

Removal of sulphates from South African mine water using coal fly ash

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A thesis submitted in fulfillment of the requirements for the degree of
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KEY WORDS

Fly ash

Circumneutral mine water

Acid mine drainage

Gypsum

Ettringite

Oxyhydroxysulphates

PHREEQC

Saturation index

Sulphate

Ettringite

ABSTRACT

South African power stations generate large amounts of highly alkaline fly ash (FA). This waste product has a serious impact on the environment. Acid mine drainage (AMD) is another environmental problem associated with mining. AMD has high heavy metal content in addition to high SO_4^{2-} concentrations. Several studies have shown that 80-90 % of SO_4^{2-} can be removed when FA is co-disposed with AMD rich in Fe and Al. In South Africa, many sources of contaminated mine waters have circumneutral pH and much lower concentrations of Fe and Al (unlike AMD), but are rich in Ca, Mg and SO_4^{2-} .

This study evaluated SO_4^{2-} removal from circumneutral mine water (CMW) collected from Middleburg coal mine using coal FA collected from Hendrina power station. The following parameters were investigated: the effect of the amount of FA, the effect of the final pH achieved during treatment, the effect of the initial pH of the mine water and the effect of Fe and Al on SO_4^{2-} removal from mine water. The precipitation of ettringite at alkaline pH was evaluated to further reduce the SO_4^{2-} concentration to below the DWAF limit for potable water.

Removal of SO_4^{2-} from mine water was found to be dependent on: the final pH achieved during treatment, the amount of FA used to treat the mine water and the presence of Fe and Al in the mine water. Treatment of CMW using different CMW:FA ratios; 5:1, 4:1, 3:1, and 2:1 resulted in 55, 60, 70 and 71 % SO_4^{2-} removal respectively. Treatment of CMW to pH 8.98, 9.88, 10.21, 10.96, 11.77 and 12.35 resulted in 6, 19, 37, 45, 63 and 71 % SO_4^{2-} removal respectively. When the CMW was modified by adding Fe and Al by mixing with Navigation coal mine AMD and treated to pH 10, 93 % SO_4^{2-} removal was observed. Further studies were done to evaluate the effects of Fe and Al separately. Treatment of simulated Fe containing AMD (Fe-AMD) to pH 9.54, 10.2, 11.8, and 12.1 resulted in 47, 52, 65, and 68 % SO_4^{2-} removal respectively. When Al containing AMD was treated to pH 9.46, 10.3, 11.5 and 12 percentage SO_4^{2-} removal of 39, 51, 55 and 67 % was observed respectively.

Ion chromatography (IC), inductively coupled plasma-mass spectrometry (ICP-MS) and inductively coupled plasma-atomic emission (ICP-AES) analysis of the product water, x-ray diffraction (XRD) and x-ray fluorescence (XRF) spectrometry analysis of FA and solid residues collected after treatment of mine water complemented with PHREEQC thermodynamic modelling have shown that the mechanism of SO_4^{2-} removal from mine water depends on the composition of the mine water. The SO_4^{2-} removal mechanism from CMW was observed to depend on gypsum precipitation. On the other hand SO_4^{2-} removal from mine water containing Fe and Al was dependent on the precipitation of gypsum and Fe and Al oxyhydroxysulphates. The oxyhydroxysulphates predicted by PHREEQC as likely to precipitate were alunite, basaluminite, ettringite, jarosites and jurbanite.

Treatment of CMW with FA to pH 12.35 removed SO_4^{2-} from 4655 ppm to approximately 1500 ppm. Addition of amorphous $\text{Al}(\text{OH})_3$ to CMW that was treated to pH greater than 12 with FA was found to further reduce the SO_4^{2-} concentration to 500 ppm which was slightly above the threshold for potable water of 400 ppm. The further decrease of SO_4^{2-} concentration from 1500 to 500 ppm was due to ettringite precipitation. Mine water treatment using FA was found to successfully remove all the major elements such as Fe, Al, Mn and Mg to below the DWAF limit for drinking water. The removal of the major elements was found to be pH dependent. Fe and Al were removed at pH 4-7, while Mn and Mg were removed at pH 9 and 11 respectively. The process water from FA treatment followed by gypsum seeding and addition of $\text{Al}(\text{OH})_3$ had high concentration of Ca, Cr, Mo and B and a pH of greater than 12.

The pH of the process water from FA treatment followed by gypsum seeding and addition of $\text{Al}(\text{OH})_3$ was reduced by reacting the process water with CO_2 to 7.06. The process water from the carbonation process contained trace elements such as Cr, Mo and B above the DWAF effluent limit for domestic use. Carbonation of the process water reduced the water hardness from 5553 ppm to 317 ppm due to

CaCO₃ precipitation, thereby reducing the Ca concentration from 2224 ppm to 126 ppm.



DECLARATION

I declare that “Removal of sulphates from South African mine water using coal fly ash” is my own work, that it has not been submitted for any degree or examination in any university, and all the resources I have used or quoted have been indicated and acknowledged by complete references.

Godfrey Madzivire

November 2009



UNIVERSITY *of the*
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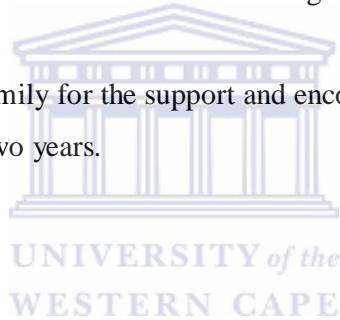
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Special thanks to my family for the support and encouragement that they accorded me during these good two years.



In reality, there is no technical limit to the quality of the water which can be achieved using current existing techniques, but the cost is the limiting factor. Therefore the selection of a treatment technique comes down to economic-environment cost benefit analysis.

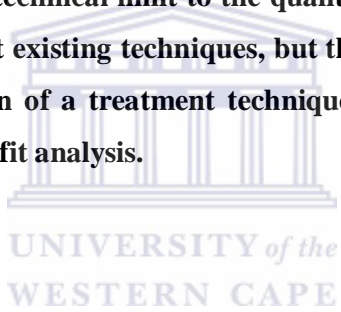


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LIST OF ABBREVIATIONS

AMD	acid mine drainage
DWAF	Department of Water Affairs and Forestry
WHO	World Health Organisation
CMW	circumneutral mine water
FA	fly ash
GpySLiM	gypsum, sulphur limestone and magnesite
CSHG	calcium silicate hydrate gel
APP	acid producing potential
ANP	acid neutralising potential
ABA	acid base accounting
NNP	net neutralising potential
ALD	anoxic limestone drain
SAPS	successive alkalinity producing systems
SRB	sulphate reducing bacteria
PRB	permeable reactive barriers
RO	reverse osmosis
ED	electro dialysis
EDR	electro dialysis reversal
CIP	cleaning –in-place
TDS	total dissolved solids
IC	ion chromatography
ICP-MS	inductively coupled plasma-mass spectrometry
ICP-AES	inductively coupled plasma-atomic emission spectrometry
XRD	x-ray diffraction
XRF	x-ray fluorescence
Al-AMD	aluminum containing acid mine drainage
Fe-AMD	iron containing acid mine drainage
EC	electrical conductivity
SEM	scanning electron microscopy
HMI	high matrix introduction

LOI	loss on ignition
FT-IR	Fourier transform-infra red
SI	saturation indices
SD	standard deviation
ND	not detected
SAMD	simulated acid mine drainage
SR1	solid residue 1
SR2	solid residue 2
CMW	circumneutral mine water
SCMW	simulated circumneutral mine water



LIST OF PUBLICATIONS

CONFERENCE PROCEEDINGS

Poster presentations

1. Madzivire, G., Petrik, L.F., Gitari, W.M., Balfour, G., Vadapalli, V.R.K. and Ojumu, T.V. “Role of pH on sulphate removal from mine water using coal fly ash”, *International mine water conference*, 19-23 October 2009, CSIR, Pretoria South Africa.
2. Madzivire, G., Petrik, L.F., Vadapalli, V.R.K. and Gitari, W.M. “Optimization of sulphate removal from circumneutral mine water using fly ash”, *39th SACI National Convention*, 30 November-5 December 2008, Stellenbosch, Cape Town, South Africa.



Oral presentations

1. Madzivire, G., Petrik, L.F., Gitari, W.M., Ojumu, T.V. and Balfour, G. “Removal of sulphate from circumneutral mine water using coal fly ash”, *Sustainable through Resource Conservation and Recycling International Conference*, 4-5 April 2009, Cape Town, South Africa.

