

# Fate of sulphate removed during the treatment of circumneutral mine water and acid mine drainage with coal fly ash: Modelling and experimental approach

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## Abstract

The treatment of acid mine drainage (AMD) and circumneutral mine water (CMW) with South African coal fly ash (FA) provides a low cost and alternative technique for treating mine wastes waters. The sulphate concentration in AMD can be reduced significantly when AMD was treated with the FA to pH 9. On the other hand an insignificant amount of sulphate was removed when CMW (containing a very low concentration of Fe and Al) was treated using FA to pH 9. The levels of Fe and Al, and the final solution pH in the AMD–fly ash mixture played a significant role on the level of sulphate removal in contrast to CMW–fly ash mixtures. In this study, a modelling approach using PHREEQC geochemical modelling software was combined with AMD–fly ash and/or CMW–fly ash neutralization experiments in order to predict the mineral phases involved in sulphate removal. The effects of solution pH and Fe and Al concentration in mine water on sulphate were also investigated. The results obtained showed that sulphate, Fe, Al, Mg and Mn removal from AMD and/or CMW with fly ash is a function of solution pH. The presence of Fe and Al in AMD exhibited buffering characteristic leading to more lime leaching from FA into mine water, hence increasing the concentration of  $\text{Ca}^{2+}$ . This resulted in increased removal of sulphate as  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ . In addition the sulphate removal was enhanced through the precipitation as Fe and Al oxy-hydroxysulphates (as shown by geochemical modelling) in AMD–fly ash system. The low concentration of Fe and Al in CMW resulted in sulphate removal depending mainly on  $\text{CaSO}_4\cdot 2\text{H}_2\text{O}$ . The

results of this study would have implications on the design of treatment methods relevant for different mine waters.

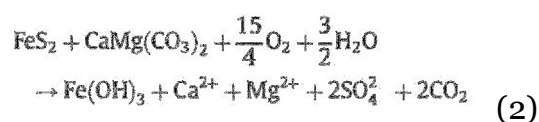
**Keywords:** Fly ash, Circumneutral mine water, Acid mine drainage, PHREEQC geochemical modelling and sulphates

## Introduction

Freshwater resources around the world are under stress due to 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 heavy metal and sulphate contamination of surface and ground water. The microbial oxidation of sulphide minerals, such as pyrite, in the presence of oxygen and water has been shown to be responsible for the presence of the sulphate ion in mine water as shown in Eq. (1) (Younger et al., 2002).



The resulting acid generated in this reaction causes chemical weathering of the surrounding rocks resulting in leaching of heavy metals into the water. The characteristics of mine water depend on the mineralogy of the surrounding rock (Lottermoser, 2007; Younger et al., 2002; Blowes and Ptacek, 1994). Circumneutral mine water is generated when the surrounding rock typically contains equal stoichiometric proportions of dolomite, limestone and pyrite. Therefore, CMW is generated when the acidity formed as a result of pyrite oxidation is neutralized in situ by dolomite dissolution. This will cause Al and Fe to precipitate as hydroxides (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 concentrations are removed from the mine water due to precipitation as gypsum.



On the other hand, acid mine drainage (AMD) is generated (Eq. (1)) when the surrounding rock contains higher proportions of pyrite than dolomite. Although sometimes the mine water contains significant amounts of Ca and Mg due to dolomite dissolution, the alkalinity produced during weathering of dolomite is not sufficient to neutralize the acidity generated by pyrite oxidation.

Several methods have been used in the treatment of polluted mine water; these include biological treatment, chemical treatment, ion exchange and membrane

methods (Madzivire, 2010). Biological treatment using sulphate reducing bacteria (SRB) and chemical treatment using lime and limestone are usually employed for heavily contaminated mine water. Ion exchange and membrane methods are too expensive for the treatment of heavily contaminated mine water and pretreatment 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; Hammack et al., 2006).

Due to the high costs associated with chemical treatment technologies and long residence time requirement for biological treatment, there has been a concerted effort towards developing a cost effective alternative technology for treatment of mine water (Madzivire et al., 2010). The treatment of mine water using coal fly ash (FA) has proved to be promising (Petrik et al., 2003; Gitari et al., 2006, 2008; Madzivire et al., 2010). Fly ash is an abundant waste material from coal power stations in South Africa. Most coal combustion power stations in South Africa are built near the coal mines to reduce the transport costs. The leachate from FA is known to be highly alkaline and the treatment of AMD with FA has been investigated extensively and it has been shown that the water produced in the treatment process is free from heavy metals such as Fe, Al, Mn, and that the sulphate concentration is reduced by 80% to the saturation level of gypsum of approximately 1500 ppm (Gitari et al., 2006, 2008; Petrik et al., 2003; Vadapalli et al., 2008).

Recently, it was shown that treatment of CMW rich in Mg and Ca to pH 9 with FA did not result in a significant sulphate removal (Madzivire et al., 2010). However, the authors showed that by raising the solution pH to 12 followed by seeding with gypsum crystals and addition of amorphous  $\text{Al}(\text{OH})_3$ , the sulphate level can be reduced to an acceptable limit. The objective of this follow up study is to provide an understanding of the mechanism of removal by the use PHREEQC geochemical modelling, which was used to investigate the effect of pH and to evaluate the effect of Fe and Al concentration on sulphate removal from CMW when reacted with FA. The Al and Fe were added by mixing AMD with CMW. This study also provides an insight into the mineral phases responsible for removal of sulphates, Fe, Al and Mn from mine water when treated with FA.

## **2. Materials and method**

The mine waters, CMW and AMD were collected from storage dams of two different coal mines in Mpumalanga, South Africa. The mine water was filtered using a hand pump through a 0.45  $\mu\text{m}$  nucleopore membrane and cation samples were acidified with concentrated  $\text{HNO}_3$  to  $\text{pH} < 2$ . The samples (100 ml) were sealed in plastic containers and kept at 4 °C until analysis. Cation analysis was performed using an inductively-coupled plasma-atomic emission spectrometry (ICP-AES) and inductively-coupled plasma-mass spectrometry (ICP-MS). The ICP-AES was used for concentration greater than 1 ppm and ICP-MS was used for concentration less than 1 ppm. Anion analysis was performed using ion chromatography (IC). To confirm the quality assurance, analysis of the certified reference material was performed using ICP-AES, ICP-MS and IC before the analysis of the samples.

Fly ash was collected from a nearby pulverized coal combustion power station in Mpumalanga. 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 mineral composition of FA was elucidated using qualitative or quantitative X-ray diffraction spectroscopy (XRD) and the morphology of FA was analyzed by scanning electron microscopy (SEM). The FA was analyzed for chemical composition using X-ray fluorescence spectroscopy (XRF).

### *2.1. Effect of final pH*

Experiments were carried out to investigate the effect of the final pH on sulphate, Mg and Mn removal by collecting water samples at different pH levels. Circumneutral mine water (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  $\mu$ m nucleopore filter membrane and analyzed using IC and ICP-AES and ICP-MS. The ICP-AES and ICP-MS samples were acidified to pH < 3 using concentrated HNO<sub>3</sub> to stabilize the cations. All the samples were stored at 4 °C before analysis. The solid residues produced at pH 9.88, 10.21, 11.77 and 12.34 were also analyzed using qualitative XRD and XRF to investigate the changes in mineralogical and chemical composition of the FA.

The pH and electrical conductivity (EC) were measured using a Hanna HI 991301 portable pH/EC/TDS/temperature pH meter after every 5 min. The pH and EC were the parameters used to measure the progress of experiment. Before using the pH meter, it was calibrated using fresh buffers of pH 4 and 7 or 10 depending on the pH range to be measured. Electrical conductivity of the water was calibrated using an EC calibration solution with a conductivity of 12.88 ms/cm.

