

ROLE OF PH ON SULPHATE REMOVAL FROM CIRCUMNEUTRAL MINE WATER USING COAL FLY ASH

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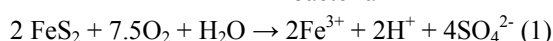
ABSTRACT

Fly ash (FA) is a coal combustion by-product. South Africa produces 27 MT of FA annually, of which a small amount (5 %) is beneficially utilized while the rest is disposed in landfill, ash dumps or ponds. This waste product has a serious impact on the environment apart from the high costs associated with its storage. Acid mine drainage (AMD) is another environmental hazard and the detrimental effects of AMD on the environment are well researched and documented in the literature. Neutralization of AMD is being achieved in various ways that include chemical and biological techniques. Low cost and effective treatment methods are constantly being sought and FA treatment is one of the promising methods due its low cost and availability in large quantities. FA has been successfully employed to neutralize and remove toxic elements from AMD. Approximately 80-90 % of sulphate was removed when FA was used as an ameliorant while treating low-pH, Fe, Al and sulphate-rich AMD. In South Africa, many contaminated mine waters are near to neutral pH (i.e., neutral mine drainage, NMD) and are often rich in Ca and Mg and poor in Fe and Al content. Such waters have been treated with FA in this study and no significant removal of sulphates was observed at final pH of less than 10. However, treatment of the NMD to pH greater than 11 has seen more than 70 % sulphate removal.

1. INTRODUCTION

The freshwater resources around the world are under stress due to the increasing population coupled with pollution of ground and surface water as a result of industrial and domestic activities. Typical pollutants of South Africa's water resources include industrial effluents, domestic and commercial sewage, mine waters, agricultural run off and litter (Davies et al., 1993). Mine water is a source of sulphate contamination in surface and groundwater. The source of sulphates in mine water is due to the bacterial catalysed oxidation of sulphide minerals, such as pyrite, in the presence of oxygen and water (Younger et al., 2002).

bacteria



The concentration of sulphates in mine water varies depending on the geologic rock that is exploited during mining. Rocks that contain more sulphide mineral than neutralizing minerals, such as dolomite and limestone, typically result in acid mine drainage (AMD) with high concentration of sulphates, Fe, Al and Mn. Rocks containing comparable amounts of neutralizing minerals to sulphide minerals generally result in neutral mine drainage (NMD), with high concentration of Ca and Mg, moderate concentration of sulphates and very low concentrations of Fe, Al and Mn (Younger et al., 2002; Blowes and Ptacek, 1994).

Typical approaches to mine water treatment include biological treatment, chemical treatment, ion exchange and membrane methods. The most common methods usually employed for heavily contaminated mine water treatment are biological treatment and chemical methods using lime and limestone. Ion exchange and membrane methods are too expensive to be used to treat heavily contaminated mine water and pre treatment is generally required to avoid fouling of membranes and resins (Adriano et al., 1980; Bosman, 1983; Conlon, 1990; Johnson and Hallberg, 2005; Maree et al., 1989; Hlabela et al., 2007 and Hammack et al., 2006).

Due to the high costs associated with chemicals, cost-effective ways are being investigated for treatment of mine water. Treatment of mine water using coal FA looks promising since it is a waste material found in close proximity to the coal mines. Most coal combustion power stations in South Africa are built near the coal mines to reduce transport costs. FA is waste material trapped from flue gas to avoid atmospheric contamination. Leachates from FA are highly alkaline. Treatment of AMD with FA has been investigated extensively (Gitari et al., 2006; Gitari et al., 2008 and Petrik et al., 2003). The water produced in the treatment process is free from heavy metals such as Fe, Al, Mn, etc. The sulphate concentrations are reduced to the saturation level of gypsum (~ 1500 ppm).

Treatment of NMD rich in Mg and Ca with FA to pH 9 has shown insignificant sulphate removal. The objectives of this research are: 1) to evaluate the effect of pH and, 2) to evaluate the effect of Fe and Al concentrations on sulphate removal.

2. MATERIALS AND METHOD

Sampling

The materials used in this study were NMD, AMD and fly ash (FA). The mine waters were collected from two different coal mines in Mpumalanga, South Africa. The mine water was filtered through a 0.45 µm pore nucleopore membrane and cation samples were acidified with concentrated HNO₃ to pH < 2. The samples were sealed in plastic containers and kept at 4 °C until analysis by inductively-coupled plasma-atomic emission/mass spectrometry (ICP-AES/MS) and ion chromatography (IC) for cations and anions, respectively (Table 3). FA was collected from a nearby pulverized coal combustion power station. The FA was collected directly from the precipitators and kept in sealed plastic bags devoid of air to avoid carbonation of free lime to calcite. The FA was analysed for elemental and mineral composition using x-ray fluorescence spectroscopy (XRF) and x-ray diffraction spectroscopy (XRD) respectively.