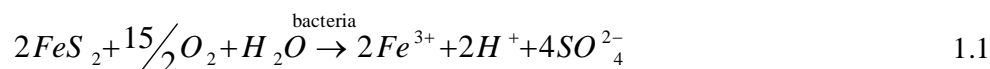
JOURNAL PUBLICATION

2. Madzivire, G., Petrik, L. F., Gitari, W. M., Ojumu, T.V. and Balfour, G. (2010), “Application of coal fly ash to circumneutral mine waters for the removal of sulphates as gypsum and ettringite”, *Mineral Engineering Journal*, **23**(3), pp 252-257

CHAPTER 1 : INTRODUCTION

Water is an indispensable natural resource, fundamental to life, the environment, food production, hygiene and sanitation, industry and power generation. Clean water is recognized around the world as a crucial element in the battle against poverty, the cornerstone of prosperity and a limiting factor to growth (Barson et al., 1997). The freshwater resources of the country 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).

Polluted mine water is a recognized problem in the coal mining areas of the country. Coal mining is a significant contributor to water pollution. Effluents need to be treated to remove SO_4^{2-} to less than 500 ppm and for metal removal. A major constituent of coal mine tailings is pyrite. When pyrite (FeS_2) is exposed to air, it is oxidized by a biologically catalysed reaction mediated by bacteria *Thioacidobacillus ferrooxidans* (Nyavor et al., 1996). The primary pollutants of acid mine drainage (AMD) are acidity, Fe, SO_4^{2-} , Mn, Mg and Al. Sulphates need to be removed from effluents to prevent salination of surface water and gypsum scaling.



Coal mines in Mpumalanga province produce mine waters that are acidic ($pH < 3$) or circumneutral ($pH = 6-7$). AMD are produced because of FeS_2 oxidation to produce acidity (Eq.1.1). The acidic nature of the water will increase the dissolution of minerals that contain heavy metals, therefore causing the water to be heavily contaminated with SO_4^{2-} and toxic heavy metals (Gazea et al., 1996; Hammack et al., 2006; Petrik et al., 2003).

Circumneutral mine waters (CMW), often referred as Ca-Mg waters are produced when acidic mine waters undergo partial neutralisation due to the surrounding

geology. If the AMD flows past dolomite rock it is partially neutralised and in the process some metal contaminants will precipitate as their respective hydroxides. Sulphates will precipitate out as gypsum or adsorb on metal hydroxides. As a result, CMW contains lower SO_4^{2-} than acid mine water, and with pH around 6.5, the concentration of toxic metals are near or below the acceptable effluents limit, but the water still contains considerable amount of SO_4^{2-} , Ca, Mg and Mn (Banks et al., 1997). Discharging the untreated mine water causes severe environmental problems to soil, surface and ground water by decreasing pH, accumulation of SO_4^{2-} and heavy metals (Petrik et al., 2003; Banks et al., 1997).

Many treatment technologies have been developed to decontaminate mine waters to produce drinking and industrial water. They can broadly be classified as passive and active treatment methods (Bosman et al., 1990). Passive treatment systems allow the mine water to pass through a system that is not monitored regularly, while active treatment involves treatment with facilities containing machines and equipment that are monitored and maintained by a responsible workforce (Hammack et al., 2006). Both passive and active treatment involves neutralisation, oxidation, adsorption and adsorption processes to remove the contaminants from mine water.

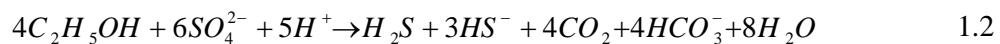
In passive treatment mine water is allowed to pass through an environment where geochemical and biological processes help to improve the quality of the mine water. The main processes that occur in passive treatment for the removal of contaminants are; dilution by water from uncontaminated sources, oxidation/hydrolysis and reduction of toxic metals to insoluble hydroxide precipitates.

A variety of passive AMD treatment systems have been developed and can be broadly classified as chemical and biological passive treatment systems (Neculita et al.; 2007). Treatment systems that rely largely on abiotic chemical processes include open limestone channels (OLC), anoxic limestone drains (ALD), and successive alkalinity-producing systems (SAPS) (Mukhopadhyay et al., 2007;

Ziemkiewicz et al., 1997). Biological passive treatment systems for AMD include bioreactors and constructed wetlands. Permeable reactive barriers (PRBs) and monitored natural attenuation (MNA) for treatment of ground water impacted by AMD can also be classified either as chemical or biological passive treatment systems based on processes that are occurring during the attenuation of contaminants in the mine water.

Passive treatment reduces the costs associated with active treatment such as chemical, operational and maintenance costs (Gazea et al., 1996, Kalin et al., 2006). The other advantages include stable sludge and high metal removal capacity. The disadvantages of passive treatment are the need for greater space and the fact that it cannot accommodate larger volumes of mine water because the water should be retained for a longer time for amelioration to occur. Also the performance and effectiveness of passive systems is not reliable and periodic depletion and breakthrough requires reinstallation (Kalin et al., 2006).

Active mine water treatment methods include chemical, biological, membrane and ion exchange treatment systems. Biological treatment of mine water is another technology that significantly reduces the metal cations and SO_4^{2-} concentrations of the effluent to the required limit. This is achieved by using sulphur reducing bacteria (SRB). The bacteria reduce SO_4^{2-} to elemental S via the H_2S intermediate. The metals react with H_2S to form metal sulphides precipitates. The pH of the water is raised during the reduction of SO_4^{2-} and this process requires a hydrocarbon as an energy source such as ethanol for the reaction to occur (Hammack et al., 2006):



If the metal content of the water is insufficient to precipitate available H₂S, the effluent should be aerated to oxidize H₂S to elemental S in order to prevent the release of H₂S to the environment:



In a conventional active treatment system alkaline materials and other chemicals are added to the AMD to neutralise it and enhance metal hydroxide precipitation. Chemicals that are usually used to treat mine water are lime, limestone and Ba salts (Bosman, 1983; Maree 1988). These chemicals are capable of removing SO₄²⁻ in the form of gypsum (in case lime/limestone treatment) and barite (in case of Ba salts).

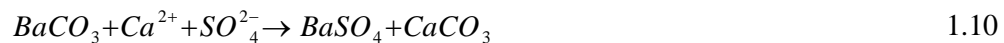


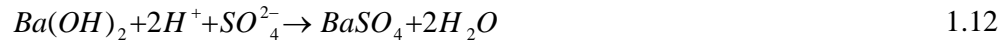
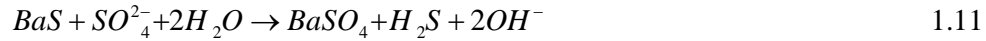
Following dissolution of the hydrated lime in mine waters, the pH is increased, metal ions are precipitated as hydroxides and SO₄²⁻ are removed from the water in the form of gypsum (Eqs. 1.8 and 1.9).



Chemical treatment of mine water using lime or limestone will remove SO₄²⁻ to between 1500 to 2000 ppm depending on the solubility of gypsum. Gypsum solubility depends on the composition and ionic strength of the solution.

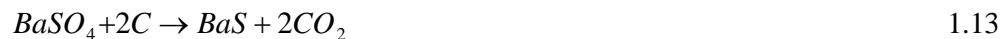
Barite (BaSO₄) is a highly water insoluble salt, this makes it a suitable phase to remove SO₄²⁻ from mine water. The Ba salts commonly used for SO₄²⁻ removal are BaCO₃, Ba(OH)₂ and BaS (Eqs. 1.10, 1.11 and 1.12). Chemical treatment of mine water using Ba salts has proved to be capable of removing SO₄²⁻ to less than 250 ppm (Bosman et al., 1990; Maree et al., 1989). The use of BaCO₃ is usually carried out after the alkali treatment to remove metal contaminants including Mg.





BaCO₃ treatment does not remove SO₄²⁻ that is associated with Mg (Hlabela et al., 2007). This means Mg should be removed from the water before Ba can be added. This is achieved by addition of an alkali to increase the pH to 11 for Mg(OH)₂ precipitation before Ba treatment. BaS treatment is capable of increasing the pH to above 11, since the treatment generates alkalinity (Eq. 1.11) thereby precipitating Mg(OH)₂. Therefore treatment of mine water using BaS does not require alkali treatment prior to addition of BaS. Metals in the mine water will react with H₂S produced to produce metal sulphides precipitates (Hlabela et al., 2007; Maree et al., 1989). Ba salts treatment of mine water introduces toxicity to the treated water if the Ba is left to be discharged with the treated water (WHO, 2008).

