD treatment process (**Figure 3**). The initial decrease in EC for the Brugspruit treatment is not sustained and stabilizes at 8.67–9.56 mS/cm. Uhlmann et al. [34] observed that the buffering observed at pH 3.5–4 is due to hydrolysis of Fe^{3+} while oxidation and hydrolysis of Fe^{2+} contributes greatly to buffering at pH 5.5–6.5 [25] (Eqs. (2) and (3)). At pH ≥ 4.5, Al^{3+} undergoes hydrolysis forming insoluble hydroxides and will buffer pH in the region of 3.5–4 (Eq. (2)) [34, 35]. It should be noted that Brugspruit AMD had very low concentration of Fe^{3+}/Fe^{2+} and Al^{3+} as compared to Navigation AMD (**Table 2**). This could explain the lack of stepwise decrease in pH and buffering during the treatment process. There are two

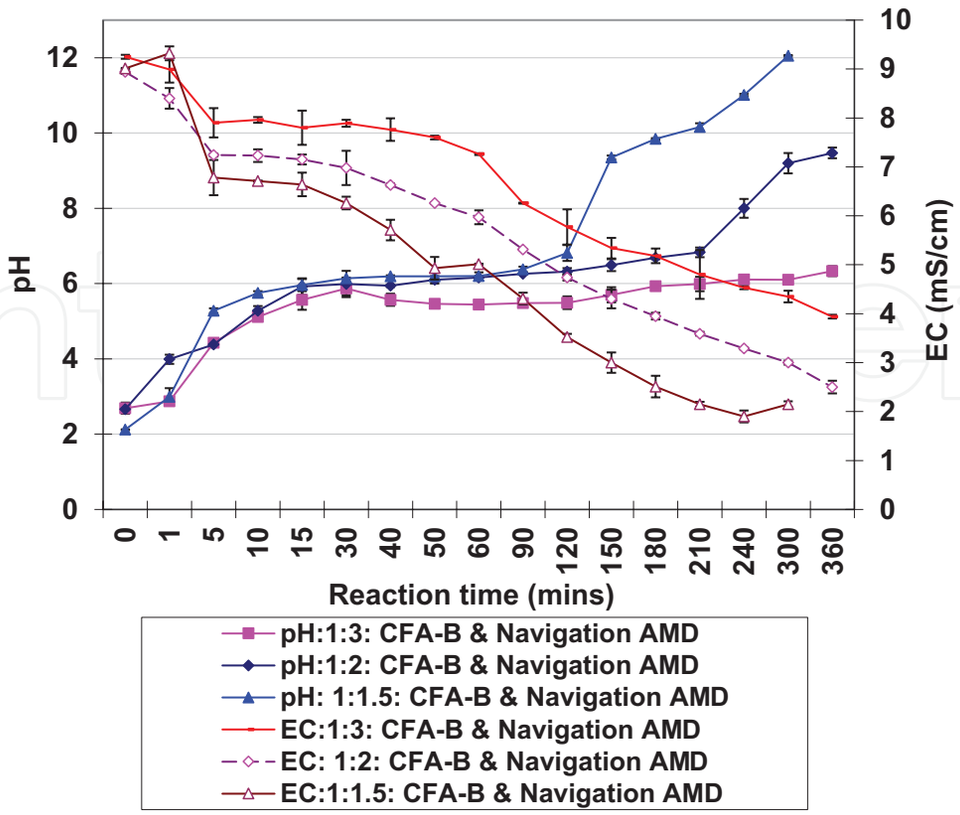

Figure 3. pH and EC for various FA:AMD ratios for reaction between CFA-B and Navigation AMD. Values reported as mean ± SD (n = 4), error bars reflect 1 SD above and below the mean.

opposing processes that finally control the final pH of the product water in this treatment process. The dissolution and hydrolysis of soluble alkaline oxides such as CaO and MgO (**Table 1**) from coal fly ash will contribute to increase in pH (Eqs. (4) and (5)). This is also confirmed by the fact that the time taken for breakthrough of the buffer zone 5.5–6.5 reduced with increase of CFA in the treatment mixture. CFA:AMD ratio of 1:1.5 took the shortest time to breakthrough this buffer zone (**Figure 3**).