### *2.2. Effect of Fe and Al on sulphate removal*

Circumneutral mine water and AMD were mixed in the following ratios; 1:0 1:1, 2:1 and 3:1 (CMW:AMD). Acid mine drainage was used as a source of Fe and Al. The CMW/AMD mixtures were then treated with FA at a liquid to solid ratio of 2:1 by stirring with an overhead stirrer. Aliquot samples were collected at pH 6, 8, 9, 10, 11 and 12, filtered through a 0.45  $\mu$ m nucleopore filter membrane and then analyzed using IC, ICP-AES and ICP-MS. The ICP-AES and ICP-MS samples were acidified to pH < 3 using concentrated HNO<sub>3</sub> to stabilize the cations. All the samples were stored at 4 °C before analysis. The solid residues formed after treatment of CMW and CMW/AMD mixtures with FA were analyzed using quantitative XRD to

understand the amount of the new mineral phases.

### 2.1. Geochemical modelling

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

$$SI = \frac{\log IAP}{K_{sp}}$$

where IAP is the ion activity product observed in solution, and  $K_{sp}$  is the solubility product.

Positive SI values indicate that a solution is supersaturated with respect to that particular mineral phase, a negative SI value indicates under saturation and a saturation index of zero indicates saturation with respect to a particular mineral. Super saturation and saturation indicate that precipitation of the respective mineral phase is thermodynamically possible. Equilibrium of the solid mineral phase with its ionic components is indicated by SI of zero. Solutions under saturated with respect to a given solid phase suggest that the phase dissolves in solution to its ionic components. Geochemical calculations performed using computer codes do not prove the presence or absence of a phase, but provide an indication of the tendency for a reaction to occur.

## 3. Results and discussion

The chemical compositions of the CMW and AMD samples are shown in Table 1. The major ions of the CMW are Ca, Mg and sulphate.

Table 1

Composition of circumneutral mine water and acid mine drainage.<sup>a</sup>

**Table 1**  
Composition of circumneutral mine water and acid mine drainage.<sup>a</sup>

Element	Circumneutral mine water	Acid mine drainage
pH	6.50 ± 0.49	2.48 ± 0.06
EC	502 ± 0.15	1138 ± 0.23
Acidity (CaCO <sub>3</sub> )	0	14.95
Alkalinity (CaCO <sub>3</sub> )	10678	0
Ca	537.55 ± 2.97	59875 ± 4687
Mg	861.72 ± 15.51	39990 ± 3328
K	2915 ± 101.4	3416 ± 37
Mn	2287 ± 1135	7622 ± 721
Na	2012 ± 1135	3042 ± 523
Fe	0.02 ± 0.002	2778 ± 223
Al	0.016 ± 0.001	2755 ± 13
Se	1.81 ± 0.03	1.02 ± 0.007
Co	0.29 ± 0.00028	1.89 ± 0.00364
Ni	0.21 ± 0.00014	2.97 ± 0.044
Zn	0.16 ± 0.00021	8.36 ± 2.42
B	0.16 ± 0.000056	0.09 ± 0.00031
Mo	0.015 ± 0.0000071	ND
Ba	0.013 ± 0.00025	ND
Cu	0.002 ± 0.0001	0.002 ± 0.0001
P	0.002 ± 0.0001	0.002 ± 0.0001
Cl	0.002 ± 0.0001	0.002 ± 0.0001
NO <sub>3</sub>	0.002 ± 0.0001	0.002 ± 0.0001
NO <sub>2</sub>	0.002 ± 0.0001	0.002 ± 0.0001
SO <sub>4</sub>	0.002 ± 0.0001	0.002 ± 0.0001

ND = not detected; all units are in mg/l. With the exception of EC which is expressed as  $\mu\text{S/cm}$ . The concentration of acidity or alkalinity is expressed as  $\text{mg/kg CaCO}_3$ .  
<sup>a</sup>The results are presented as the mean of triplicates and the errors as the standard deviation of the mean.

Circumneutral mine water also contains substantial amounts of Mn but 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 CMW.

The FA mineral composition was analyzed using XRD and results obtained are as depicted in Fig. 1. The FA is composed of mullite ( $3\text{Al}_2\text{O}_3\text{-}2\text{SiO}_2$ ), quartz ( $\text{SiO}_2$ ), hematite ( $\text{Fe}_2\text{O}_3$ ) and lime ( $\text{CaO}$ ). The SEM images showed (Fig. 1) that FA is typically composed of irregular and numerous spherical shaped particles having an average diameter of less than 10  $\mu\text{m}$ .

The elemental composition of FA was also determined using XRF and the results are shown in Table 2.

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).

### 3.1. Effect of the final pH

After addition of FA to CMW the pH changed rapidly such that after 20 min the pH had reached 12.35 after which it remained constant. The results reveal that the concentration of sulphate, Mg and Mn removed from the CMW depends on the final pH of the water (Fig. 2). Also Fig. 2b shows that the amount of Ca increases

with increase in the final pH. Treatment of mine water to pH 9.88 removes 6% of sulphate from mine water. Treatment of the mine water to a pH of 12.35 results in 71% of sulphate being removed from mine water (Fig. 2a).

The XRD results obtained for FA and solid residues (SR) taken at pH 11.77 and 12.34 show that the only new mineral phase formed during treatment of mine water with FA was gypsum (Fig. 3). This means that the sulphate is being removed in the form of gypsum during the treatment of mine water with FA. The CaO in FA leaches into the mine water causing the pH and the Ca concentration to increase (Fig. 2). This resulted in the disappearing of the lime peaks in the solid residue XRD spectra (Fig. 3).

A comparison of the elemental composition of FA and solid residues (SR) shows that the % SO<sub>3</sub>, MnO and MgO increases in the SR as the final pH end point was increased (Table 3). This correlates well with the results obtained from cation and anion analysis which showed a decrease in the sulphate, Mn and Mg concentration of the water as the final pH increased (Fig. 2).

The percentage composition of CaO increased from fresh FA to pH 9.88 and then decreased slightly in the solid residue as the final

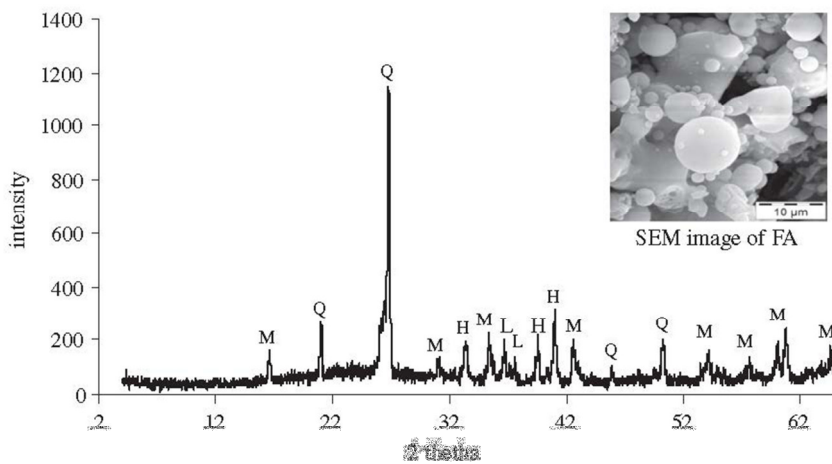


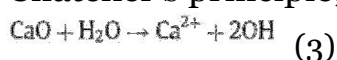
Fig. 1. XRD spectrum and SEM image for FA (M-mullite, Q-quartz, H-hematite and L-lime).

**Table 2**  
Elemental composition of FA.<sup>a</sup>

Major elements		Minor elements	
Species	% w/w composition	Element	Concentration (mg/kg)
SiO <sub>2</sub>	54.01 ± 0.28	Sr	1265.68 ± 8.43
Al <sub>2</sub> O <sub>3</sub>	29.01 ± 0.13	Zr	806.41 ± 2.57
CaO	4.63 ± 0.09	V	380.91 ± 1.00
Fe <sub>2</sub> O <sub>3</sub>	3.99 ± 0.07	Ce	274.69 ± 6.32
TiO <sub>2</sub>	1.79 ± 0.03	Ba	219.69 ± 7.06
MgO	1.12 ± 0.03	Pb	111.58 ± 3.17
Total		Mo	6.44 ± 0.358
		As	0.04 ± 0.03

<sup>a</sup> The results were presented as the mean of triplicates and the error as the standard deviation from the mean.

pH was further increased and this correlates with an increase in Ca concentration (Fig. 2b). During treatment of mine water with FA, lime from FA dissolves into solution thereby causing the pH of the water to increase (Eq. (3)). As the final pH of process water is increased, more CaO is available in the mine water (Eq. (3)) and more Ca<sup>2+</sup> 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. 2a).