Effect of the Amount of FA or Final PH on Sulphate Removal

a) Effect of the amount of FA.

These experiments were conducted to evaluate the effect of the amount of FA on sulphate removal. NMD was mixed with different amounts of FA to give a pre-determined NMD: FA ratio. The mixture was stirred in a beaker using an overhead stirrer until pH ≥ 12 as shown in Table 1. The mixtures were then filtered through a 0.45µm filter paper and the supernatant analysed using IC and ICP-MS for anions and cations respectively.

Table 1. Different amounts of FA mixed with neutral mine drainage

Experiment	Volume of mine water (ml)	Mass of FA (g)	Mass Ratio
1	200	100.05	2:1
2	200	66.68	3:1
3	200	50.04	4:1
4	200	40.03	5:1

b) Effect of final pH.

This set of experiments was conducted to investigate the effect of the final pH on sulphate removal. NMD (500 ml) of pH 6.5 was mixed with FA (250 g) and stirred using an overhead stirrer. Aliquot samples were collected at pH 9.88, 10.21, 11.77 and 12.34. The samples were filtered through a 0.45 µm nucleopore filter membrane and the supernatant analysed for anions and cations using IC and ICP-MS. The solid samples at pH 9.88, 10.21, 11.77 and 12.34 were also analysed using XRD and XRF to investigate the changes in mineralogical and chemical composition of the FA.

Effect of FE and AL on Sulphate Removal

NMD and AMD were mixed in the following ratios; 1:0 1:1, 2:1 and 3:1 (NMD:AMD). AMD was used as a source of Fe and Al. The mixtures were then treated with FA at a L/S ratio of 2:1 by stirring the mixture with an overhead stirrer. Aliquot samples were collected at pH 6, 8, 9, 10, 11 and 12, filtered through a 0.45 µm nucleopore filter membrane. The supernatant was then analysed for elemental composition using IC and ICP-MS.

The mineral phases that were likely to form during treatment of NMD and NMD/AMD mixtures were predicted using PHREEQC geochemical modeling code and WATEQ4F database. Saturation indices were calculated at different final pH values. The WATEQ4F database was edited to include the thermodynamic parameters of ettringite as calculated by Perkins and Palmer (1999).

3. RESULTS AND DISCUSSION

Characterization of FA, NMD and AMD

The chemical compositions of the NMD and AMD samples are shown in Table 2. The major ions of the NMD are Ca, Mg and sulphate. It also contains substantial amounts of Mn and very low concentration of Fe and Al. The AMD contains substantial amounts of Fe, Al and Mn. Its sulphate content is far greater than that of the NMD.

The type of mine water depends on the geology of mine (Lottermoser, 2007; Younger et al., 2002). The mine producing NMD is situated in a geologic setting that includes dolomite and pyrite. The coal mine producing AMD is located in a geologic setting that also contains dolomite, but is dominated by pyrite.

The AMD results from oxidation of pyrite and a lack of buffering by dolomite. Although the mine water contains substantial amounts of Ca and Mg due to dolomite dissolution. In this case, the alkalinity produced during weathering of dolomite is not sufficient to neutralize the acidity generated by pyrite oxidation.

NMD results from the oxidation of the pyrite followed by neutralization due to dolomite dissolution. This will cause Al and Fe to precipitate as hydroxides ($\text{pH} > 3.5$) while the weathering of dolomite causes the mine water to contain elevated concentrations of Ca and Mg (Eq. 2). Some of the sulphate is removed from the water due to precipitation of gypsum.

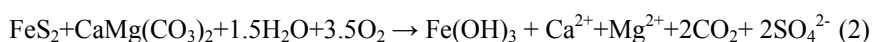


Table 2. Composition of circumneutral mine water and AMD.

	Neutral mine drainage	Acid mine water
element	concentration (ppm)	concentration (ppm)
pH	6.85	2.48
EC (ms/m)	5.02	13.98
Al	0.016	473.95
K	29.19	34.16
Mn	24.96	88.22
Co	0.29	1.89
Ni	0.21	2.97
Ca	557.55	598.73
Fe	0.07	8158.20
Mg	851.77	398.90
Na	20.12	70.48
Sr	1.81	1.02
F	0.79	1.75
Cl	115	9.80
NO_3^-	49.69	8.01
PO_4^{3-}	1.15	167
SO_4^{2-}	4583	42862

FA mineral composition was analyzed using XRD and the results obtained are as depicted on Fig 3. The FA is composed of mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), quartz (SiO_2), hematite (Fe_2O_3) and lime (CaO). The elemental composition of FA was also analyzed using XRF and the results are shown in Table 3. Based on the XRF data obtained, the FA used in this study is Class F according to the American Society for Testing and Measurement (ASTM C618) classification since $\text{SiO}_2 + \text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3 = 86.99\% > 70\%$. Class F fly ash is formed during the combustion of either bituminous or anthracitic type of coal (Mattigod et al., 1990).