$$CaO + H_2O \Rightarrow Ca^{2+} + 2OH^- \text{ pH increase} \tag{4}$$

$$MgO + H_2O \Rightarrow Mg^{2+} + 2OH^- \text{ pH increase} \tag{5}$$

Hydrolysis of AMD constituents such as Fe^{3+}, Al^{3+} and Fe^{2+} releases protons (acidity increase) (Eqs. (2) and (3)) and offsets the pH increase attributed to the dissolution of the alkaline oxide from coal fly ash. The net result is a pH buffer zone, this buffer zone is only overstepped when the components leading to release of acidity are completely hydrolyzed. These hydrolysable components will finally determine if the final pH of the product water will be acidic or alkaline at any given treatment time. It will also be observed that the final pH of the product water also depended on the CFA:AMD ratio applied. Higher CFA:AMD led to higher pH of product water regardless of treatment time. It can therefore be concluded that factors that will control

the product water chemistry and quality would be, CFA:AMD ratio, the treatment time and the chemistry of the AMD.

3.5. Inorganic contaminants removal: product water quality compared to South African water quality guidelines

Acid mine waters are highly reactive solutions that can dissolve most primary minerals when reacted with an alkaline solid waste material such as coal fly ash with subsequent formation of a variety of secondary minerals that can potentially adsorb trace chemical species. Dissolution of coal fly ash by AMD triggers several processes such as hydrolysis of soluble alkaline oxides leading to increase in pH. Several authors observe that pH is the most important parameter in coal fly ash solutions and accounts for significant inorganic toxic elements removal through precipitation, ion exchange and adsorption processes [13, 30].

Tables 3 and **4** present results of inorganic contaminants removal as a function of final solution pH and CFA:AMD ratios for Brugspruit and Navigation AMD treatment with CFA-B. The results are discussed with respect to pH of precipitation of the various metal species as determined from thermodynamic calculations and experimental observations from titration of solutions containing the stated species as reported by Britton [36].

3.6. Brugspruit AMD treatment with CFA-B: inorganic contaminants removal

Brugspruit AMD had different chemistry compared to that of Navigation AMD, it had low concentration of the major hydrolysable chemical species Al^{3+}, Fe^{3+}, Fe^{2+} and Mn^{2+}. Major inorganic contaminants Fe, Mn, Al and Mg were reduced significantly in all the ratios investigated (**Table 3**). Fe and Al were reduced by >95% at pH ≥ 9.16 attained in the final process waters for CFA:AMD ratios, 1:3, 1:5, 1:8, 1:2 and 1:3. It should be noted that final pH also depended on the treatment time employed. Mn removal was ≥90% for all CFA:AMD ratios evaluated except for 1:3 ratio at 80%. Jenke et al. [25] observed that at the pH of minimum solubility of the hydroxides of Fe^{3+} (pH 3.0), of Fe^{2+} (pH 6.0–8.0), of Mn^{2+} (pH 8.41–9.0) and of Zn^{2+} (pH 6.0–6.5), a significant proportion of the initial concentration should be precipitated out of solution. Gitari et al. [19] observed that at pH ≥ 4.5, most of the mineral phases bearing these species were at saturation or oversaturation (SI ≥ 1). At pH ≥ 12, a slight increase in Al, Fe and Mn was observed. At pH 12.0–12.5 attained for ratios 1:8, 1:2 and 1:3, the formation of hydroxy complexes was attributed to the decreased removal. Drever [37] observes that Al^{3+} hydroxide exhibits minimum solubility at pH 6–6.5, therefore at pH > 6.5, the Al-hydroxy complexes become more important [38].