The results obtained have shown that the removal of sulphates, Mg and Mn from CMW is dependent of pH. Approximately 71% of sulphate can be removed when the pH is increased from 6.5 to greater than 11, while almost 100% of Mn and Mg could be removed when the pH is increased beyond 9 and 11 respectively.

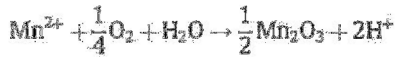
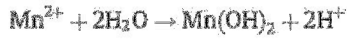
### 3.2. Effect of Fe and Al on sulphate removal

The 1:0, 1:1, 2:1 and 3:1 CMW and AMD mixtures had pH values of 6.5, 2.3, 2.65 and 2.63 before adding FA respectively. The 1:0 mixture was purely CMW, while 1:1, 2:1 and 3:1 had AMD characteristics. The AMD characteristics are more pronounced in the 1:1 mixture followed by 2:1 and lastly 3:1. The converse is true for CMW characteristics. The mixtures were treated with FA and the pH profiles over time of different mixtures are as shown in Fig. 4.

As observed in Fig. 4, the treatment of CMW with FA resulted in a rapid change in pH from 6.5 to 12.35 with a buffering plateau at a pH 10, which was not as prominent for the CMW/AMD mixtures. The buffering plateau at pH 10 is ascribed to the hydrolysis of Mn<sup>2+</sup> (Eq. (5)) and oxidation and precipitation of Mn<sup>2+</sup> (Eq. (6)) (Younger et al., 2002). The higher Mn<sup>2+</sup> concentration in the CMW/AMD



mixtures has resulted in a more prominent buffering plateau at pH 10 compared to<sup>469</sup> CMW trend.



The pH trends for the 3:1, 2:1 and 1:1 mixtures show gradual changes with multiple buffering plateaus. The buffering at pH 6–6.5 can be attributed to the hydrolysis of Fe and Al that was introduced as a result of mixing AMD with CMW (Eqs. (7) and (8)).

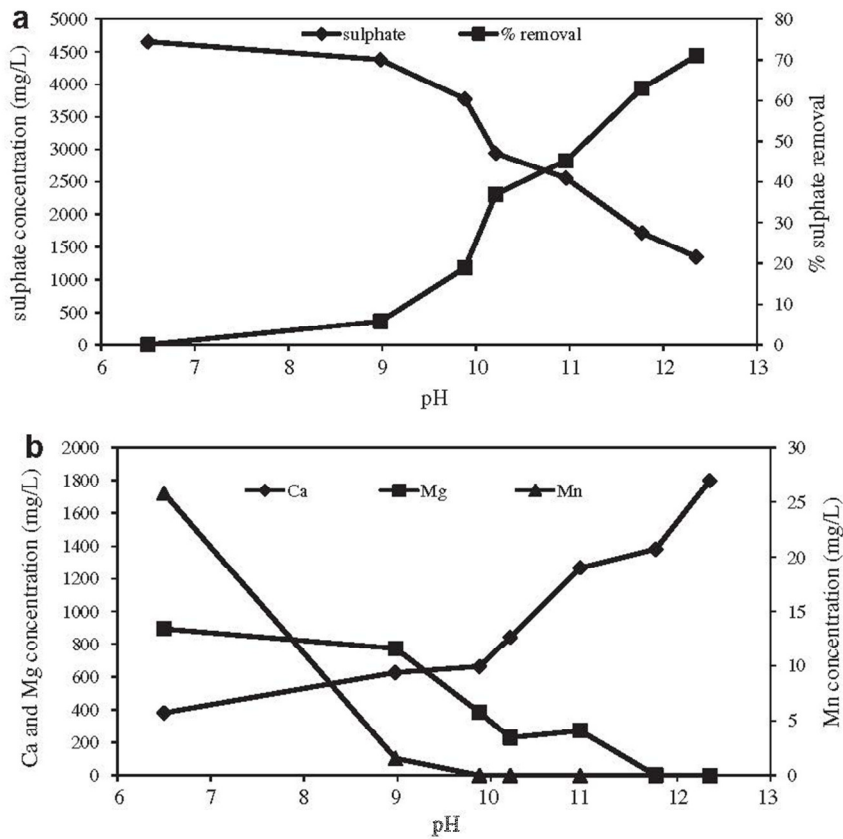


Fig. 2. Sulphate concentration and % sulphate removal (a) and Ca, Mg and Mn concentration (b) at different final pH end points of treatment of CMW with FA.

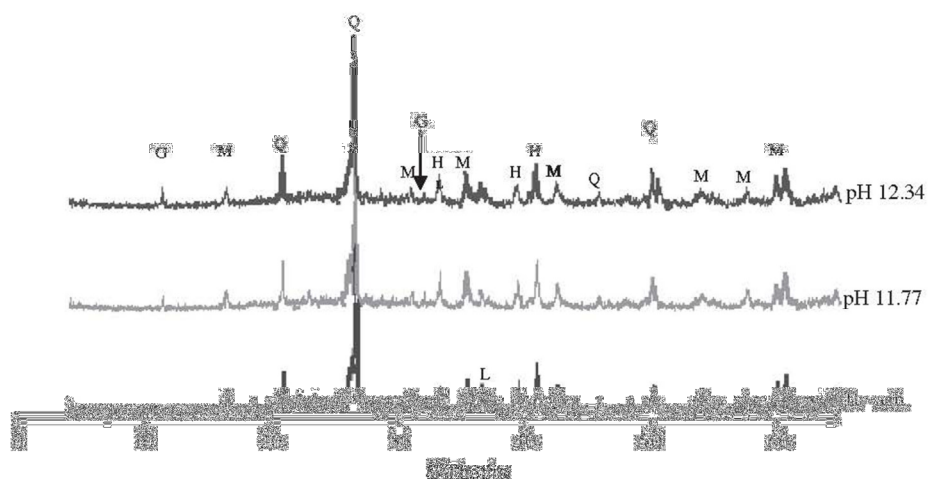


Fig. 2. XRD spectra of solid residues after treatment of wastewater by coagulation-flocculation process at different pH values.

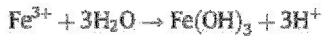
**Table 3**  
Elemental composition of FA and solid residues at different pH values of treatment.

% Oxide	Fresh FA	pH 9.88	pH 10.21	pH 11.77	pH 12.34
SiO <sub>2</sub>	54.01	53.12	52.88	52.72	53.28
Al <sub>2</sub> O <sub>3</sub>	29.01	26.92	26.70	26.51	26.75
CaO	4.63	4.73	4.63	4.57	4.56
Fe <sub>2</sub> O <sub>3</sub>	3.99	4.30	4.28	4.34	4.37
MgO	3.12	1.88	1.96	1.97	1.98
TiO <sub>2</sub>	1.79	1.475	1.459	1.440	1.49
K <sub>2</sub> O	0.78	0.75	0.74	0.73	0.74
SO <sub>3</sub>	0.24	0.70	0.71	1.24	1.30
P <sub>2</sub> O <sub>5</sub>	0.54	0.535	0.531	0.525	0.529
Na <sub>2</sub> O	0.14	0.03	0.06	0.08	0.07
MnO	0.04	0.063	0.060	0.06	0.06
LOI	3.7	4.882	4.820	4.953	4.87
Total	99.99	99.40	98.84	99.14	99.98

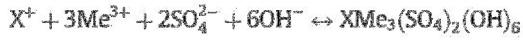
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Al <sub>2</sub> O <sub>3</sub>	29.01	26.92	26.70	26.51	26.75
CaO	4.63	4.73	4.63	4.57	4.56
Fe <sub>2</sub> O <sub>3</sub>	3.99	4.30	4.28	4.34	4.37
MgO	3.12	1.88	1.96	1.97	1.98
TiO <sub>2</sub>	1.79	1.475	1.459	1.440	1.49
K <sub>2</sub> O	0.78	0.75	0.74	0.73	0.74
SO <sub>3</sub>	0.24	0.70	0.71	1.24	1.30
P <sub>2</sub> O <sub>5</sub>	0.54	0.535	0.531	0.525	0.529
Na <sub>2</sub> O	0.14	0.03	0.06	0.08	0.07
MnO	0.04	0.063	0.060	0.06	0.06
LOI	3.7	4.882	4.820	4.953	4.87
Total	99.99	99.40	98.84	99.14	99.98

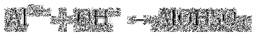
Moreover, the buffering between pH 4 and 7 can be attributed to the precipitation of Fe and Al hydroxides: Fe(OH)<sub>3</sub>, Fe(OH)<sub>2</sub> and Al(OH)<sub>3</sub> (Uhlmann et al., 2004; Jenke and Gordon, 1983).