Effect of the Amount of FA or the Final PH on Sulphate Removal

The results show that the amount of FA added to the mine water has a great effect on the amount of sulphates that can be removed from the water. As more FA was added to mine water, more sulphates were removed, as shown in Fig 1 (a) and (b). For the 5:1 ratio, approximately 55 % sulphate removal was observed, while for the 2:1 ratio, approximately 71 % sulphate removal was observed. Maximum values for pH were 10.13, 11.77, 12.12 and 12.34 for ratios 5:1, 4:1, 3:1 and 2:1, respectively.

The results also reveal that the amount of sulphates removed from the mine water depends on the final pH of the water (Fig 1c and 1d). Treatment of mine water to pH 9.88 only removes 6 % of sulphates from mine water. Treatment of the mine water to a pH of 12.35 results in 71 % of sulphates removed from mine water.

XRD results obtained for FA and solid residues (SR) taken at pH 11.77 (SR1) and 12.34 (SR2) show that the only new mineral phase formed during treatment of mine water with FA was gypsum (Fig 2). This means that the sulphates are being removed in the form of gypsum during the treatment of mine water with FA. The lime in FA causes the pH of the water to increase and the lime peaks disappear from the spectra of the solid residues (SR).

As more FA is added or final pH is increased, more lime is available to neutralize the mine water (Eq. 3) and more Ca^{2+} ions are present, causing Eq. 4 to shift to the right according to Le Chatelier's principle, resulting in enhanced removal of sulphate as gypsum (Fig 2).

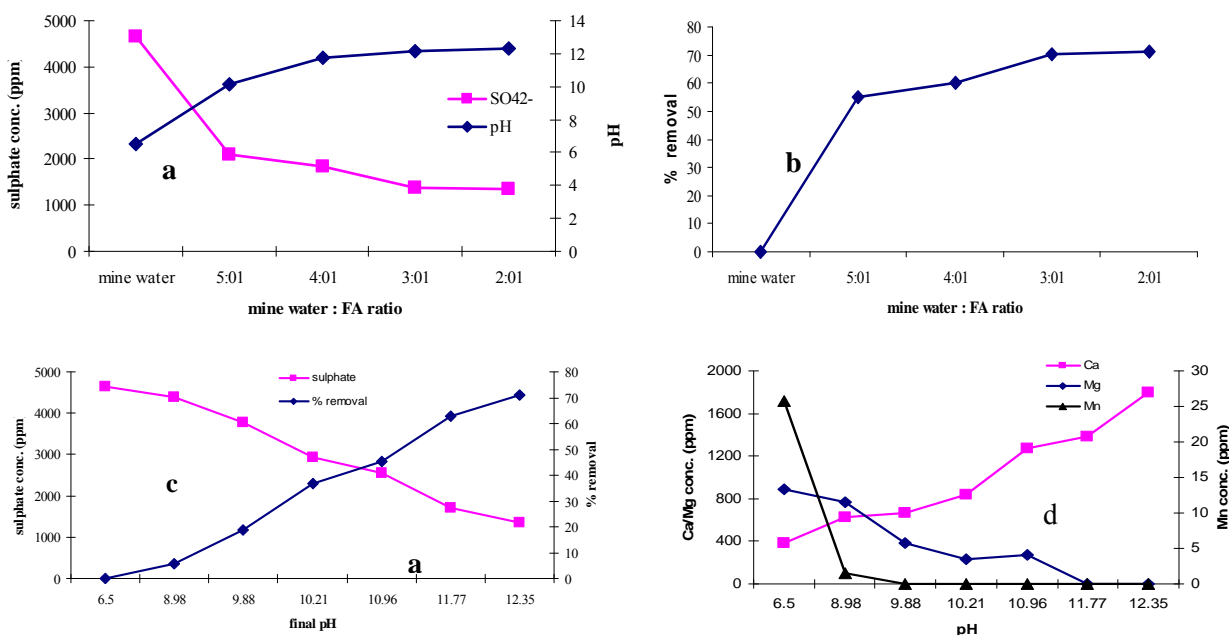
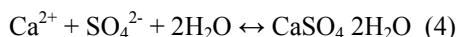
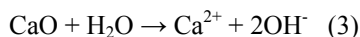


Fig 1. Sulphate concentration during treatment of NMD with different amounts of FA (a), % sulphate removal of sulphates using different amounts of FA (b), % removal of sulphates at different NMD: FA ratios (c) and the Ca/Mg and Mn concentration trends (d) during treatment of NMD to different final pH.