The major disadvantage of active chemical treatment of mine water is the costs associated with chemicals. Also chemical treatment of mine water produces voluminous sludge that is expensive to store and dispose. In order to counter the expenses associated with Ba chemicals, BaS and CaO can be regenerated and recycled from BaSO₄ and CaCO₃ mixture produced during the Ba²⁺ treatment of mine water. This is achieved by thermally reducing BaSO₄/CaCO₃ using coal.



In the process there is production of S and CaO. Sulphur can be used by the fertilizer manufacturing industry, while CaO can be reused to neutralise mine water therefore reducing the expenses incurred by buying of raw materials.

Membrane technology involves two basic processes; electro dialysis and reverse osmosis to remove impurities from contaminated water. In electro dialysis an electric potential is used to move dissolved ions selectively through cation and anion selective membranes leaving behind a stream of pure water and streams of

concentrated brines across the membranes (Conlon, 1990). In contrast, in reverse osmosis a semi permeable membrane selectively allows water to pass through leaving behind concentrated brine and producing pure water across the membrane (Mattson and Lew, 1982).

Ion exchange involves the exchange of ions in the contaminated water with those on the cationic or the anionic resin. The cationic resin is used for the removal of cations such as Ca^{2+} in exchange with H^+ , while in anion resin the anions like SO_4^{2-} are exchanged with OH^- resulting in the removal from water of ions that are detrimental to the environment (Schoeman and Steyn, 2001).

The major advantage of membrane technology and ion exchange is that they can be used to produce potable water that can be sold as drinking water, and thereby offsetting the running expenses associated with these processes. The disadvantage of ion exchange and membrane technology is the resulting brine waste stream that is produced, which is difficult to handle since it is much more concentrated and contaminated than the mine water. Also the processes require pretreatment of the mine water to avoid fouling, mineral precipitation and microbial growth, which may contribute additional cost to the economics of these processes.

While these active treatment processes work well to raise pH and to precipitate the metals, the treatment plants are very expensive to operate and maintain, and disposal of the metal-laden sludge can be a problem. In order to counter the expenses associated with the running of the treatment plants, ways are being found to recover valuable metals or compounds from the sludge to offset treatment costs such as the GypSliM process that is being championed by CSIR (Naido, 2007). Ingwe Collieries and Anglo Coal mines in Mpumalanga province have built the Emalahleni water treatment plant that uses limestone/lime treatment followed by membrane technology which will convert contaminated mine water into high-quality potable water at the rate of 20 Ml per day (Tzoneva, 2008). Research is being conducted to convert waste gypsum produced during chemical treatment to elemental S, MgCO_3 and CaCO_3 (GypSliM process). The produced

CaCO_3 is recycled in the process while S can be sold as a by-product or used as a raw material for manufacturing of sulphuric acid, thus replacing imported S, offsetting the costs associated with chemical imports (Naido, 2007).

Due to high costs associated with treatment of mine water, cheaper technologies to deal with mine water are constantly being sought. One of these ways is the use of FA, a waste material produced from coal fired power stations (Adriano et al., 1980; Petrik et al., 2003; Klink et al., 2003; Gitari et al., 2006; P'erez-L'opez et al., 2007; Gitari et al., 2008). FA is a ferroaluminosilicate waste compound that results from coal combustion during power generation. FA tends to accumulate toxic elements such as heavy metals at the high temperatures involved during its generation, and is considered an environmental hazard in South Africa and other parts of the world. The toxic elements contained in ash could leach out when FA is mixed with water and therefore FA should be disposed safely to avoid pollution of the environment (Van den Berg et al., 2001). It has been shown that the aqueous extracts from FA are strongly alkaline ($\text{pH} = 12$) due to the presence of free soluble alkaline components (CaO and MgO).







Treatment of AMD using FA has been studied extensively and it has been shown that significant levels of toxic elements can be removed by precipitation, co precipitation and adsorption (Gitari et al., 2008; Petrik et al., 2003; Klink, 2003). The authors have shown that about 80-90 % of total mine water SO_4^{2-} can be removed, although the remaining SO_4^{2-} concentration was still above the acceptable limit (500 ppm) for the effluent. Al, Fe, Mn and other toxic elements are removed from during treatment of AMD with FA to below the required Department of Water Affairs and Forestry (DWAF) effluent limit (DWAF, 1996)






The main disadvantage of using FA to treat water that may be used for domestic consumption is that toxic elements such as B, Mo and Sr leach from the FA. Further research is being pursued to produce zeolites that will refine the water by removing these toxic elements after the removal of major contaminants using FA (Moreno et al., 2001; Petrik et al., 2003).

1.1: PROBLEM STATEMENT

Elevated concentration of SO_4^{2-} in water has detrimental effects on human health. Sulphate concentrations of greater than 600 ppm causes diarrhoea to most individuals and adaptation may not occur (DWAF, 1996; WISA, 2009).

Table 1.1: Effects of SO_4^{2-} on aesthetics and human health

Concentration (ppm)	Effect	Classification
600 - 1000	Possibility of diarrhoea. Poor adaptation in sensitive individuals	
< 100	No effects	
100 - 200	No effects	
200 - 400	Insignificant health effects	
400 - 600	Slight chance of initial diarrhoea in sensitive groups, but disappear with adaptation	
> 1000	High chance of diarrhoea. No adaptation	

Ideal	Good	Marginal	Poor	Unacceptable
				

Exposure to high SO_4^{2-} concentrations in drinking water for long periods, usually cause people to become adapted and they may no longer experience these effects. Higher SO_4^{2-} concentration in water causes water to taste salty or bitter. The taste threshold for SO_4^{2-} concentration is 400 ppm (DWAF, 1996; WISA, 2009).

High SO_4^{2-} concentrations in industrial waster cause an increase in the corrosion rate of metal fittings in distribution systems because SO_4^{2-} promotes the growth of SRB, which in turn enhances damage through microbially-induced corrosion (MIC). Elevated SO_4^{2-} in water causes degradation of concrete structures due to gypsum formation. Water containing high SO_4^{2-} causes CaSO_4 scale on steam generating equipment surfaces thereby reducing the heat transfer capacity (DWAF, 1996).

Treatment of AMD using alkalis and fly ash (FA) has been studied and the chemistry of the removal of toxic metals is well understood (Adriano et al., 1980; Bosman, 1983; Cravotta et al., 1990; Gitari et al., 2006; Petrik et al., 2003). It has been shown that FA treatment of AMD that contains high concentration of Fe and Al can remove 70-80 % of SO_4^{2-} coupled with removal of almost all of the heavy metals found in AMD (Gitari et al., 2006; Gitari et al., 2008). Unlike AMD, the concentrations of toxic metals in CMW are near or below the acceptable effluents limit but it still contains a considerable amount of SO_4^{2-} (Banks et al., 1997). An attempt to remove SO_4^{2-} using FA treatment in CMW (with high concentration of Mg and Ca and very low concentration of Fe and Al) using FA has shown little or no SO_4^{2-} removal (Madzivire et al., 2008). Therefore treatment of Ca, Mg and SO_4^{2-} rich CMW with alkalis or FA, the concentration of SO_4^{2-} that remained in the water is of concern.

The above discussion highlights the problems that need to be addressed in order to reduce SO_4^{2-} levels in CMW from Mpumalanga area to within DWAF target ranges. This will require the understanding of the fundamental chemistry of SO_4^{2-} removal mechanisms during treatment of CMW with FA.

1.2: OBJECTIVES

The major aim of this research is to remove SO_4^{2-} from CMW and to understand the mechanism of SO_4^{2-} removal from Middleburg mine water using Hendrina FA. To develop an understanding of the fundamental chemistry of SO_4^{2-} removal in circumneutral mine water the following variables were evaluated:

1. The effect of the final pH of the water after mixing with FA on SO_4^{2-} removal.
2. The effect of the initial pH of the mine water.
3. The effect of the amount of FA on SO_4^{2-} removal.
4. The role of Fe and Al ions in SO_4^{2-} removal from mine water.

5. Whether it is possible to remove SO_4^{2-} to the required effluent limit by step wise precipitation techniques using FA, gypsum seeding and $\text{Al}(\text{OH})_3$.