The precipitation of oxy-hydroxysulphate consumes alkalinity thereby causing pH buffering according to Eqs. (9)–(11). According to Younger et al. (2002) the precipitation of the oxyhydroxysulphate occurs between pH 4 and 9.



where X can be K, Na or H<sub>3</sub>O and Me is either Al or Fe



Sulphate removal as function of pH for different CMW/AMD mixtures is shown in Fig. 5.

The sulphate concentration for the CMW (1:0) was reduced from 4655 mg/L to 4381 mg/L when CMW was treated with FA to pH 10, which is approximately 19% sulphate removal. In the case of the mixtures; the sulphate concentration of 3:1 CMW/AMD mixture was reduced from 15797 mg/L to 2731 mg/L, for 2:1 CMW/AMD mixture the sulphate concentration was reduced from 17142 mg/L to 2435 mg/L and for the 1:1 mixture the sulphate concentration was reduced from 20870 to 1970 mg/L when the mixtures were treated with FA to pH 10. This translates to more than 80% sulphate removal when 3:1, 2:1 and 1:1 mixtures were treated with FA to pH 10. It can be concluded from the above set of experiments that the presence of Fe and Al in mine water has enhanced the sulphate removal.

The small sulphate removal observed for CMW when treated with FA to pH 10 was because the pH rise only required a very small amount of CaO to be released from FA due to the absence of Fe and Al to buffer the sharp rise in pH (Fig. 4). This resulted in small amounts of Ca<sup>2+</sup> being released into solution to react and precipitate out to form gypsum (Eq. (4)).

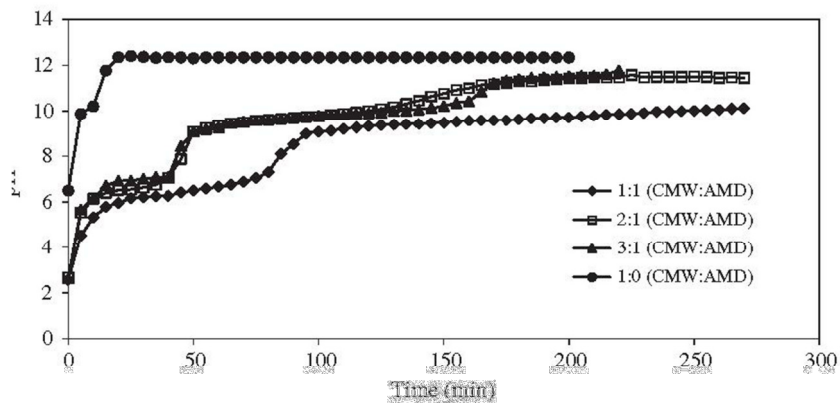


Fig. 4. Changes of pH during treatment of CMW and different CMW/AMD mixture with FA.

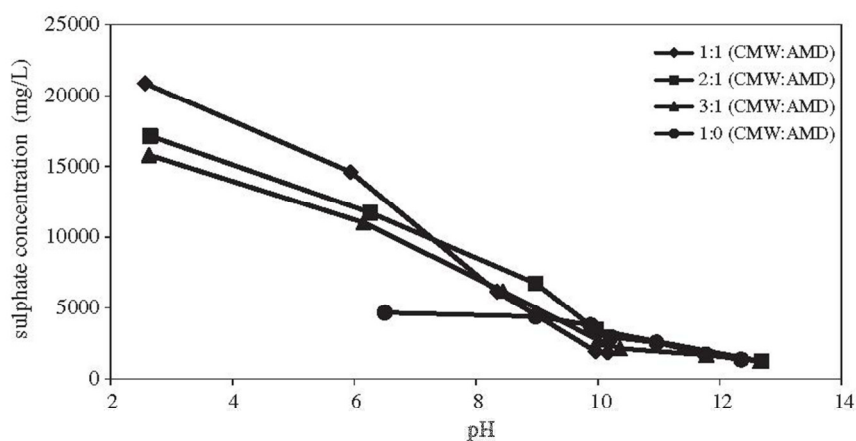


Fig. 5. Sulphate concentration during treatment of CMW and different CMW/AMD mixtures with FA.

**Table 4**  
The percentage composition of the mineral phases in fly ash and solid residues produced after treatment of CMW and CMW/AMD.

Minerals (%)	Fly ash	CMW solid residue	CMW/AMD solid residue
Quartz	46.8	49.2	52.8
Alite	33.8	33.8	33.8
Sulphate	1.5	1.5	1.5
Hydroxide	1.8	1.8	0
Other	14	13.5	11.4

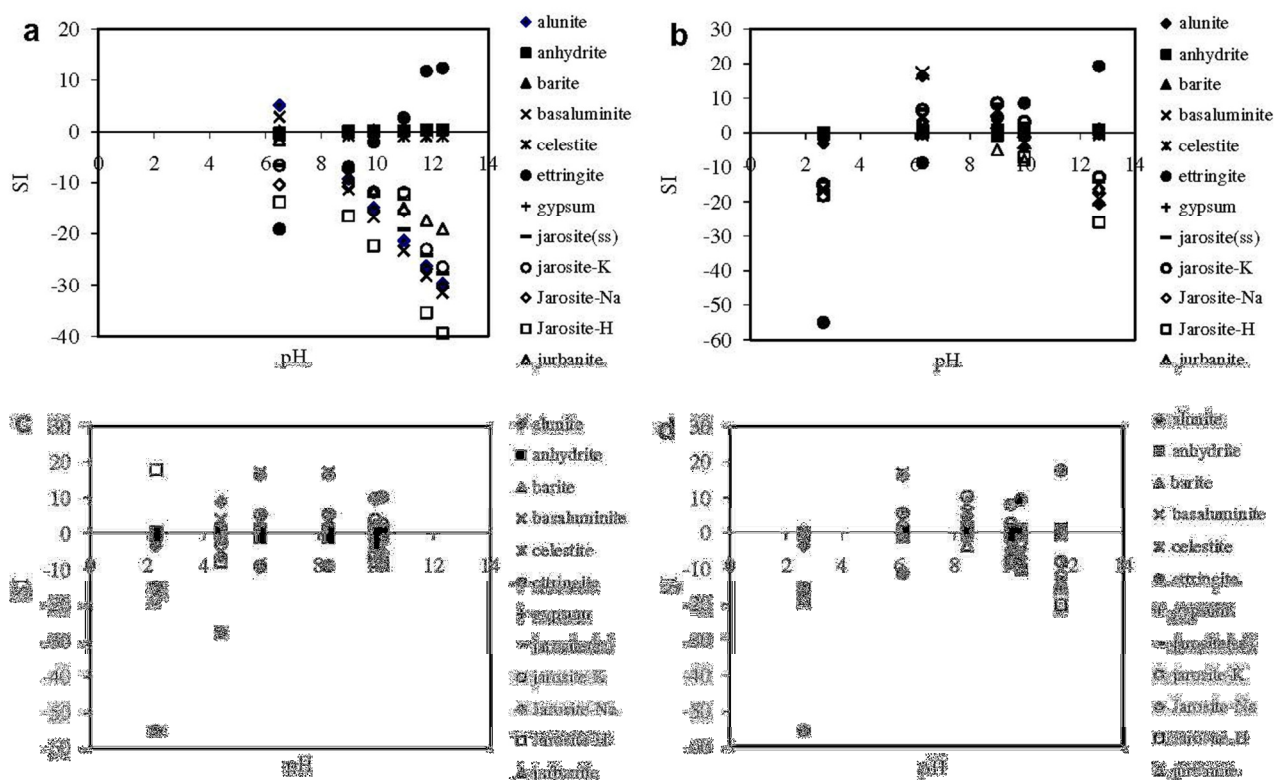


Fig. 6. Saturation indices of sulphate mineral phases at different final pH for treatment of CMW (a) and CMW/AMD mixtures (b-1:1, c-2:1 and d-3:1) with FA. Saturation index < 0 means under saturation, saturation index = 0 means saturation and saturation index > 0 means super saturation. Supersaturation and saturation with respect to a particular mineral means precipitation of that mineral can occur.