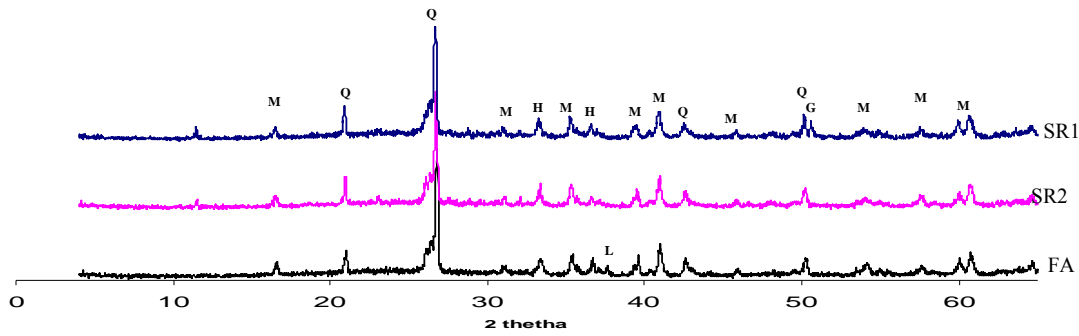


Figure 2. XRD spectra of FA, solid residues (SR1 and SR2) after treatment of CMW with FA.

A comparison of the elemental composition of FA and solid residues shows that the % SO_3 increases in the SR as the final pH increases (Table 3). This correlates well with the results obtained from IC which shows a decrease in the sulphate content of the water as the final pH increases (Fig 2a). During treatment of mine water with FA, lime in FA dissolves into solution thereby causing the pH of the water to increase (Eq. 3).

Table 3. Elemental composition of FA and solid residues at different pH values of treatment

Oxide	Hendrina	pH 9.88	pH 10.21	pH 11.77	pH 12.34
SiO_2	54.01	53.115	52.880	52.717	53.278
Al_2O_3	29.01	26.950	26.696	26.505	26.745
CaO	4.63	4.725	4.634	4.574	4.556
Fe_2O_3	3.99	4.302	4.284	4.340	4.372
MgO	1.12	1.881	1.956	1.971	1.975
TiO_2	1.79	1.475	1.459	1.440	1.485
K_2O	0.78	0.747	0.740	0.734	0.738
SO_3	0.24	0.697	0.713	1.238	1.301
P_2O_5	0.54	0.535	0.531	0.525	0.529
Na_2O	0.14	0.028	0.063	0.080	0.068
MnO	0.04	0.063	0.060	0.059	0.063
LOI	3.7	4.882	4.820	4.953	4.870
Total	99.99	99.400	98.835	99.137	99.979

Effect of FE and AL on Sulphate Removal

The mixtures of NMD and AMD had pH values less than 3. Treatment profiles of different NMD to AMD ratios are shown in Fig 3.

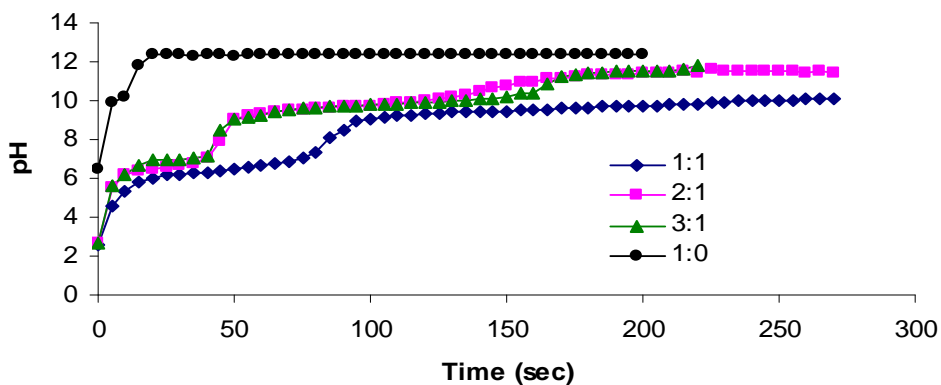
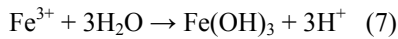
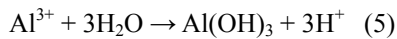


Fig 3. Changes of pH during treatment of circumneutral and different CMW:AMD ratio with FA

A slight buffering was noticed for NMD treatment at pH 10, which was not pronounced as compared to NMD/AMD mixtures. The buffering is observed at multiple pH plateaus is due to hydrolysis reactions coupled with precipitation of Fe(OH)₃ and Al(OH)₃ at pH 4-7 (Uhlman et al., 2004; Jenke and Gordon, 1983). Mn(OH)₂ hydrolysis occurs at pH 9-10. PHREEQC geochemical modeling done on NMD and NMD/AMD post process waters predicts hydroxides, oxyhydroxides and oxyhydroxysulphate of Fe and Al to be precipitating (Table 4).