The above information will be used to come up with the best treatment method that can be used for treatment of mine water to remove SO_4^{2-} to below the allowed DWAF effluent limit of 500 ppm.

1.3: HYPOTHESIS

It is possible to remove SO_4^{2-} from Ca-Mg rich CMW to below the DWAF effluent limit of 500 ppm using FA, gypsum seeding and addition of amorphous $\text{Al}(\text{OH})_3$.

1.4: RESEARCH APPROACH

A number of experiments were designed in order to understand the effect of:

1. The amount of FA on SO_4^{2-} removal.
2. The initial pH of mine water on SO_4^{2-} removal from circumneutral mine water.
3. The final pH of the process water on SO_4^{2-} removal from circumneutral mine water.
4. Fe and Al in mine water on SO_4^{2-} removal from circumneutral mine water.
5. Gypsum seeding followed by ettringite precipitation on SO_4^{2-} removal.

In this study simulated CMW (made according to the composition of Middleburg mine water) and FA obtained from Eskom's Hendrina power station were used. The chemistry involved during the treatment of CMW with Hendrina FA was elucidated by analysing the water before and after treatment with FA with ion chromatography (IC), inductively coupled plasma-mass spectrometer spectrometry (ICP-MS) and inductively coupled plasma-atomic emission

spectrometry (ICP-AES). Fresh Hendrina FA and solid residues (SR) produced when CMW was treated with FA were analysed using X-ray diffraction (XRD) and X-ray fluorescence (XRF) techniques to compare the changes in elemental and mineral phases composition of the fresh Hendrina FA and SR. PHREEQC geochemical modelling was applied to predict the mineral phases that precipitated during treatment of CMW with Hendrina FA. This complemented the results of physical measurements from XRF and XRD.

1.5: SCOPE AND DELIMITATIONS OF STUDY

The study involved the use of FA from Hendrina coal power station and waters from Middleburg and Navigation coal mines. The Hendrina FA was used to treat Middleburg coal mine water to remove SO_4^{2-} by gypsum precipitation and to take up the pH to greater than 12 followed by gypsum seeding and addition of $\text{Al}(\text{OH})_3$ in order to remove SO_4^{2-} to below 500 ppm from Middleburg mine water by ettringite precipitation. Navigation coal mine water was only used as a source of Fe and Al in order to study the effect of the presence of these two cations in CMW on SO_4^{2-} removal during treatment of CMW with Hendrina FA. The pH of the process water from FA treatment followed by gypsum seeding and addition of $\text{Al}(\text{OH})_3$ was greater than 12 and was reduced by reacting the process water with CO_2 . The process water from the carbonation process contained trace elements such as Cr, Mo and B above the DWAF effluent limit for domestic use, which could be removed by adsorption using zeolites synthesized from FA.

In this study FA from other nearby coal power plants close to Middleburg coal mine such as Arnot, Duvha, Komati and Kendal (Figure 1.4.1) were not used investigated to treat Middleburg coal mine water. Also the refinement of the process water after the carbonation stage using zeolites was not carried out to remove Cr, Mo and B to the DWAF limit levels.

1.6: THESIS OUTLINE

Chapter 2: Literature review

A comprehensive geochemistry of the formation of mine water and the formation of FA in coal power generating plants is outlined in chapter 2. The detrimental effects of these two waste materials are also highlighted. A review of mine water treatment techniques is outlined, with advantages and disadvantages of each treatment method being identified.

Chapter 3: Methodology

Steps followed in order to address the research objectives are outlined in chapter 3. A detailed outline of how the CMW and FA samples were collected from Middleburg coal mine and Hendrina coal power station respectively and also how these samples were stored and analysed is described in this chapter. The water used in this study was simulated mine water and its preparation is presented in the experimental section. The methodology addresses the steps taken to answer the research objectives.

Chapter 4: Results and discussion

Chapter 4 outlines a detailed presentation and discussion of the results obtained by applying methods specified in chapter 3. In this chapter the chemistry of the treatment experiments conducted in the previous chapter is explained with chemical equations and PHREEQC geochemical modelling, and results are compared to literature and significant findings are highlighted.

Chapter 5: Conclusion

In Chapter 5 the hypothesis of this research is verified based on the results and discussion of the previous chapter. Conclusions are drawn based on the results obtained and future work is specified.

CHAPTER 2 : LITERATURE REVIEW

2.1: INTRODUCTION

Mine water and fly ash (FA) are two waste products produced in close proximity at coal mines and coal power stations respectively. These two waste products have detrimental effects on the environment, and therefore alternative cheap ways of using these wastes in a sustainable way are being investigated. Pulverised coal FA is a ferroaluminosilicate material that contains readily soluble CaO. Mine water is highly saline water (containing high concentration of SO_4^{2-}) which can be either acidic, circumneutral or alkaline (Younger et al., 2002). Application of FA for mine water remediation seeks to exploit the free CaO in FA.

2.2: FLY ASH

FA is the mineral matter in coal that remains after coal has been thermally altered through the combustion process to produce electricity. FA is a waste product that is collected from flue gas using electrostatic precipitators or filter bags (Adriano, 1980). The major constituents of coal are C, O, H, N and S, which are thermally oxidized during coal combustion to produce electricity. Coal also contains trace elements such as As, Hg, B, Pb, Ni, Se, Sr, V and Zn in association with different types of inorganic minerals such as aluminosilicates (clay minerals), carbonates (calcite and dolomite), sulphides (pyrites), and silica (quartz). The inorganic minerals make up 5 to 40 % of coal. South African power stations burn low quality coal with very high inorganic content containing up to 40 % inorganic material (Pinetown et al., 2007). It is these incombustible materials that form the ash that remains after combustion of coal. The chemical composition of FA is made up of Si, Ca, Al, Fe, Mg and S oxides along with C and various trace elements. The silica in the form of mineral quartz passes through the combustion process and remains as quartz in the FA. The clay minerals transform into crystalline and non-crystalline (amorphous) aluminosilicates materials. Elements

such as Fe, Ca, and Mg are oxidized to form oxide minerals such as magnetite (Fe_3O_4), hematite (Fe_2O_3), lime (CaO) and periclase (MgO) (Mattigod et al., 1990).

The constituents of FA mainly depend on the chemical composition of the coal burnt. However, FA produced from the same coal can have significantly different mineral composition depending on the coal combustion technology employed. Therefore the FA hydration properties and the leaching characteristics can vary significantly depending on the type of coal burnt and generation facilities. The amount of crystalline material and glass phase material depends largely on the combustion and glassification (cooling of the ash) process used at a particular power plant. When the maximum combustion temperature is greater than 1200°C and the cooling time is very short, the ash produced is mostly glassy phase material (McCarthy et al., 1988). Where boiler design or operation allows a more gradual cooling of the ash, crystalline calcium compounds are formed.

The relative proportion of the spherical glassy phase and the crystalline materials, the size distribution, the chemical nature of the glassy phase, the type of the crystalline material and the nature and the percentage of unburnt carbon are the factors that can affect the hydration and leaching properties of FA (Roy et. al., 1985). The primary factors that influence the mineralogy of coal FA are:

- The boiler operation including coal pulverization, combustion, flue gas clean up and collection operations also determines the composition of FA.
- Additives used, including oil additives for flame stabilization and corrosion control additives.

The minerals present in the coal dictates the elemental composition of the FA.

2.2.1: Fly ash classification

According to the American Standard of Testing and Measurement (ASTM) C 618 FA can be classified into two categories, Class F and Class C. For class F the total amount of SiO_2 , Al_2O_3 and Fe_2O_3 is greater than or equal to 70 % and Class C is

between 50 to 70 % (McCarthy, 1988). Class F FA is produced from burning anthracite and bituminous coals. This FA has siliceous or siliceous and aluminous material, which itself possesses little or no cementitious value, but will, in finely divided form and in the presence of moisture, chemically react with CaO at ordinary temperature to form cementitious compounds. Class C FA is produced from lignite and sub-bituminous coals and usually contains significant amount of CaO (Wesche, 1991). This class of FA, in addition to having pozzolanic properties, also has some cementitious properties. South African coal FA is classified as class F (Gitari et al., 2006).