The qualitative XRD spectra for the solid residues produced during treatment of AMD or CMW with FA showed similar spectra to those in Fig. 3. Quantitative XRD was conducted in order to see the difference of the changes in the amount of new minerals that were formed during treatment of AMD or CMW with FA (Table 4).

The results showed that the new mineral phase after treatment of mine water with FA is gypsum. The appearance of gypsum occurs as lime disappears, meaning that the Ca that leaches as a result of the dissolution of lime (resulting in a pH increase as depicted in Fig. 4), reacts with the sulphates in the mine water to form gypsum (Eq. (4)). More gypsum was formed in the solid residues produced from FA that was used to treat CMW/AMD mixtures because more lime had to leach to offset the pH buffering caused by the presence of Fe and Al (Eqs. (7)–(11)). Other mineral phases that were formed were amorphous as shown by the increase in the percentage in the solid residue. The identity of these amorphous mineral phases was elucidated using PHREEQC geo-chemical modelling.

### 3.2.1. PHREEQC geochemical modeling

The possible sulphate mineral phases that were precipitating at different pH levels were predicted

using PHREEQC thermodynamic geochemical model and the results are shown in Fig. 6. The saturation indices (SI) obtained by PHREEQC geochemical modelling predicted the following sulphate-bearing mineral phases; ettringite ( $\text{CaO} \cdot 3\text{CaSO}_4 \cdot \text{Al}_2\text{O}_3 \cdot 31\text{H}_2\text{O}$ ); alunite ( $\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$ ), anhydrite ( $\text{CaSO}_4$ ), barite ( $\text{BaSO}_4$ ), basaluminite ( $\text{Al}_4(\text{OH})_{10}\text{SO}_4$ ), jurbanite ( $\text{AlOHSO}_4$ ), jarosite-ss ( $\text{K}_{0.77}\text{Na}_{0.03}\text{H}_{0.2}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ), jarosite-K ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), jarosite-Na ( $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), jarosite-H ( $\text{H}_3\text{OFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), celestite ( $\text{SrSO}_4$ ) and gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) to be precipitating at various pH values (Fig. 6).

Saturation indices of different sulphate-bearing mineral phases for CMW/FA mixtures at different pH end points (Fig. 6a) show that gypsum, barite, celestite, anhydrite and ettringite are the only mineral phases that could precipitate out sulphate when CMW was mixed with FA. The amount of sulphate that could be removed as ettringite, barite and celestite was insignificant since the concentration of Al, Ba, and Sr was in CMW.

Saturation indices calculated for the 3:1, 2:1 and 1:1 CMW/ AMD mixtures (Fig. 6b–d) using PHREEQC geochemical software show that, in addition to gypsum, celestite, ettringite and anhydrite, other Fe and Al oxyhydroxysulphates (alunite, basaluminite, jarosite(ss), jarosite-k, jarosite-Na, jarosite-H and jurbanite) can contribute to sulphate removal. All the oxyhydroxysulphates are super saturated at pH 4–10 except ettringite. Above pH 10 they become under saturated and ettringite becomes supersaturated. This explains why the 3:1, 2:1 and 1:1 CMW/AMD mixtures tend to precipitate out more sulphate compared to CMW when pH was raised to below 10 as the removal of sulphate is not as pronounced for AMD after pH 10 as compared to below pH 10 and the converse is true for CMW.

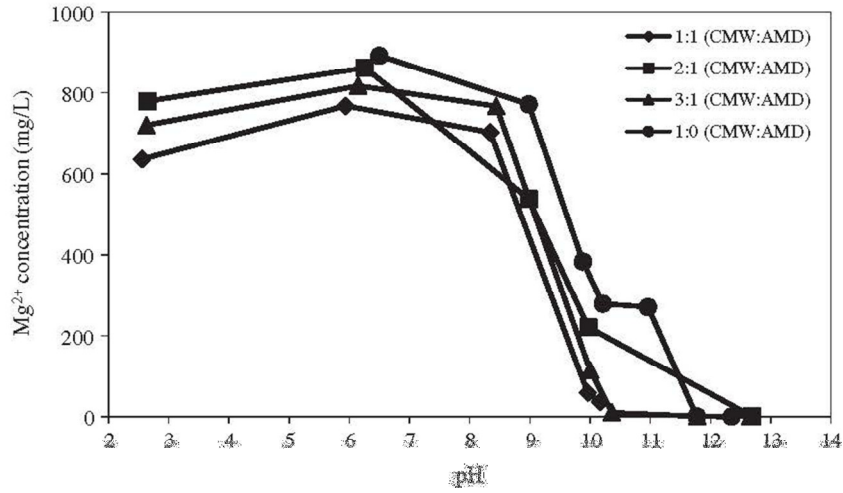


Fig. 7. The concentration of dissolved magnesium as a function of pH for different CMW:AMD ratios.

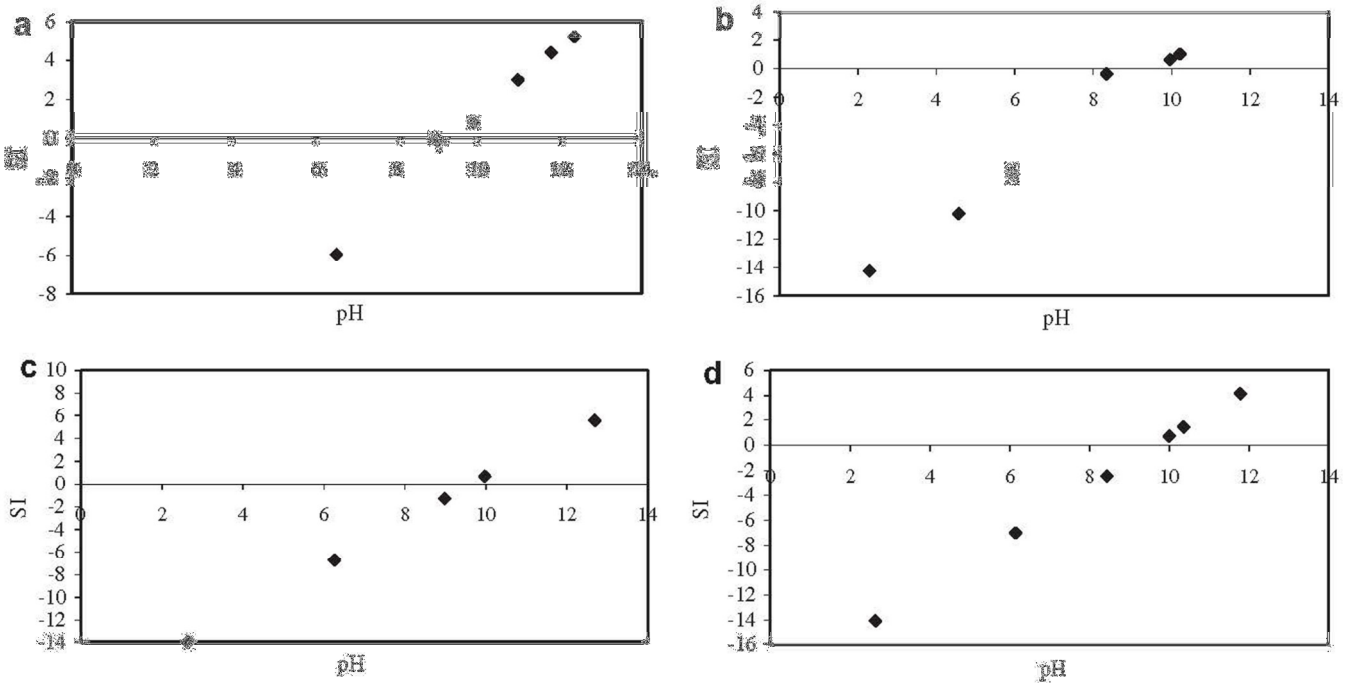


Fig. 8. Saturation indices of brucite at different final pH end points during treatment of CMW (a) and CMW/AMD mixtures (b-1:1, c-2:1 and d-3:1) with FA. Saturation index < 0 means under saturation, saturation index = 0 means saturation and saturation index > 0 means super saturation. Super saturation and saturation with respect to a particular mineral means precipitation of that mineral can occur.