Sulphate removal as a function of different NMD:AMD ratios is shown in Fig 4. Treatment of NMD to pH less than 10 shows insignificant sulphate removal. This is because the pH increase to pH 10 requires very small amount of lime due the absence of Fe and Al to buffer a sharp rise in pH. This means only a small concentration of Ca²⁺ will be available for gypsum precipitation. Treatment of NMD:AMD mixtures shows more than 80 % sulphate removal when the pH is raised to 10.

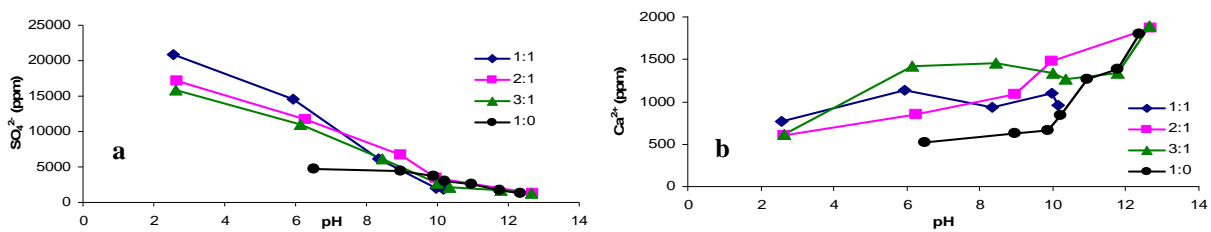


Fig 4. Trends of sulphate (a) and Ca (b) concentrations during treatment of CMW and different CMW:AMD ratios with FA

Table 4. Saturation indices of sulphates and Ca bearing mineral phases calculated at various pHs for NMD and 1:1, 2:1 and 3:1 NMD/AMD mixtures.

ion	sample	NMD to different final pH						1:1 mixture to different final pH					
		6.5	8.9	9.88	10.96	11.7	12.35	2.3	4.57	5.94	8.34	9.96	10.21
SO ₄ ²⁻	Alunite	5.14	-	-	-	-	-	-	-	16.4	16.4	-	-
	Anhydrite	-0.3	0.1	0.2	0.2	0.3	0.4	0.2	0.7	1.0	1.0	1.1	1.1
	Barite	0.1	0.03	0.00	0.0	0.0	0.0	-0.1	-0.1	-0.2	-0.2	-0.1	-0.1
	Basaluminite	2.9	-	-	-	-	-	-	3.8	16.9	16.9	-	-
	Celestite	-0.8	-0.8	-0.9	-0.9	-0.9	-0.9	-0.7	-0.7	-0.8	-0.8	-0.8	-0.8
	Ettringite	-	-	-	2.7	11.8	12.4	-	-	-	-	9.85	10.7
	Gypsum	-0.1	0.2	0.4	0.4	0.5	0.5	0.4	0.9	1.2	1.2	1.3	1.3
	Jarosite(ss)	-	-	-	-	-	-	-	-	5.4	5.4	3.1	1.9
	Jarosite-K	-	-	-	-	-	-	-	-	5.2	5.2	3.8	2.6
	Jarosite-Na	-	-	-	-	-	-	-	-	1.9	1.9	0.5	-0.7
JarositeH	-	-	-	-	-	-	-	-	-	-1.0	-1.0	-	
Ca	Anhydrite	-0.3	-0.1	0.2	0.2	0.3	0.4	0.15	0.69	1.00	1.00	1.12	1.12
	Diopside	-	0.7	3.9	6.5	8.0	8.7	-	-	-	-	-	-
	Gypsum	0.1	0.2	0.4	0.4	0.5	0.6	0.37	0.91	1.21	1.22	1.33	1.33
	Hydroxyapatite	-	5.0	7.4	8.9	10.2	11.1	-	-	-	-	-	-
	Tremolite	-	10.3	21.0	29.0	33.0	34.1	-	-	-	-	-	-
ion	sample	2:1 mixture to different final pH					3:1 mixture to different final pH						
		2.65	6.26	8.98	9.97	12.69	2.63	6.15	8.44	10.0	10.36	11.78	
SO ₄ ²⁻	Alunite		16.4	1.7	-	-	-	16.2	4.7	-	-		
	Anhydrite	0.03	0.7	0.9	0.9	0.9	0.04	0.5	0.77	0.86	0.87		
	Barite	0.1	0.1	0.1	0.1	0.1	0.25	0.2	0.25	0.23	0.23		
	Basaluminite	-	-	3.1	-	-	-	16.7	5.9	-	-		
	Celestite	-0.6	-0.6	-0.6	-0.6	-0.6	-	-0.7	-0.7	-0.7	-0.7		
	Ettringite	-	-	4.36	8.6	19.3	-	-	1.1	8.0	9.5		
	Gypsum	0.2	0.9	1.1	1.2	1.2	0.26	0.7	1.0	1.1	1.1		
	Jarosite(ss)	-	6.7	8.0	2.5	-	-	5.65	10.02	1.90	-0.29		
	Jarosite-K	-	6.6	8.5	3.2	-	-	5.6	10.4	2.6	0.5		
	Jarosite-Na	-	3.3	5.1	-0.2	-	-	2.08	6.9	-0.9	-		
	JarositeH	-	0.03	-0.8	-	-	-	-1.0	1.6	-	-		
Jurbanite	-0.3	2.6	-	-	-	-0.4	2.6	-	-	-			