Among the minor and trace species, Ni, Cu, Pb, Mg, Cr, Ni,Co, Cu, As and Cd were all observed to decrease as the pH increased. The Cu, Cr, Zn and Pb removal efficiency was observed to decrease at CFA:AMD ratio of 1:8 which attained a pH of 12.04. The decrease in removal of these species could be attributed to soluble hydroxo species formed at pH > 12.0. Another reason for the increase could be reduced adsorption due to reduced formation of amorphous $Fe(OH)_3$, MnOOH and $Al(OH)_3$ due to the low concentration of Fe^{3+}, Mn and Al^{3+} in Brugspruit AMD. Mg^{2+} removal efficiency approached 100% at pH 9.16 with a decrease observed as the pH increased to 12.62. Decreased removal could be due to the formation of

FA:AMD	AMD		1:3		1:2.5		1:2		1:1.5		DWAF limits	
Species	**ave**	**SD**	**ave**	**SD**	**ave**	**SD**	**ave**	**SD**	**ave**	**SD**	**Irrigation**	**Domestic use**
B	1.37	0.163	23.44	3.44	24.38	2.56	17.57	2.356	17.86	3.456	0.5	0–0.5
Na	358.72	2.946	71.76	10.23	72.53	9.87	68.21	10.12	62.02	21.8	70	100
Mg	2661.67	35.008	636.85	80.45	618.06	70.8	200.04	34.5	1.5	0.02		30
Al	1068.00	11.279	2.85	0.05	3.26	0.35	2.35	0.56	9.41	1.97		
Si	82.01	1.238	4.39	0.52	2.05	0.003	2.3	0.16	1.09	0.03		
K	23.03	2.856	16.27	2.45	19.45	1.56	14.87	2.35	10.33	2.45		50
Ca	653.33	10.626	368.19	23.8	495.11	20.45	448.53	19.67	477.92	35.63		32
Cr	1.11	0.009	0.069	0.003	0.163	0.013	0.141	0.001	0.083	0.015		
Mn	226.2.5	4.742	56.65	5.68	5.15	0.456	1.11	0.005	0.133	0.005		
Fe	5599.92	80.862	293.3	19.57	52.25	6.78	43.23	4.578	4.7	0.67		
Ni	6.95	0.018	0.58	0.04	0.134	0.002	0.088	0.004	0.051	0.001	0.2	0–0.02
Co	4.3	0.105	0.312	0.012	0.014	0.001	0.019	0.003	0.002	0.0015	0.05	0–0.05
Cu	0.355	0.007	0.045	0.003	0.055	0.011	0.073	0.005	0.034	0.006	0.2	1
Zn	48.99	30.624	1.3	0.012	1.2	0.05	1.26	0.02	0.736	0.012	1	3
As	0.193	0.012	0.003	0.0005	0.005	0.0015	0.003	0.0005	0.004	0.001		
Se	0.032	0.002	0.037	0.002	0.026	0.003	0.052	0.001	0.112	0.003		
Sr	7.69	0.226	15.71	1.34	17.18	2.543	14.48	2.87	17.72	1.48		
Mo	0.04	0.002	0.025	0.002	0.622	0.002	0.665	0.002	0.77	0.04	0.01	0–0.05
Cd	0.032	0.001	0.003	0.0015	0.004	0.001	0.003	0.0015	0.002	0.0004		
Ba	0.209	0.002	0.369	0.003	0.347	0.032	0.336	0.034	0.319	0.013		
Pb	0.314	0.107	0.019	0.002	0.041	0.004	0.0301	0.005	0.0154	0.0021		

FA:AMD	AMD		1:3		1:2.5		1:2		1:1.5		DWAF limits	
Species	**ave**	**SD**	**ave**	**SD**	**ave**	**SD**	**ave**	**SD**	**ave**	**SD**	**Irrigation**	**Domestic use**
SO_4	11949.6	61.5	5483.3	14.9	2414.3	28.1	2508.1	247.6	4570.7	110.3		
NO_3	163.17	10.01	68.43	7.82	23.69	5.34	<0.1	0	9.3.44	10.21		
Cl	729.27	100.1	65.8	3.21	63.168	6.21	44.744	3.03	88.172	9.65		
pH	2.69	0.21	6.33	0.15	8.72	0.62	9.47	0.43	12.1	0.18		6–9

ave, average; SD, standard deviation.

Table 4. Concentration of inorganic contaminants at various final pH of solution and CFA:AMD ratios for treatment of Navigation AMD with CFA-B (concentrations are in mg/L except for pH).