The presence of Fe and Al ions generates acidity ( $H^+$  ions) as Al and Fe (oxy) hydroxides precipitate according to Eqs. (7) and (8). Precipitation of oxyhydroxysulphates consumes alkalinity as shown in Eqs. (9)–(11) (Younger et al., 2002). The acidity generated by hydrolysis reactions during the precipitation of Al and Fe (oxy)hydroxides and the consumption of alkalinity during precipitation of oxyhydroxysulphates facilitates dissolution of more CaO for pH to increase to 10, releasing more  $Ca^{2+}$  ions. The  $Ca^{2+}$  ions combine with sulphate to form gypsum leading to removal of  $SO_4^{2-}$ . Precipitation of Al, Fe (oxy)hydroxides and oxyhydroxysulphates in addition to gypsum precipitation thereby contributes to

more sulphate removal through adsorption and structural incorporation of  $\text{SO}_4^{2-}$ . Treatment of CMW and all the mixtures of CMW/AMD to pH levels beyond pH 10 show similar trends of sulphate removal (Fig. 6). This is because the sulphate phases that are supersaturated above pH 10 and hence responsible for sulphate removal are; barite, ettringite, gypsum and anhydrite for CMW and all CMW/AMD mixtures.

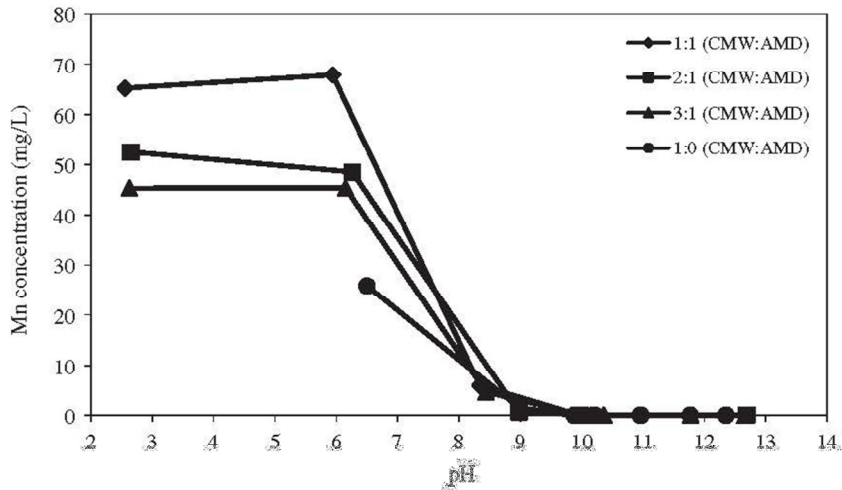


Fig. 9. Mn concentration during treatment of CMW and CMW/AMD mixtures with FA.

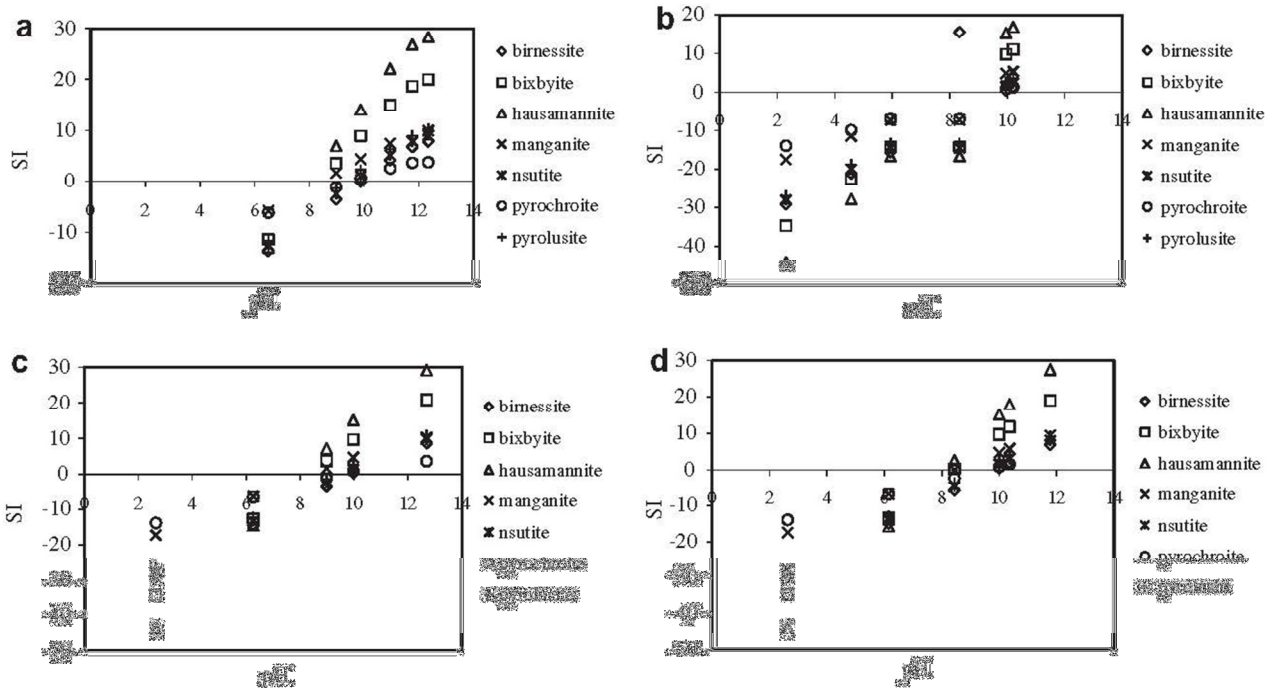


Fig. 10. Saturation indices of Mn bearing minerals phases at different final pH end points during treatment of CMW (a), CMW/AMD mixtures (b-1:1, c-2:1 and d-3:1) with FA. Saturation index < 0 means under saturation, saturation index = 0 means saturation and saturation index > 0 means super saturation. Super saturation and saturation with respect to a particular mineral means precipitation of that mineral can occur.

Treatment of CMW and CMW/AMD mixtures with FA results in approximately 100% removal of Mg from 600–800 mg/L to 0.3 mg/L (Fig. 7). The degree of removal is dependent on the final pH of treatment. Between pH 2 and 6 a slight increase of Mg concentration is observed because of the dissolution of Mg salts from FA, at pH 9 Mg



starts precipitating rapidly and eventually precipitating to below 0.3 mg/L at pH greater than 10 (Fig. 7).

PHREEQC geochemical modelling predicts that Mg would start to precipitate at pH greater than 8 (Fig. 8) as brucite ( $\text{Mg}(\text{OH})_2$ ). The saturation index shows that  $\text{Mg}(\text{OH})_2$  is saturated when the pH is approximately 8.5. At pH above 10,  $\text{Mg}(\text{OH})_2$  is supersaturated, consequently the Mg concentration decreased to below 0.3ppm due to the formation of  $\text{Mg}(\text{OH})_2$ .