Note: (-) undersaturation, (0) at equilibrium and positive numbers means supersaturation and precipitation of that mineral phase is possible.

This is because more lime is consumed (Fig 4b) to counter the acidity/H⁺ ions generated through hydrolysis of Al and Fe ions. Precipitation of Al and Fe (oxy)-hydroxides, oxyhydroxysulphate tends to adsorb or incorporate sulphates leading to more sulphates being removed (Seth and Ghazi, 1997). The possible oxyhydroxysulphate complexes predicted using PHREEQC geochemical modeling include alunite(KAl₃(SO₄)₂(OH)₆), basaluminite (Al₄(OH)₁₀SO₄), jurbanite (AlOHSO₄), jarosite-ss (K_{0.77}Na_{0.03}H_{0.2}Fe₃(SO₄)₂(OH)₆), jarosite-K (KFe₃(SO₄)₂(OH)₆), jarosite-Na (NaFe₃(SO₄)₂(OH)₆) and jarosite-H (H₃OFe₃(SO₄)₂(OH)₆).

The presence of Fe and Al ions generates acidity (H⁺ ions) when Al and Fe (oxy) hydroxides and oxyhydroxysulphates forms. This facilitates dissolution of lime (releasing more Ca²⁺ and OH⁻). The Ca²⁺ ions combine with SO₄²⁻ to form gypsum leading to removal of SO₄²⁻. The OH⁻ combine with H⁺ leading to the buffer plateaus observed (Fig 3). Precipitation of Al, Fe (oxy) hydroxides and oxyhydroxysulphates contribute to sulphate removal through adsorption and structural incorporation respectively.

Treatment of NMD beyond pH 10 shows similar trends of sulphate removal for NMD:AMD mixtures. This is because sulphates that precipitate on metal hydroxide surfaces in the form of oxyhydroxysulphates tend to desorb at high pH due to competition with hydroxide ions. At pH 7, the sulphates start to desorb from metal hydroxides surfaces due to competition with OH⁻ ions according to Seth and Ghazi (1997). Saturation indices calculated using PHREEQC show that Fe and Al oxyhydroxysulphate complexes are undersaturated at pH > 10. The only sulphate phases that are supersaturated are barite, ettringite, gypsum and anhydrite for all the NMD and NMD/AMD mixtures.