2.2.2: Uses of fly ash

FA is a heterogeneous compound composed of mullite, quartz, hematite, lime and amorphous material that has pozzolanic properties. The use of FA mainly depends on the exploitation of these compounds. The uses of FA include; cement and concrete making, treatment of AMD and treatment of acidic soils

2.2.2.1: Cement and Concrete making

FA is an inexpensive replacement for Portland cement used in concrete, because it improves strength, segregation, and ease of pumping of the concrete. FA consists mostly of silica, alumina and Fe, and thus is a pozzolan; a substance containing aluminous and siliceous material that forms cement in the presence of water.

When mixed with lime and water it forms a compound similar to Portland cement. The spherical shape of the particles reduces internal friction thereby increasing the concrete's workability and mobility, permitting longer pumping distances.

Addition of FA to Portland cement results in the decrease in water demand during concrete making (Foner et al., 1999). Addition of FA to concrete increases corrosion resistance by forming calcium silicate hydrate gel (CSHG) which reduces the leaching of Ca(OH)_2 . Also the CSHG fills up the capillary voids in concrete hence reducing concrete permeability (Taylor, 1998).

2.2.2.2: Treatment of acidic soils

Addition of FA to contaminated soils reduces the mobility of most toxic metals. FA was found to reduce the mobility of Cu and Pb by approximately 98 % when added to Cu and Pb contaminated soils (Kumpiene et al., 2006). This results in reduced uptake of these metals by plants and hence reduced toxicity along the food chain. Application of FA to acidic soils reduces acidity due to neutralization by CaO present in FA. This results in neutralised soils suitable for plant inhabitation (Yunusa et al., 2006; Summers et al., 1998). FA can be applied to land contaminated by mine tailings. The FA will neutralise the acidity generated by oxidation of sulphide minerals such as pyrite resulting in better soils suitable for agriculture (Taylor, 1998). Excess application of FA causes the soils to have reduced hydraulic conductivities. This is because of the pozzolanic nature of FA which makes the soil become cementitious.

2.2.2.3: Treatment of AMD

Acid mine drainage (AMD) are acid waters generated because of the oxidation of pyrite in the presence of water and oxygen. FA application to treat AMD was found to be able to neutralize the acidity. This is because of the lime present in FA (Gitari et al., 2006; Klink, 2003). As a result of the neutralization metals precipitate out as hydroxides. Most metals were removed by approximately 100 % when the pH of minimum solubility of hydroxides was achieved. Sulphate removal was found to be approximately 80 % due to gypsum precipitation.

2.2.3: Environmental impacts of FA

FA contains trace elements (As, Hg, B, Pb, Ni, Se, Sr, V and Zn) in higher concentrations compared to coal and soil. An estimated 36 Mt of FA are produced by Eskom annually. Approximately 1 % is used in the production of bricks and cement. The surplus ash is stacked on large dumps which require complex dust control systems and rehabilitation (Eskom, 2008).

The way FA is disposed presents an environmental problem because it increases the possibility of leaching of toxic elements such as B, Pb, etc when the FA is infiltrated with rain water (Mattigod et al., 1990; Adriano et al., 1980). Leaching of these toxic metals leads to contamination of groundwater and surface water. Plants grown on acidic soils mixed with FA have increased concentration of Se, Mo, B, Al and Sr in their tissues (Adriano, 1980). B contamination makes FA an environmental hazard due to phytotoxic effects of B (Furr et al., 1978).

2.3: MINE WATER

Mine waters have become a major hydrological and geochemical problem arising from human exploitation of the geosphere. Mine water composition depends on the mined ore and the chemical additives used in the mineral processing and hydrometallurgical processing. This means that there is no typical composition of mine waters and as a result, the classification of mine water based on its composition is difficult to achieve. A number of classification schemes of mine water have been proposed using one or several water parameters such as major cations and anions, pH and alkalinity vs acidity of the mine water (Lottermoser, 2007).

a) Major cations and anions

The classification of mine waters in terms of their major cations and anions involves plotting the major cation (Ca^{2+} , Mg^{2+} , Na^+ , K^+) and anions (Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^-) on Piper or trilinear diagrams. The plots are then applied in classifying the waters according to their cation and anion abundances.

b) pH

Another way of classification is by the pH of the water which classifies mine water according to pH as acidic, alkaline or circumneutral (Morin and Hutt, 1997).

c) Alkalinity vs acidity

A further method to classify mine water is to distinguish mine waters according to their ability to be treated using either anaerobic or aerobic passive treatment. Acidic mine water requires anaerobic treatment while alkaline mine water require aerobic treatment (Younger et al., 2002). Acidic mine water is characterized by low pH (usually <3), being heavy-metal-laden and very rich in SO_4^{2-} . Circumneutral and mine water are characterized by neutral pH, heavy-metal-poor with moderate concentration of SO_4^{2-} .

2.3.1: Acid mine drainage

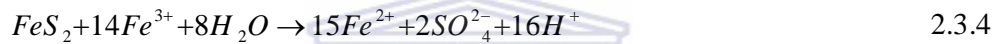
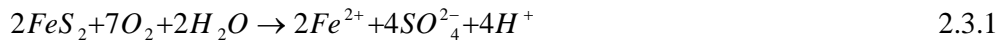
Mining exposes geology that is being mined to oxygen and water therefore allowing the oxidation of minerals that are in reduced state. The oxidation can occur either underground or on the surface. The most common types of these minerals are the metal sulphides (Table 2.1).

Table 2.1: Important metal sulphides that occur in mining regions

Chemical formula	Name of compound
FeS_2	Pyrite
FeS_2	Marcosite
Fe_xS_x	Pyrrhotite
Cu_2S	Chalcocite
CuS	Covellite
CuFeS_2	Chalcopyrite
MoS_2	Molybdenite
NiS	Millerite
PbS	Galena
ZnS	Sphalerite
FeAsS	Arsenopyrite

Pyrite and marcasite are the most common metal sulphides found in coal deposits and other mineral deposits. The oxidation of pyrite in the presence of water produces sulphuric acid that in turn interacts with the bedrock leading to the leaching and dissolution of the toxic heavy metals into the water. The sulphuric acid acidifies the water, introducing SO_4^{2-} and heavy metals creating AMD which in turn pollutes groundwater and surface water.

The oxidation of FeS_2 to form AMD in the presence of air and water follows a complex set of reactions (Stumm and Morgan, 1981):



In the initial step, FeS_2 reacts with O_2 and water to produce Fe^{2+} , SO_4^{2-} and acidity (Eq. 2.3.1). The conversion of Fe^{2+} to Fe^{3+} in Equation 2.3.2 has been termed the rate determining step for the overall sequence, because at pH values below 5 under abiotic conditions the rate of this reaction is very slow (Stumm and Morgan 1981). However, Fe-oxidizing bacteria, principally *Acidithiobacillus sp.*, accelerate this reaction, so the activities of the bacteria enhance the generation of AMD (Johnson and Hallberg, 2003). The third step involves the hydrolysis of Fe^{3+} to form the $Fe(OH)_3$ precipitates and the release of additional acidity (Eq.2.3.3). This third reaction is pH dependent. Under very acid conditions ($pH < 3.5$), the solid hydroxide does not form and Fe^{3+} remains in solution, and at high pH values, $Fe(OH)_3$ precipitate forms. The fourth step involves the autocatalysis oxidation of additional FeS_2 by Fe^{3+} (Eq.2.3.4). The Fe^{3+} is generated by the initial oxidation reactions in steps one and two. This cyclic propagation of acid generation by iron takes place very rapidly and continues until the supply of Fe^{3+} or FeS_2 is exhausted. Oxygen is not required for the fourth reaction to occur.

The overall pyrite reaction series is among the most acid-producing of all weathering processes in nature. AMD is produced if acid producing minerals are far more abundant than acid neutralizing minerals. Acid base accounting for acid producing minerals and acid neutralizing minerals can be used as an initial step to predict if a certain geology can produce AMD, circumneutral or alkaline mine water during and after mining.

The oxidation of sulphide minerals produces acidity and this enhances the leaching of heavy metals (Fe, Cu, Pb, Zn, Cd, Co, Cr, Ni, and Hg), metalloids (As and Sb), other elements (Al, Mn, Si, Ca, Na, K, Mg and Ba) and SO_4^{2-} from other minerals associated with the FeS_2 rock. AMD is characterized by low pH, high concentration of Fe and Al (greater than 100 ppm), elevated amounts of Cu, Cr, Ni, Pb, and Zn (greater than 10 ppm) and SO_4^{2-} (greater than 1000 ppm) (Lottermoser, 2007).