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soluble hydroxo species at the high pH. Na and K were removed by 50% as the pH increased. Gitari et al. [19] observed that as pH increases and in presence of SO_4^{2-}, several Na-K bearing mineral phases such as jarosite are precipitated and would account for this decrease. Sulfate did not register significant removal and in some CFA:AMD ratios (1:2) was observed to increase, this increase is attributed to release from the coal fly ash.

3.7. Navigation AMD treatment with CFA-B: inorganic contaminants removal

The pH increase with increase of CFA:AMD ratios was observed to be gradual for Navigation AMD treatment as compared to that of Brugspruit AMD (**Tables 3** and **4**). Several inorganic contaminants removal trends are observed as the pH increases. At final pH 6.33 achieved for the CFA:AMD ratio of 1:3, a sharp decrease in concentration is observed for Fe, Al and Mn. These are the major inorganic contaminants that characterize Navigation AMD. With subsequent CFA:AMD ratios, the removal efficiency of ≥90% are observed. Gitari et al. [19] observed that as pH increases, mineral phases bearing these chemical species are precipitated and account for their increased removal in solution. Minor and trace inorganic species such as Si, Cr, Ni, Co, Cu, Zn, As, Se, Cd and Pb were all observed to decrease as the pH increased with subsequent CFA:AMD ratios. Their removal could be attributed to several mechanisms such as precipitation of mineral phases and adsorption to high surface area Fe and Al oxyhydroxy precipitates. Gitari et al. [19] observed that co-precipitation of Fe, Al-oxyhydroxides, oxyhydroxy sulfates and adsorption could be responsible for attenuation of Cu^{2+}, Zn^{2+} species.

Britton [36] observes that the pH of minimum solubility of the hydroxides/oxyhydroxides of Fe^{3+}, Fe^{2+}, Al^{3+}, Zn^{2+}, Cu^{2+} and Ni^{2+} are 3.0, 6.0–8.0, 4–4.5, 6.0–6.5 and 6.66, respectively. The pH attained for CFA:AMD ratio of 1:3–1:2 is within this range. This would explain the high removal of these species within this pH range. However, Cu and Pb registered an increase in concentration in final process waters for CFA:AMD 1:2 and 1:2.5 ratios whose final pH ranged from 8.7 to 9.5 (**Table 4**). This would be attributed to the formation of soluble hydroxo complexes for both species at this pH range.

Mg, Na, K and Ca removal increased with increasing pH of the final process water. These chemical species are highly soluble in the pH range generated in process waters and likely removed through incorporation in precipitating mineral phases. Gitari et al. [19] observed that mineral phases such as alunite, basaluminite, jurbanite, brucite and jarosite are likely to precipitate out in CFA:AMD reactions leading to removal of these species. Sulfate was likely removed through formation of gypsum, incorporation into Al, Fe-oxyhydroxysulfates. A direct relationship between percent sulfate removal and FA content in the reaction mixture suggests that dissolution of CaO and subsequent formation of gypsum accounts for the sulfate removal in both AMD treatments. XRD analysis identified gypsum in the solid residues of the CFA:AMD reactions [3, 39].

3.8. Leaching of chemical species from coal fly ash in the treatment process

Coal fly ash is a reactive material and on contact with aqueous solutions such as AMD undergoes dissolution with subsequent release of chemical species. An observation of results in **Tables 3** and **4** show that interaction of coal fly ash and AMD leads to the release of B, Sr, Mo

and Ba. The fact that these chemical species increased with increase in the ratio of CFA in the treatment mixture attests to the fact they were being released from the coal fly ash. Mattigod et al. [17] and Eary et al. [20] reported that the glassy phase in coal fly ash is enriched with As, Na, Mg, K, Sr, B, Mo and Ba as soluble salts which are released into solution when the CFA contacts aqueous solutions.