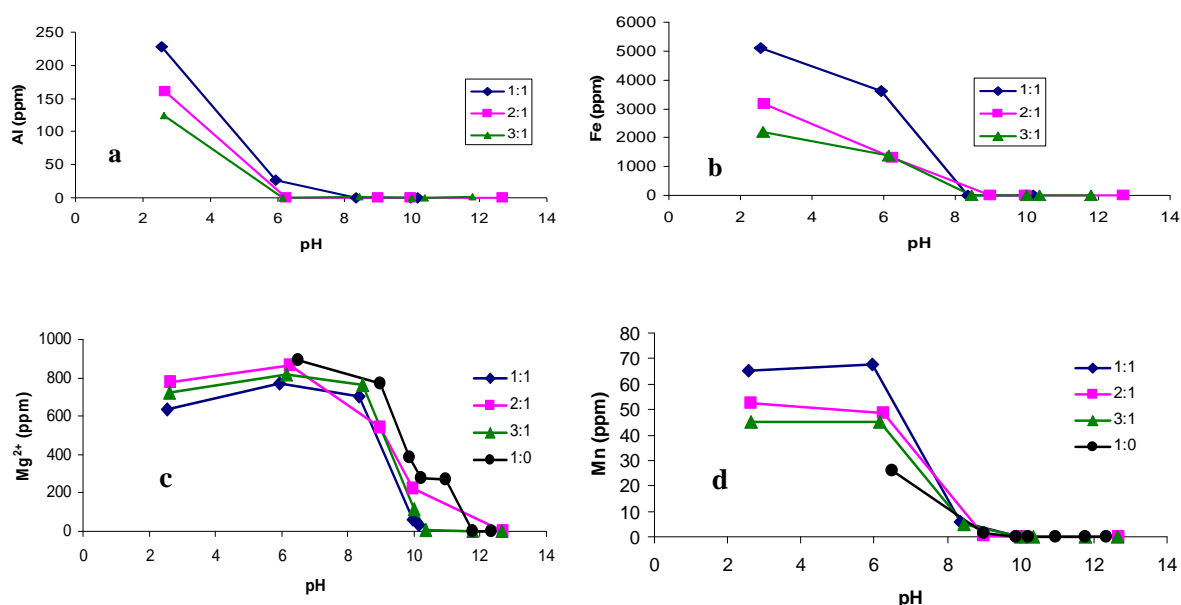


Fig 5. Trends of Al (a), Fe (b), Mg (c) and Mn (d) concentrations during treatment of different CMW and different CMW:AMD ratios with FA.

Treatment of mine water with FA results in removal of Mg, Fe, Mn and Al, but the removal depends on the final pH of treatment. Fe and Al precipitate at pH 6-8 (Fig 6a and 5b), Mn precipitates at pH > 9 (Fig 5c) and Mg precipitates out at pH > 10 (Fig 5d).

Table 5. Saturation indices of Al, Fe, Mn and Mg mineral phases calculated using PHREEQC geochemical model at various pHs for NMD and 1:1, 2:1 and 3:1 NMD/AMD mixtures.

ion	sample phases	NMD to different final pH						1:1 mixture to different final pH					
		6.5	8.9	9.88	10.96	11.7	12.35	2.3	4.57	5.94	8.34	9.96	10.21
Al	Al(OH) ₃	-0.7	-	-	-	-	-	-	-	2.5	2.5	-0.3	-0.5
	Alunite	5.1	-	-	-	-	-	-	8.8	16.4	16.4	-	-
	Basaluminite	2.9	-	-	-	-	-	-	3.8	16.9	16.9	-	-
	Boehmite	1.6	-0.7	-	-	-	-	-	0.7	4.7	4.7	1.9	1.7
	Diaspore	3.3	1.0	0.1	-	-	-	-	2.4	6.4	6.4	3.6	3.4
	Etringite	-	-	-	2.65	6.4	8.9	-	-	-	-	9.9	10.7
	Jurbanite	-	-	-	-	-	-	-0.2	1.8	2.9	2.9	-	-
	Gibbsite	2.0	-0.3	-	-	-	-	-	1.2	5.2	5.2	2.4	2.2
Mn	Birnessite	-	-	-0.1	4.1	6.7	7.8	-	-	-	-	0.5	1.3
	Bixbyite	-	3.5	8.9	15.0	18.7	20.0	-	-	-	-	9.8	11.0
	Hausmannite	-	6.9	14.1	22.1	26.8	28.3	-	-	-	-	15.3	16.9
	Manganite	-	1.6	4.3	7.4	7.9	9.9	-	-	-	-	4.8	5.35
	Nsutite	-	-	1.0	5.1	7.7	9.0	-	-	-	-	1.5	2.3
	Pyrochroite	-	-	0.6	2.5	3.6	3.7	-	-	-	-	0.9	1.3
	Pyrolusite	-	-	2.2	6.3	8.9	10.2	-	-	-	-	2.7	3.5
Fe	Fe(OH) _{2.7} Cl _{0.3}	-	5.5	4.4	3.2	2.2	1.4	-	3.6	7.4	7.4	9.64	9.4
	Fe(OH) ₃	-	1.1	0.5	-0.6	-	-	-	-	2.1	2.1	5.6	5.4
	Fe ₃ (OH) ₈	-	-	-	-	-	-	-	-	3.8	3.8	10.2	9.4
	Goethite	4.6	7.0	6.4	5.3	4.5	3.9	-	3.8	8.0	8.0	11.5	11.3
	Hematite	11.2	16.1	14.7	12.6	11.0	9.9	-	9.6	18.0	18.0	24.9	24.6
	Maghemite	-	5.7	4.3	2.2	0.6	-0.5	-	-0.8	7.6	7.6	14.5	14.2
	Magnetite	9.6	14.4	11.5	7.3	4.0	1.7	-	9.09	20.3	20.3	26.7	25.9
	Jarosite(ss)	-	-	-	-	-	-	-	-	5.4	5.4	3.1	1.9
	Jarosite-K	-	-	-	-	-	-	-	-	5.2	5.2	3.8	2.6
	Jarosite-Na	-	-	-	-	-	-	-	-	1.9	1.9	0.5	-0.7
	JarositeH	-	-	-	-	-	-	-	-	-1.0	-1.0	-	-
Mg	Brucite	-	-0.1	0.8	3.0	4.4	5.2	-	-	-	-	0.6	1.0
ion	sample phase	2:1 mixture to different final pH					3:1 mixture to different final pH						
		2.65	6.26	8.98	9.97	12.69	2.63	6.15	8.44	10.0	10.36	11.78	
Al	Al(OH) ₃	-	2.7	0.5	-0.5	-	-	2.5	1.0	-0.6	-1.0	-	-
	Alunite	-	16.4	1.7	-	-	-	16.2	4.7	-	-	-	-
	Basaluminite	-	-	3.1	-	-	-	16.7	5.9	-	-	-	-
	Boehmite	-	5.0	2.8	1.8	-1.0	-	4.7	3.2	1.6	1.3	-0.2	-
	Diaspore	-	6.7	4.5	3.5	0.8	-	6.4	4.9	3.3	3.0	1.6	-
	Etringite	-	-	4.36	8.59	19.27	-	-	1.1	7.99	9.53	15.16	-
	Jurbanite	-0.3	2.6	-	-	-	-0.4	2.6	-	-	-	-	-
	Gibbsite	-	5.4	3.2	2.2	-	-	5.2	3.7	2.1	1.7	0.3	-
Mn	Birnessite	-	-	-	0.4	8.7	-	-	-	0.46	1.88	6.93	-
	Bixbyite	-	-	3.7	9.7	20.9	-	-	0.33	9.71	11.83	19.10	-
	Hausmannite	-	-	7.2	15.1	29.2	-	-	2.64	15.2	17.97	27.5	-
	Manganite	-	-	1.7	4.7	10.3	-	-	0.03	4.72	5.78	9.41	-
	Nsutite	-	-	-	1.4	-	-	-	-	1.50	2.91	7.97	-
	Pyrochroite	-	-	-	0.9	3.7	-	-	-	0.86	1.56	3.77	-
Fe	Fe(OH) _{2.7} Cl _{0.3}	-	8.0	10.5	9.44	5.9	-	7.5	10.7	9.3	8.8	7.0	-
	Fe ₃ (OH) ₈	-	2.8	6.1	5.3	2.7	-	4.10	13.50	8.92	7.54	1.9	-
	Fe(OH) ₃	-	5.6	12.8	9.5	-	-	2.3	6.2	5.2	4.8	3.4	-
	Goethite	-	8.7	12.0	11.2	8.6	-	8.2	12.1	11.0	10.7	9.3	-
	Hematite	-	19.4	26.0	24.4	19.1	-	18.3	26.1	24.1	23.41	20.6	-
	Maghemite	-	9.0	15.6	14.1	8.7	-	7.9	15.7	13.7	13.0	10.2	-
	Magnetite	-	22.1	29.3	26.0	15.2	-	20.6	30.0	25.4	24.0	18.4	-
	Jarosite(ss)	-	6.70	8.03	2.49	-	-	5.7	10.0	1.9	-0.3	-	-
	Jarosite-K	-	6.6	8.5	3.2	-	-	5.6	5.6	2.6	0.5	-	-
	Jarosite-Na	-	3.3	5.1	-0.2	-	-	2.1	6.9	-0.9	-	-	-
JarositeH	-	0.03	-0.8	-	-	-	-1.0	1.6	-	-	-	-	
Mg	Brucite	-	-	-	0.71	5.54	-	-	-	0.73	1.45	4.15	-