The results obtained when CMW and CMW/AMD mixtures when treated with FA show that Mn is also removed from between 40 and 70 mg/L to below 0.04 mg/L (Fig. 9) when the pH was higher than 8.

Saturation indices obtained using PHREEQC show that Mn-bearing mineral phases start precipitating at pH greater than 8 (Fig. 10) as birnessite ( $\text{MnO}_2$ ), bixbyite ( $\text{Mn}_2\text{O}_3$ ), hausmannite ( $\text{Mn}_3\text{O}_4$ ), manganite ( $\text{MnOOH}$ ), nsutite ( $\text{MnO}_2$ ), pyrochroite ( $\text{Mn}(\text{OH})_2$ ) and pyrolusite ( $\text{MnO}_2$ ). All these mineral phases approach saturation at pH 8.5 and are supersaturated at pH greater than 9, and thus precipitate out rapidly and completely.

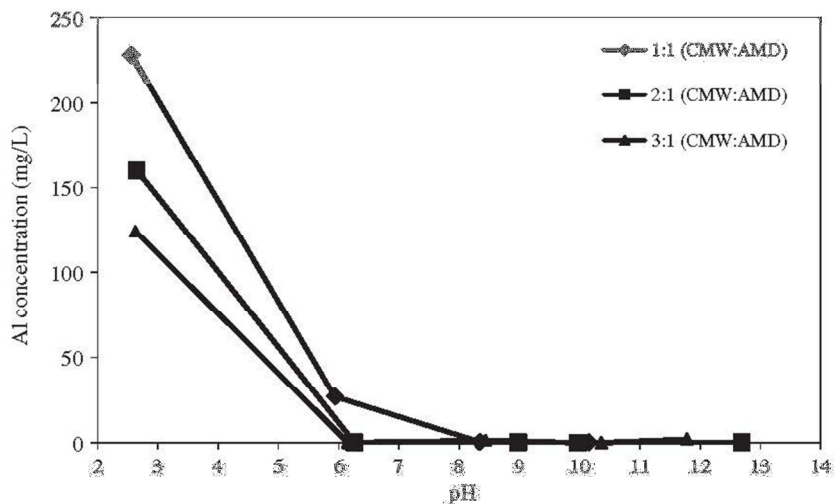


Fig. 11. Al concentration during treatment of CMW/AMD mixtures to various pH end points with FA.

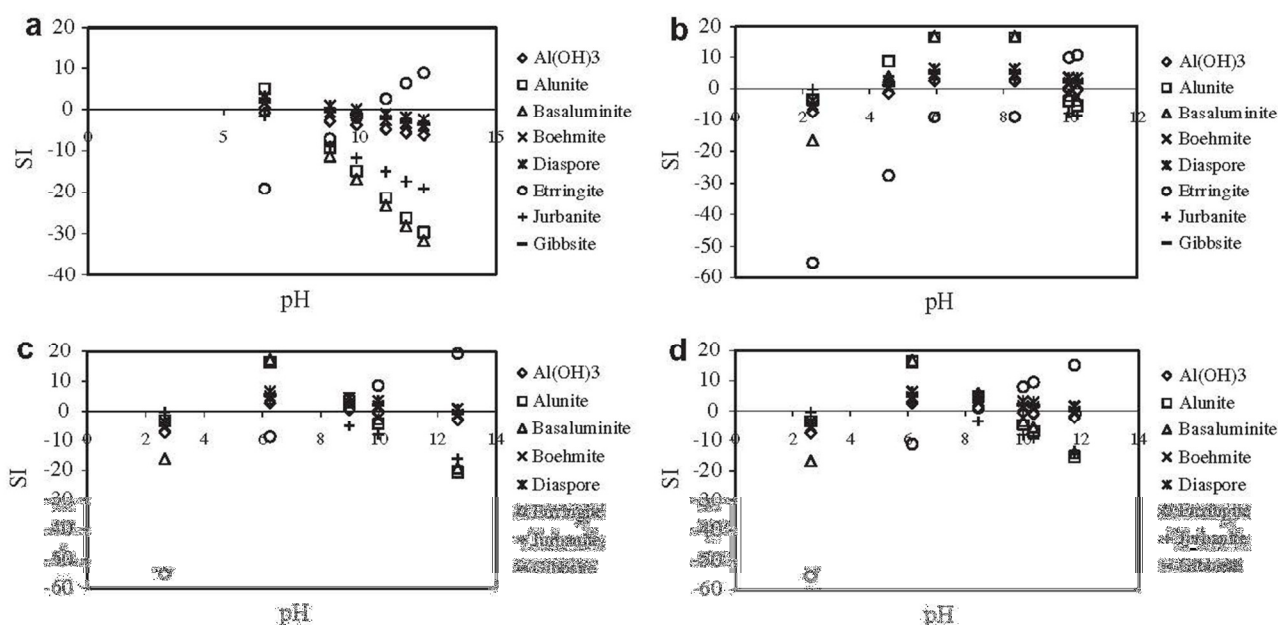


Fig. 12. Saturation indices of Al bearing mineral phases at different pH end points during treatment of CMW (a) and CMW/AMD mixtures (b-1:1, c-2:1 and d-3:1) with FA. Saturation index < 0 means under saturation, saturation index = 0 means saturation and saturation index > 0 means super saturation. Super saturation and saturation with respect to a particular mineral means precipitation of that mineral can occur.

When 3:1, 2:1 and 1:1 CMW/AMD mixtures were treated with FA to various pH end points the Al concentration was reduced from between 124 and 228 mg/L to as low as 48 mg/L when the pH was raised to 6. The Al concentration further decreased to below mg/L when the pH was raised to above 9 (Fig. 11).

The SI indices were calculated for Al-bearing mineral phases using PHREEQC geochemical model (Fig. 12). The calculated SI indicated that amorphous  $\text{Al}(\text{OH})_3$ , alunite ( $\text{KAl}_3(\text{SO}_4)(\text{OH})_6$ ), basaluminite ( $\text{Al}_4(\text{OH})_{10}\text{SO}_4$ ), boehmite ( $\text{AlOOH}$ ), diaspore ( $\text{AlOOH}$ ), ettringite, jurbanite ( $\text{AlOHSO}_4$ ) and gibbsite ( $\text{Al}(\text{OH})_3$ ) could precipitate out when mine water was treated with FA (Fig. 12). Amorphous  $\text{Al}(\text{OH})_3$ , alunite, basaluminite and jurbanite are super-saturated between pH 4 and 9, while

boehmite, diaspore and gibbsite are supersaturated at pH greater than 4. Ettringite is supersaturated at pH greater than 10.

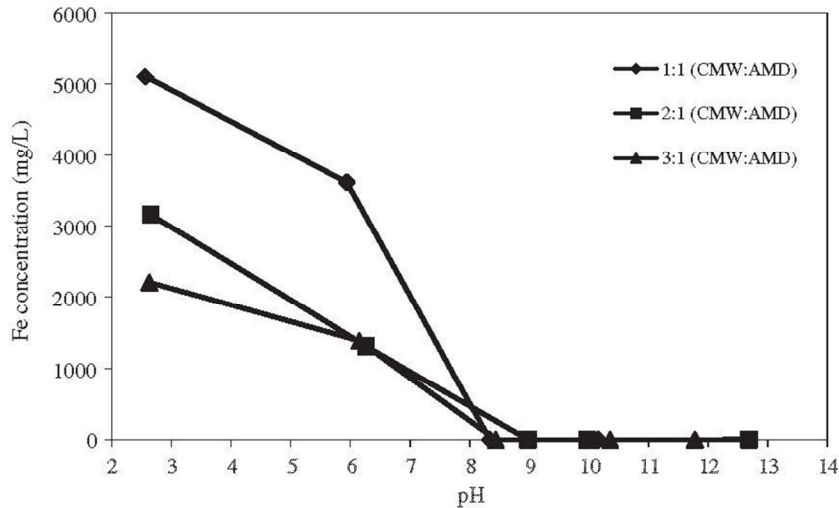


Fig. 13. Fe concentration during treatment of different CMW/AMD mixtures to various pH end points with FA.