3.9. Comparison to South Africa water quality guidelines

The product water for various CFA:AMD ratios was compared to the Department of Water Affairs and Forestry [32] water quality limits for irrigation and domestic use. Treatments of Navigation AMD with CFA-B resulted in much cleaner water with Cu, K, Mo, Na and Zn being within the domestic water use limits for 1:3 CFA:AMD ratio and Co, Cu, K, Na and Zn being within the domestic water limits for 1:2.5 CFA:AMD ratio. Treatment of Brugspruit AMD with CFA-B produced less clean water although breakthrough to alkaline pH was established within less than an hour. Only Cu and K were within the domestic limits for 1:3 FA:AMD ratio. This comparison includes only the FA:AMD ratios that resulted in process water in the pH range 6–9. The alkali and alkaline earth metal species (Na, B, Mg, Ca, Sr and Ba) remained largely in the process water in concentrations beyond the guideline limits. B, Mg, Sr, Mo and Ba were largely released from dissolution of coal fly ash and additional treatment options such as reverse osmosis will be required to further clean the water to required standards.

4. Conclusions

The dissolution and hydrolysis of basic oxides such as MgO and CaO from coal fly ash on contacting AMD led to an increase in pH. On the other hand, hydrolysis of AMD chemical species such as Al^{3+}, Fe^{3+}, Fe^{2+} and Mn^{2+} led to release of acidity that counteracted the pH increase leading to stepwise increase in pH of process water and buffer zones as the treatment processes progressed. This was clearly observed for Navigation AMD as opposed to Brugspruit AMD that had low hydrolysable species. These two processes initiated several processes such as precipitation and adsorption that led to attenuation of the major and minor chemical species leading to much cleaner product water. Efficiency of the inorganic contaminants removal was directly linked to amount of FA in the reaction mixture and to the final pH in product water. Three processes were identified that would finally control the quality of the product water, these were (1) CFA:AMD ratios, (2) treatment time and (3) chemistry of the AMD. Most of the major contaminants were reduced to below South African water quality guidelines; however, the coal fly ash was observed to release other contaminants in solution and this could be a drawback for the proposed treatment process. Other factors that would improve the sustainability of the treatment process are beneficial application of the treatment residues as backfill material. Economic viability of this process would also depend on closeness of the AMD generating mines and the coal power utilities generating the coal fly ash.

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References

[1] Simate GS, Ndlovu S. Acid mine drainage: Challenges and opportunities. Journal of Environmental Chemical Engineering. 2014;**2**:1785-1803. http://dx.doi.org/10.1016/j.jece.2014.07.021

[2] Younger PL, Banwart SA, Hedin RS. Mine water chemistry. In: Brian JA, Jack TT, editors. Mine Water: Hydrology, Pollution, Remediation. Dordrecht: Kluwer Academic Publishers; 2002. pp. 65-117

[3] Gitari MW, Petrik LF, Etchebers O, Key DL, Iwuoha E, Okujeni C. Treatment of acid mine drainage with fly ash: Removal of major contaminants and trace elements. Journal of Environmental Science Health-Part A. 2006;**A41**:1729-1747. DOI: 10.1080/10934520600754425

[4] Feng D, Aldrich C, Tau H. Treatment of acid mine water by use of heavy metal precipitation and ion exchange. Mineral Engineering. 2000;**13**:623-642. http://dx.doi.org/10.1016/S0892-6875(00)00045-5

[5] Gunther P, Mey W, Van Niekerk A. A sustainable mine water treatment initiative to provide potable water for South African City _ a public-private partnership. Water in Mining Conference; 2006; Brisbane

[6] Gitari WM. Attenuation of metal species in acidic solutions using bentonite clay: Implications for acid mine drainage remediation. Toxicological & Environmental Chemistry. 2014;**96**:201-217. DOI: 10.1080/02772248.2014.923426

[7] Nordstrom DK. Aqueous pyrite oxidation and the consequent formation of secondary iron minerals. In Acid Sulfate Weathering (eds. J. A. Kittrick, D. F. Fanning, and L. R. Hossner). Soil Science Society of America Special Publication. 1982;**10**:37-56. ISBN-13: 978-0-08-044643-1

[8] Potgieter-Vermaak SS, PotgieterJH, Monama P, Van Grieken R. Comparison of limestone, dolomite and fly ash as Pre-treatment agents for acid mine drainage. Minerals Engineering. 2006;**19**:454-462. http://dx.doi.org/doi:10.1016/J.MINENG.2005.07.009

[9] Maree JP, du Plessis P, van der Watt CJ. Treatment of acidic effluents with limestone instead of lime. Water Science Technology. 1992;**26**:345-355