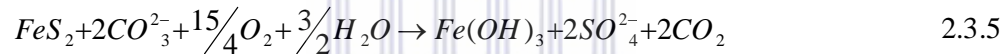
The products of AMD formation, acidity and Fe, can devastate water resources by lowering the pH and coating stream bottoms with $\text{Fe}(\text{OH})_3$, forming the familiar orange colored "yellow boy" common in areas with abandoned mines. As acidity increases, very few living things can tolerate the harsh conditions. The corrosive acid water also attacks culverts and bridge abutments, resulting in a shorter than normal life span for exposed infrastructure.

Small amounts of AMD can harm the life in streams because the metals, SO_4^{2-} and/or other suspended solids precipitate out of the water and coat the rocks and gravel on the stream bottom. When this happens, the flora and fauna that live on and under the rocks literally are smothered because they cannot get oxygen out of the water. High levels of Na make the water unsuitable for irrigation while hardness influences the toxicity of heavy metals such as Zn (Lottermoser, 2007).

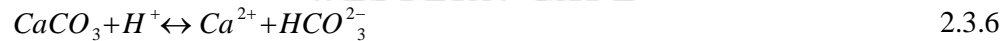
2.3.2: Circumneutral mine water

A low pH is not a universal characteristic of all the mine waters. In acid waters, SO_4^{2-} is the principal anion and Fe, Mn and Al are major cations. In contrast circumneutral mine waters (CMW), SO_4^{2-} and HCO_3^- are principal anions and the concentrations of Ca, Mg and Na are generally elevated compared to Fe and Al (Cravotta et al., 1990).

Depending on the geology that is being exploited by mining the resultant water that comes from the mine water or from the mine tailings can be either acidic, circumneutral or alkaline. Naturally occurring carbonates and silicates are capable of neutralising the acidity that is produced during sulphide mineral oxidation. Carbonate minerals include calcite (CaCO_3), dolomite ($\text{CaMg}(\text{CO}_3)_2$), magnesite (MgCO_3) and ankerite ($\text{Ca}_2\text{MgFe}(\text{CO}_3)_4$) deposits which neutralise acidity (eq. 2.3.5) that is produced during pyrite oxidation.



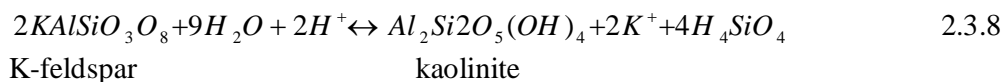
The most common and fast reacting carbonate is CaCO_3 and its solubility depends on the proton concentration as shown in the following equation.



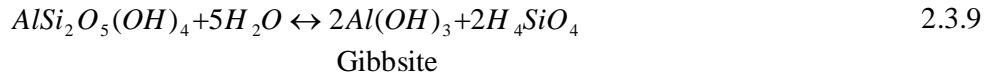
This reaction will buffer pH at near neutral (6.5-7), while in more acidic environments the following equation can be written:



Silicate minerals also consume H^+ ions and contribute base cations (Ca, Mg, and Fe), alkali elements (Na, K) and dissolved Si and Al to the tailing water (Blowes and Ptacek, 1994). The dissolution of aluminosilicate minerals is slower than of metal hydroxides and much slower than that of carbonates. Feldspar weathering is mainly controlled by pH, silica, Na, K, and Ca concentrations. The reaction path is feldspar to kaolinite and then gibbsite (Eqs 2.3.8 and 2.3.9).



Kaolinite may hydrolyse to form gibbsite and the reaction does not consume acidity or generate acidity.



CMW is produced when the acid producing capacity and the neutralising capacity of the geology to be exploited during mining is almost equal. The CMW is characterised by pH 6-7, moderate amounts of SO_4^{2-} and low concentration of metals especially Fe and Al. This is due to the precipitation of the metals as hydroxides and SO_4^{2-} as gypsum due to the neutralisation by the carbonates that are found associated with the FeS_2 . Although the generic term AMD (or acid rock drainage) is used frequently to describe mine water discharges, the pH of these waters may be above 6, particularly at the point of discharge (where dissolved O_2 concentrations are frequently very low). In the case of Fe and Mn, these metals are generally present in their reduced (Fe^{2+} and Mn^{2+}) ionic states in anoxic AMD, and these forms of the metals are much more stable at higher pH than the fully oxidized (Fe^{3+} and Mn^{4+}) ions.

Some AMD streams remain neutral-to-alkaline, although others show a marked decline in pH as they oxygenate. This is because the total (or net) acidity derived both from proton acidity (H^+ concentration) and mineral acidity (the combined concentration of soluble metals, notably Fe, Al, and Mn, which produce protons when they are hydrolysed) is greater than acid neutralising capacity (Lottermoser 2007). The net acidity in AMD needs to be offset against any alkalinity present; this is chiefly in the form of bicarbonate (HCO_3^-) deriving from the dissolution of basic minerals (calcium carbonate), although biological processes may also generate alkalinity in AMD streams (Johnson and Hallberg, 2005).

2.3.3: Prediction of mine water type

Predicting the type of mine water that can be produced from a particular geology to be exploited during mining is essential for deciding the treatment strategies of

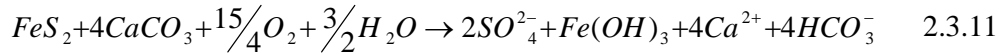
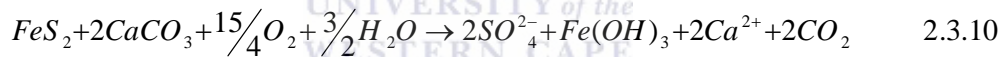
treating the effluent. In predicting the type of mine water that can be produced the following information need is required:

- The amount of acid producing minerals
- The amount of acid neutralising minerals
- The kinetics of acid producing processes
- The kinetics of acid neutralising processes

Determining the amount of acid producing and acid neutralising minerals is the first step in predicting the type of mine water to be produced. The amount of acid producing minerals gives the value of acid producing potential (APP) and the amount of acid neutralising minerals give the acid neutralising potential (ANP). This is achieved by acid base accounting (ABA) technique, which involves the determination of APP and ANP values (Skousen et al., 1990). The difference between ANP and APP gives the net neutralising potential (NNP):

$$\text{ANP} - \text{APP} = \text{NNP}$$

APP values are obtained based on the following stoichiometric equations (Cravotta et al., 1990):



Equation 2.3.10 represents an open FeS₂ oxidation neutralisation system which allows CO₂ gas produced to escape into the atmosphere, while equation 2.3.11 represents a closed system. APP is attributed to the potential of the sample to oxidise sulphide minerals to SO₄²⁻ (sulphuric acid). Sulphide minerals include the common iron minerals pyrite (FeS₂) and pyrrhotite (Fe_{1-x}S), and metallic sulphides such as chalcopyrite (CuFeS₂), sphalerite (ZnS), galena (PbS), etc. The sulphide sulphur is determined stoichiometrically from equations 2.3.10 and 2.3.11 depending on the system hence acid generation potential in % w/w CaCO₃ can be determined. However some SO₄²⁻ containing minerals such as FeSO₄·7H₂O, brochantite (Cu₄(SO₄)(OH)₆), jarosite (KFe₃(SO₄)₂(OH)₆), and alunite (KAl₃(SO₄)₂(OH)₆) produce acidity on hydrolysis. If these minerals occur in substantial amounts there is a need to include their contribution (Sobek et al.,

1978); otherwise sulphide S may be assumed as the acid producing parameter for calculation of the APP value.

Translating mineralogical data into ANP values proved to be a complex process that is prone to errors; chemical procedures have therefore been developed as a substitute for mineralogical procedures (Lawrence and Wang, 1997). However, to maximise the information obtained from chemical procedures in mine water prediction, mineralogical data should be complemented with chemical data for ANP determination.