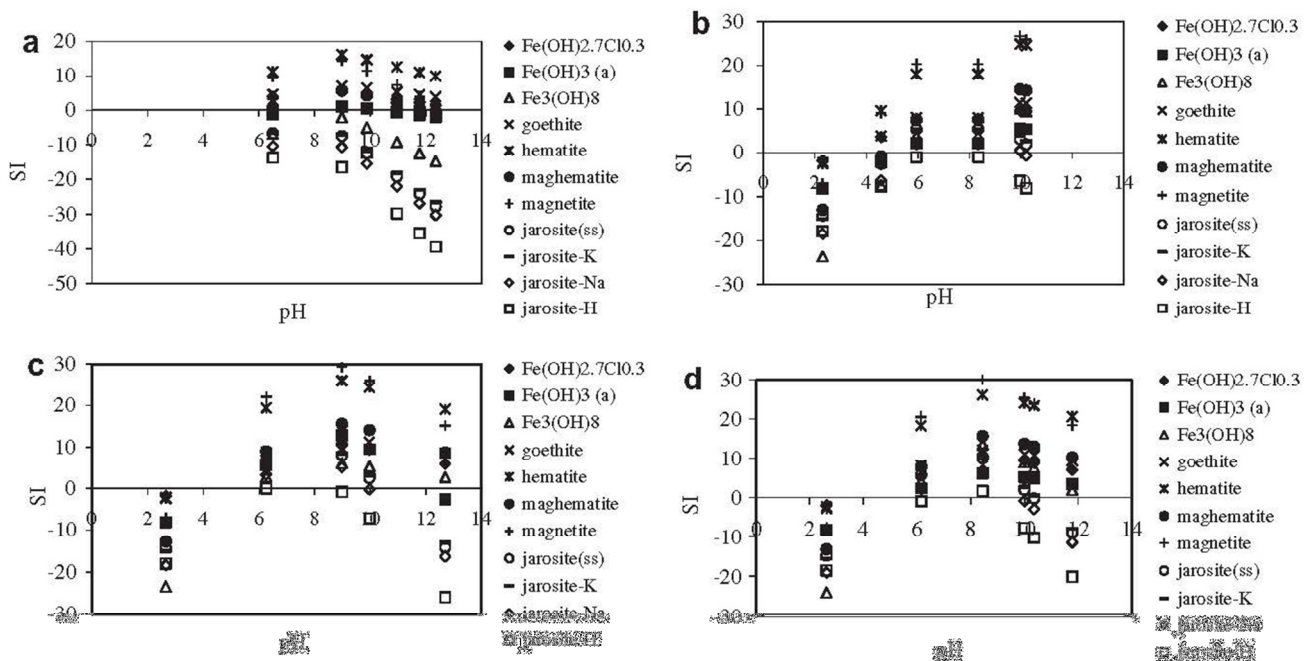


Fig. 14. Saturation indices of Fe-bearing mineral phases at different pH end points during treatment of 1:1, 2:1 and 3:1 CMW/AMD mixtures with FA. Values in index <math>0</math> means under saturation, <math>0</math> index = 0 means saturation and <math>0</math> index > 0 means supersaturation. Under saturation and saturation with respect to particular mineral phase are represented by the filled and empty symbols, respectively.

Treatment of 3:1, 2:1 and 1:1 CMW/AMD mixtures with FA have shown that the Fe concentration was reduced from between 2202 and 5108 mg/L to between 0.03 and 0.05 mg/L when pH was raised to 9. Iron starts precipitating from solution at pH greater than 5 when FA was mixed with the CMW/AMD mixtures (Fig. 13).

The SI indices were calculated for Fe-bearing mineral phases using PHREEQC model (Fig. 14). Calculated SI, show that Fe hydroxides, oxyhydroxides and oxyhydroxysulphate mineral phases started precipitating at pH 5 (Fig. 14). The

minerals controlling Fe removal according to the model are  $\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$ ,<sup>1471</sup> amorphous  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}_3(\text{OH})_8$ , goethite ( $\text{FeOOH}$ ), hematite ( $\text{Fe}_2\text{O}_3$ ), maghematite ( $\text{Fe}_2\text{O}_3$ ), magnetite ( $\text{Fe}_3\text{O}_4$ ), jarosite(ss) ( $\text{K}_{0.77}\text{Na}_{0.03}\text{H}_{0.2}\text{Fe}_3(\text{SO}_4)_2(\text{OH})_6$ ), jarosite-K ( $\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$ ), jarosite-Na ( $\text{NaFe}_3(\text{SO}_4)_2(\text{OH})_6$ ) and jarosite-H ( $\text{HFe}_3(\text{SO}_4)_2(\text{OH})_6$ ). All other Fe bearing mineral phases are capable of precipitating at pH greater than 4 except jarosite-H which is stable at pH 6–7, jarosite-Na is stable at pH 4–9, while jarosite-K and jarosite(ss) are stable between pH 4 and 10.

### *3.3. General discussion*

This study has shown that sulphate, Fe, Al, Mn and Mg concentrations in CMW and AMD can be reduced by manipulating their solution chemistry using South African coal fly ash. It has been revealed in this study that AMD can be used as a source of Al and Fe to facilitate sulphate removal from CMW–fly ash system. A geochemical modelling tool (PHREEQC) can be used to explore the unique properties of CMW and AMD with a view to provide an understanding of appropriate treatment options for these waters. The PHREEQC software has been used successfully as a predictive tool to determine mineral phases and the forms in which sulphate; Fe, Al, Mn and Mg can be precipitated from mine water–fly ash systems. It has shown through modelling and experimentation that different precipitates are formed at different pH values and these precipitates are removed in different forms depending on the type of mine water.

South Africa is water scarce country. This water scarcity is exacerbated by the contamination of surface and groundwater with mine water. Treatment of mine water is very expensive and cheap ways are continually being sort. Coal FA is waste product and therefore treatment of mine water will go a long way in reducing the exorbitant costs associated with mine water treatment. Also use of coal FA in mine water treatment will be a step ahead in achieving zero effluent discharge in coal mines and coal fired power stations since both mine water and coal FA are environmental liabilities.

## **4. Conclusion**

The results obtained in this study showed that treatment of mine water using FA is

dependent on its elemental composition. These results are vital for mining companies in coming up with a suitable treatment methods for the water they pump during their operations. Removal of sulphates, Fe, Al, Mg and Mn when CMW and AMD were treated with coal FA was found to be pH dependent. About 16% of sulphate were removed when CMW was treated with FA to pH 10 and 71% of sulphate was removed when pH was increased beyond 10. In case of AMD blended with CMW 80% of sulphates were removed when the pH was raised to 10 and 90% was removed when pH of AMD was raised to greater 10. The enhanced removal of sulphate from AMD/CMW mixture is due to the presence of Fe and Al that tend to buffer the rise in pH thereby increasing CaO dissolution hence more gypsum precipitation. In addition the presence of Fe and Al in AMD enhanced sulphate removal through precipitation of Fe and Al oxyhydroxysulphates. If the mine water pH was raised to greater than 6, 8, 9 and 11 it was found that approximately 100% of Al, Fe, Mn and Mg were removed respectively. The mineral phases that were responsible for sulphate removal were found to be alunite, anhydrite, barite, basaluminite, jurbanite, jarosites, jarosite-K, jarosite-Na, jarosite-H, celestite and gypsum. Iron was found to be precipitating in the form of  $\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$ , amorphous  $\text{Fe}(\text{OH})_3$ ,  $\text{Fe}_3(\text{OH})_8$ , goethite, hematite, maghematite, magnetite, jarosite(ss), jarosite-K, jarosite-Na and jarosite-H, while Al was found to precipitate out as amorphous  $\text{Al}(\text{OH})_3$ , alunite, basaluminite, boehmite, diaspore, ettringite, jurbanite and gibbsite. Magnesium was found to be removed as brucite and Mn was found to remove as birnessite, bixbyite, hausmannite, manganite, nsutite, pyrochroite and pyrolusite.

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