[10] Maree JP, Van Tonder GJ, Millard P. Underground Neutralization of Mine Water with Limestone. Pretoria, South Africa: Water Research Commission, Report no. 609/1/96; 1996. ISBN: 1-86845-241-7

[11] Allison AE, Nathoo J, Thomson K, Kramer HJ, Witkamp GJ, Reddy ST, Randall DG. Design of a eutectic freeze crystallization process for multicomponent waste water stream. Chemical Engineering Research and Design. 2010;**88**:1290-1296. http://dx.doi.org/10.1016/j.cherd.2010.01.023

[12] Mulopo J. Continuous pilot scale assessment of the alkaline barium calcium desalination process for acid mine drainage treatment. Journal of Environmental Chemical Engineering. 2015;**3**:1295-1302. http://dx.doi.org/10.1016/j.jece.2014.12.001

[13] Cravotta III AC, Trahan MK. Limestone drains to increase pH and remove dissolved metals from acidic mine drainage. Applied Geochemistry. 1999;**14**:581-606. http://dx.doi.org/10.1016/S0883-2927(98)00066-3

[14] Cogho VE,van Niekerk AM. Optimum coal mine water reclamation project. In: Proceedings of the International Mine Water Conference; 2009; Pretoria, South Africa. ISBN Number: 978-0-9802623-5-3

[15] Bhattacharyya KG, Gupta SS. Kaolinite and montmorillonite as adsorbents for Fe^{3+}, Co^{2+} and Ni^{2+} in aqueous medium. Applied Clay Science. 2008;**41**:1-9. http://dx.doi.org/10.1016/j.clay.2007.09.005

[16] Sammy MN, Chuks PE, Richard OA, Gitari WM, Segun AA, Olanrewaju OF, Petrik LF. The leaching behavior and geochemical fractionation of trace elements in hydraulically disposed weathered coal fly ash. Journal of Environmental Science and Health, Part A: Toxic/Hazardous Substances and Environmental Engineering. 2014;**49**:233-242. DOI: 10.1080/10934529.2013.838929

[17] Mattigod SV, Rai D, Eary LE, Ainsworth CC. Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel residues: Review of the major elements. Journal of Environmental Quality. 1990;**19**:188-201. DOI: 10.2134/jeq1990.00472425001900020004x

[18] Gitari WM, Fatoba OO, Petrik LF, Vadapalli VR. Leaching characteristics of selected South African fly ashes: Effect of pH on the release of major and trace species.

Journal of Environmental Science and Health, Part A. 2009;**44**:206-220. DOI: 10.1080/10934520802539897

[19] Gitari WM, Petrik LF, Etchebers, Key DL, Okujeni C.Utilization of fly ash for treatment of coal mines wastewater: Solubility controls on major inorganic contaminants. Fuel. 2008;**87**:2450-2462. DOI: 10.1016/j.fuel.2008.03.018

[20] Eary LE, Dhanpat R, Mattigod SV, Ainsworth CC. Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion residues: II. Review of the minor elements. Journal of Environmental Quality. 1990;**19**:202-214. DOI: 10.2134/jeq1990.00472425001900020005x

[21] Foner HA, Robl TL, Hower JC, Graham UM. Characterization of fly ash from Israel with reference to its possible utilization. Fuel 1999;**78**:215-223. http://dx.doi.org/10.1016/S0016-2361(98)00140-9

[22] Eze CP, Sammy MN, Richard OA, Gitari WM, Segun AA, Olanrewaju OF, Petrik LF. Chemical, mineralogical and morphological changes in weathered coal fly ash: A case study of a brine impacted wet ash dump. Journal of Environmental Management. 2013;**129**:479-492. http://dx.doi.org/10.1016/j.jenvman.2013.07.024

[23] Grace NM, Leslie FP, Olanrewaju OF, Gitari WM, Frédéric JD, Jaco N, Sammy MN, Paul EC. Comparison of CO_2 capture by ex-situ accelerated carbonation and in in-situ naturally weathered coal fly ash. Journal of Environmental Management. 2013;**127**:212-220. http://dx.doi.org/10.1016/j.jenvman.2013.05.027