A number of chemical procedures for the determination of ANP exist (Lapakko, 1994; Lawrence and Wang, 1997; Skousen et al, 1997). These are:

- Lapakko Neutralisation Potential Test
- BC Research Inc. Initial Test
- Modified Acid Base Accounting Procedure for Neutralization Potential
- Peroxide Siderite Correction for Sobek Method

These methods all involve the following steps in the determination of ANP:

- reaction of a sample with a mineral acid of measured quantity
- determination of the base equivalency of the acid consumed
- conversion of the measured values to % w/w CaCO₃

2.4: MINE WATER TREATMENT TECHNOLOGIES

Mine waters have high SO₄²⁻ and metal concentrations which need to be treated before being discharged into the environment (Blowes et al., 2003). Several methods exist for the treatment of mine waters, depending on the volume of the effluent, the type and concentration of contaminants present. Effective treatments are constantly being sought to generate water of neutral pH and low acidity, and to reduce the levels of the SO₄²⁻, Fe and other metals present down to the environmental limits. Ideally, a sustainable solution to any industrial problem

should be economically viable, generate little or no waste, be energy efficient and not be a source, in itself of pollution.

Mine water should not be seen as an environmental problem but can also be perceived as a useful raw material for industrial or drinking water. Many treatment methods have been implemented to treat mine water to remove heavy metals and SO_4^{2-} to the required effluent limits. These methods can be broadly classified as passive treatment and active treatment systems. Passive treatment is when mine water is passed through an environment where geochemical and biological processes help to improve the quality of the mine water and require relatively little resource input once in operation (Kalin et al., 2006).

Active treatment is when the water is treated in a constructed plant where processes are controlled and require continuous input of resources to sustain the process. Types of active treatment include biological treatment, chemical treatment, membrane technology and ion exchange.



2.4.1: Passive treatment of mine water

Passive treatment schemes take advantage of naturally occurring geochemical and biological processes in order to improve the quality of the influent waters with minimal operation and maintenance requirements. Passive treatment can be broadly classified as chemical or biological depending on the processes that are occurring to ameliorate the mine water (Figure 2.1) (Neculita et al., 2007).

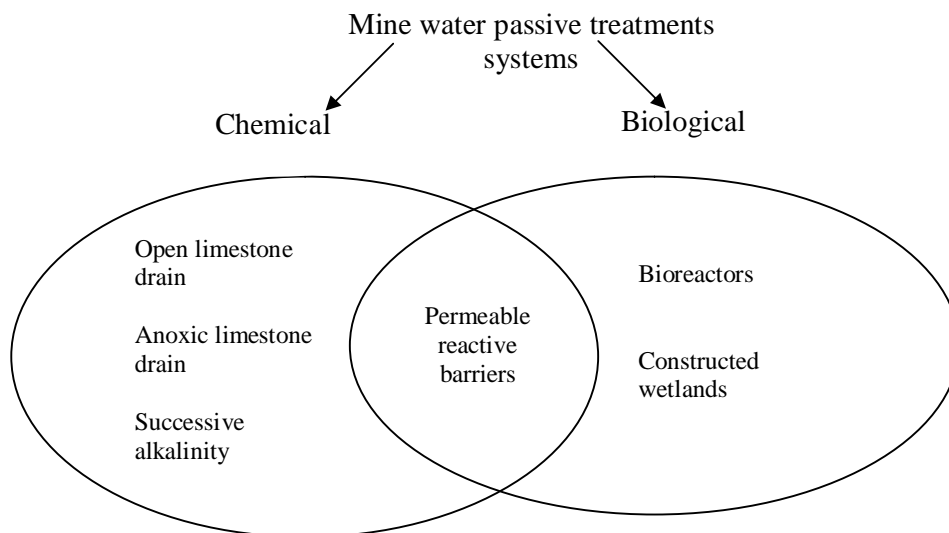
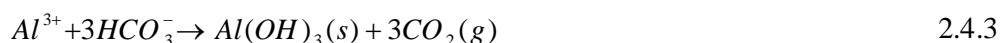
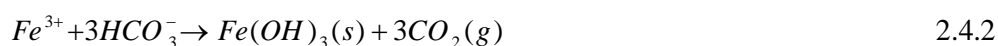


Figure 2.1: Passive treatment systems of mine water (Neculita et al., 2007)

Passive treatment systems that rely more on chemical processes are open limestone drains (OPD), anoxic limestone drains (ALD) and successive alkalinity producing systems (SAPS). The pH of mine drainage is raised when the water mixes with alkaline water or through direct contact with carbonate rocks (Mukhopadhyay et al., 2007; Ziemkiewicz et al., 1997). The removal of metal contaminants is then effected through the precipitation of hydroxides, oxyhydroxides and sulphides. Local conditions such as O₂ content, water and soil chemistry dictate whether these reactions will occur under oxidizing (aerobic) or reducing (anaerobic) environments (Gazea et al., 1996).

2.4.1.1: Open limestone drains

OLD are open ditches filled with crushed limestone. As the AMD flows over the limestone, the stone dissolves, which produces alkalinity to increase pH and remove soluble Al, Fe and Mn due to mineral precipitation (Mukhopadhyay et al., 2007; Ziemkiewicz et al., 1997).



Sulphates in the mine water will be precipitate out as gypsum (Nairn et al., 1991)



These systems generally only work with low flow rates with a long distance to the nearest receiving stream because, as Fe and Al precipitate from the AMD, the limestone gets coated by the metal hydroxides and thereby the solubility of limestone is reduced and the system becomes ineffective over time.

2.4.1.2. Anoxic limestone drains

In ALD, limestone is buried in trenches Fig 2.2. As the AMD flows through, the limestone dissolves, alkalinity is added and pH is increased. To prevent the limestone from becoming coated or armored with precipitated metal hydroxides, the AMD must be oxygen free (Cravotta and Trahan, 1999; Hedin et al., 1994).

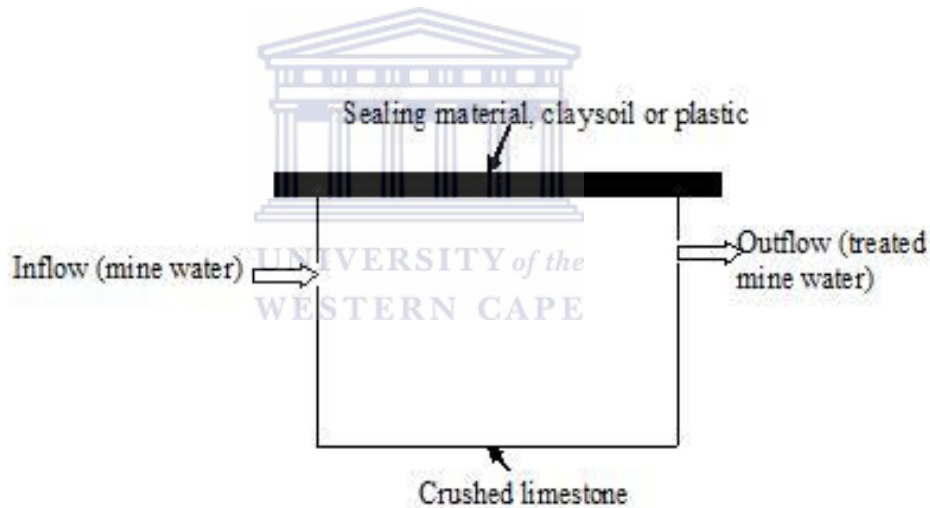
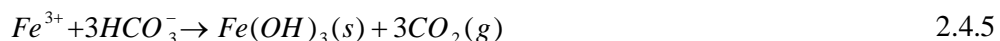


Figure 2.2: Schematic diagram of an anoxic limestone drain (Younger et al., 2002)

Deep mine discharges often have no O_2 , so the water can be channeled directly into the drain, which is covered with clay and/or plastic liners to avoid O_2 ingress. If the AMD is already has oxygenated, the water must be put through an anaerobic wetland in which organic material removes the O_2 , after which the water is channeled into the ALD. After the net alkaline waters pass through the ALD, then the water is exposed to atmospheric conditions and $Fe(OH)_3$ is produced by the oxidation of Fe^{2+} to Fe^{3+} .



A major source of HCO_3^- in many anoxic environments is the dissolution of carbonate minerals, such as CaCO_3 .



Sulphates are removed during ALD treatment of mine water through the precipitation of gypsum (Nairn et al., 1991).

Carbonate dissolution can result in higher concentrations of HCO_3^- in anoxic mine water environments than oxic environments. This is because of the absence of $\text{Fe}(\text{OH})_3$ in most anoxic environments that may armour carbonate surfaces and inhibit further CaCO_3 dissolution in oxic environments. The solubility of carbonate compounds are directly affected by the partial pressure of dissolved CO_2 (Stumm and Morgan, 1996; Butler, 1991). Anoxic mine water environments commonly contain high CO_2 partial pressures due to the decomposition of organic matter and the neutralisation of proton acidity.