Note: (-) undersaturation, (0) at equilibrium and positive numbers means supersaturation and precipitation of that mineral phase is possible.

Saturation indices calculated using PHREEQC geochemical code show that Al and Fe hydroxides, oxyhydroxides and oxyhydroxysulphate complexes start precipitating at pH 5 and 6 respectively (Table 5). The saturation indices for Mn phases (i.e MnO₂, Mn₂O₃, Mn₃O₄, MnOOH, MnO₂, Mn(OH)₂) show that they are supersaturated at pH > 8. Mg was found to precipitate as brucite (Mg(OH)₂) at pH > 10 (Table 5).

4. CONCLUSION

Sulphate removal during treatment of mine water with FA results in sulphate removal to 1000 - 1500 ppm. For NMD/AMD mixtures approximately 80 % of sulphate concentration is removed up to pH 10 and a further 5 – 10 % is removed when pH is increased beyond pH 10. On the other hand NMD treatment shows a gradual decrease of sulphate concentration at pH 6 to 10 and a sharp decrease of sulphate concentration were observed at pH beyond 10. The sulphates are removed in the form of gypsum. The presence of Fe, Al and Mn results in more lime demand from the FA due to pH buffering, thereby precipitating more sulphates as gypsum if the mine water is treated to pH below pH 10. The oxyhydroxysulphates also contribute to removal of sulphates in addition to adsorption on the surfaces of precipitating oxyhydroxides. Fe, Al, Mn and Mg are removed to below detection limit during treatment of mine water with FA. In order to remove Fe and Al, the pH needs to be raised to 8, while for removal of Mn and Mg; the pH has to be raised to 10 and 11, respectively.

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