[24] Fatoba OO, Petrik LF, Akinyeye RO, Gitari WM, Iwuoha EI. Long-term brine impacted fly ash. Part 1: Chemical and mineralogical composition of the ash residues. International Journal of Environmental Science and Technology. 2015;**12**:551-562. DOI 10.1007/s13762-013-0439-1

[25] Jenke RD, Gordon KP. Chemical changes in concentrated, acidic, metal-bearing waste waters when treated with lime. Environmental Science and Technology. 1983;**17**:217-223. DOI: 10.1021/es00110a007

[26] Doye I, Duchesne J. Neutralization of acid mine drainage with alkaline industrial residues: Laboratory investigation using batch-leaching tests. Applied Geochemistry. 2003;**18**:1197-1213. http://dx.doi.org/10.1016/S0883-2927(02)00246-9

[27] Xenidis A, Evangelia M, Ioannis P. Potential use of lignite fly ash for the control of acid generation from sulphidic wastes. Waste Management. 2002;**22**:631-641. http://dx.doi.org/10.1016/S0956-053X(01)00053-8

[28] Seoane S, Leiros CM. Acidification-Neutralization processes in a lignite Mine Spoil Amended with Fly Ash or Limestone. Journal of Environmental Quality. 2001;**30**:1420-1431. DOI: 10.2134/jeq2001.3041420x

[29] Phung HT, Lund LJ, Page AL, Bradford GR. Trace elements in fly ash and their release in water and treated soils. Journal of Environmental Quality. 1979;**8**:171-175. DOI: 10.2134/jeq1979.00472425000800020007x

[30] Erol M, Kucukbayrak S, Ersoy-Mericboyu A, Ulubas T. Removal of Cu^{2+} and Pb^{2+} in aqueous solutions by fly ash. Energy Conservation Management. 2005;**46**:1319-1331. http://dx.doi.org/10.1016/j.enconman.2004.06.033

[31] Polat M, Eli L, Ithamar P, Haim C. Chemical neutralization of acidic wastes using fly ash in Israel. Journal of Chemical Technology and Biotechnology. 2002;**77**:377-381. DOI: 10.1002/jctb.567

[32] Department of Water Affairs and Forestry. South African Water Quality, Guidelines, second ed, Domestic Use. Vol. 1. 2nd ed. Pretoria, South Africa: Department of Water Affairs and Forestry; 1996. ISBN 0-7988-5339-5

[33] American Society for Testing and Materials. Standard Specification for Fly Ash and Raw or Calcined Natural Pozzolan for Use as a Mineral Admixture in Portland Cement Concrete. Philadelphia, PA: ASTM; 1988. pp. C618-88

[34] Uhlmann WH, Buttcher O, Totsche CE, Steinberg W. Buffering of acidic mine lakes: The relevance of surface exchange and solid bound sulphate. Mine Water and Environment. 2004;**23**:20-27. DOI: 10.1007/s10230-004-0032-4

[35] Fillipek HL, Nordstrom DK, Ficklin HW. Interaction of acid mine drainage with waters and sediments of west squaw creek in the West Shasta Mining District, California. Environmental Science and Technology, 1987;**21**:388-396. DOI: 10.1021/es00158a009

[36] Britton HTS. Hydrogen Ions: Their Determination and Importance in Pure and Industrial Chemistry. 4th ed. Vol. 2. London, UK:Chapman and Hall Ltd; 1956

[37] Drever IJ. The Geochemistry of Natural Waters: Surface and Groundwater Environments. 3rd ed. Prentice-Hall, Inc, New Jersey, United states; 1997. pp. 25-37. ISBN-13: 978-0132727907

[38] Shum M, Lavkulich L. Speciation and solubility relationships of Al, Cu and Fe in solutions associated with sulfuric acid leached mine waste rock. Environmental Geology. 1999;**38**:59-68. DOI: 10.1007/s002540050401

[39] Godfrey Madzivire, Leslie F. Petrik, Wilson M. Gitari, Tunde V. Ojumu, Gillian Balfour. Application of coal fly ash to circumneutral mine waters for the removal of sulphates as gypsum and ettringite. Minerals Engineering; 2010;**23**:252-257. http://dx.doi.org/10.1016/j.mineng.2009.12.004

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