Although ALDs produce alkalinity at a lower cost than constructed compost wetlands, they are not suitable for treating all AMD waters. In situations where the AMD contains significant concentrations of Fe^{3+} or Al^{3+} , the short-term performance of ALDs may be good, but the buildup of hydroxide precipitates gradually decreases drain permeability, which may cause failure of the drain within six months of construction (Johnson and Hallberg, 2005).

2.4.1.3: Successive alkalinity producing systems

In SAPS, mine water is channeled through alternating series of wetlands of anaerobic and aerobic conditions (Fig 2.3). The wetland is made up of organic matter that removes O_2 , creates a good environment for sulphate reducing bacteria (SRB) and converts Fe^{3+} to Fe^{2+} . The water that enters the limestone region is O_2 and Fe^{3+} free preventing armoring of limestone with $\text{Fe}(\text{OH})_3$. Alkalinity is generated through SRB or limestone dissolution in wetlands followed by metal removal in the aerobic ponds as a result of oxidation, hydrolysis, and precipitation and settling. Sulphates are removed either by bacterial action (Eq 1.2 and 1.3) or by

precipitation as gypsum in cases where the alkalinity is produced by limestone dissolution (Keplar and McCleary, 1994; Nairn and Mercer, 2000).

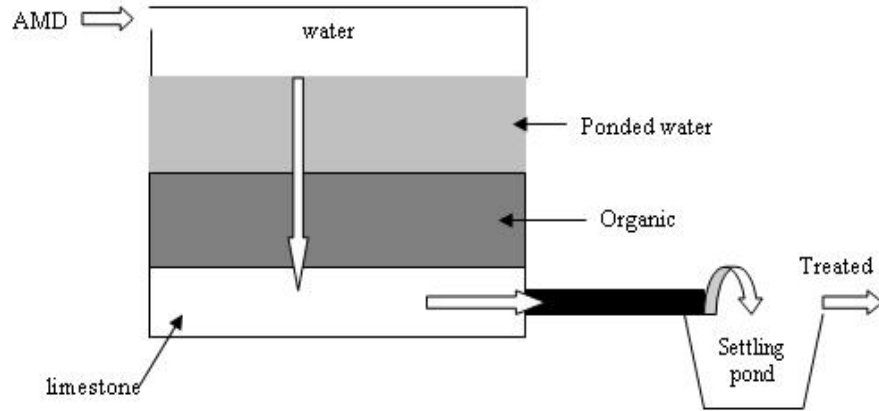


Figure 2.3: Schematic diagram of SAPS (Brown et al., 2002)

The alkalinity produced by SRB or limestone dissolution should be enough to buffer the acidity that is produced in the aerobic ponds in order to produce effluent water with a suitable pH that can be discharged into the environment (Nairn and Mercer, 2000).

2.4.1.4: Sulphate reducing passive bioreactors

Biological passive treatment systems for AMD include bioreactors and constructed wetlands. Sulphate-reducing passive bioreactors have received recent attention as promising technologies for mine water treatment (Neculita et al., 2007; Steed et al., 2000). The advantages of this technology are high metal removal capacity, stable sludge, and low operation costs. The chemical basis for treatment of AMD by SRB involves microbially-mediated sulphate reduction coupled to organic matter oxidation (Eq. 2.4.7). The hydrogen sulphide produced in equation 2.4.7 precipitates out metal contaminants (Eq. 2.4.8).



Other metal attenuation mechanisms including adsorption and precipitation of metal hydroxides occur in passive bioreactors (Neculita et al., 2007).

Generally, passive bioreactors operate over relatively short periods of time meeting their treatment objectives in terms of increasing the pH, for SO_4^{2-} and metal removal (Younger et al., 2002). However long-term operation has seen their efficiency decreasing due to substrate composition depletion, hydraulic retention time as well as AMD toxicity and variations in flow (Younger et al., 2002; Neculita et al., 2007).

2.4.1.5: Constructed wetlands

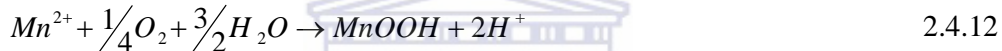
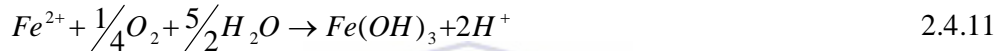
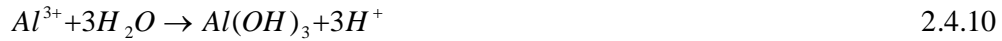
It was observed in the early 1980s that the quality of mine water significantly improved as it flowed through natural, sphagnum moss-dominated wetlands and this led to the idea that constructed wetlands could be used to remediate AMD (Wieder and Lang, 1982). Subsequently, much work in the development and engineering of wetlands to treat mine water discharges was carried out and the majority of early facilities were installed to treat mine water from coal mines (Hedin et al., 1994). Wetlands have been successfully applied in many locations to treat mine water, but they are usually applied to coal mine drainage, which is relatively low in metals and only mildly acidic to alkaline compared to AMD from metal mines (Younger et al., 2002).

Constructed wetlands fall into two categories; aerobic and anaerobic wetlands. Aerobic wetlands are suitable for treatment of net alkaline mine waters, while anaerobic wetlands are suited for passive remediation of acidic mine waters (Johnson and Hallberg, 2004).

Aerobic wetlands are designed to allow metal oxidation and precipitation are normally shallow, vegetated and have surface flow predominating (Robb and Robinson, 1995). Oxidation and hydrolysis reactions commonly cause concentrations of Fe^{2+} , Fe^{3+} , Mn^{2+} , and Al^{3+} to decrease when mine water flows through an aerobic environment. Whether these reactions occur quickly enough to lower metal concentrations to an acceptable level depends on the availability of oxygen for oxidation reactions, the pH of the water, the activity of microbial

and/or other catalysts and inhibitors, and the retention time of water in the treatment system.

The pH is an especially important parameter because it influences both the solubility of metal hydroxide precipitates and the kinetics of the oxidation and hydrolysis processes. The relationship between pH and metal-removal processes in passive treatment systems is complex because it differs among metals and also between abiotic and biotic processes. The stoichiometries of the major metal removing reactions in passive treatment systems are:

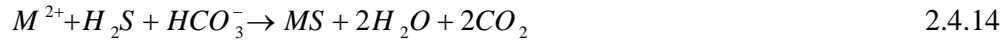


The first two reactions (2.4.9 and 2.4.10) are simple hydrolysis reactions, which require only the presence of water (and enough alkalinity to neutralize the H^+ produced). The last two reactions (2.4.11 and 2.4.12) require the presence of O_2 to oxidize the metal prior to hydrolysis. All of the reactions produce acidity. The goal of passive treatment systems is to drive these reactions to completion and collect the resulting solids before the water enters a receiving stream and hence the prerequisite that the input water should be net alkaline for aerobic wetlands to be effective (Hedin et al., 1994).

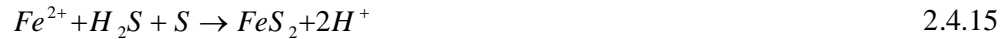
Anaerobic constructed wetlands require that the mine water flows through an organic layer containing SRB. When mine water flows through an anaerobic environment that contains an organic substrate, the water chemistry can be affected by bacterial sulphate reduction. In this process, bacteria oxidize organic compounds using SO_4^{2-} as the terminal electron acceptor and release H_2S and HCO_3^- :



CH₂O is used to represent organic matter (Postgate, 1984). Bacterial SO₄²⁻ reduction not only improves water quality by the addition of bicarbonate alkalinity, it can also lower the concentrations of dissolved metals, M²⁺ (Fe²⁺, Mn²⁺, Zn²⁺, Ni²⁺, Cu²⁺, Cd²⁺, Pb²⁺) by precipitating them as metal sulfide solids:



For Fe, the formation of FeS and even pyrite is possible:



The removal of dissolved metals as sulphide compounds depends on pH, the solubility product of the specific metal sulphide, and the concentrations of the reactants (Hammack et al. 1993). The first metal sulphide that forms is CuS, followed by PbS, ZnS, and CdS. FeS is one of the last metal sulfides to form. MnS is the most soluble metal sulfide known, and is not expected to form. Due to the low solubility of some of these metal sulphides relative to their solubilities as oxides or hydroxides, SO₄²⁻ reduction can be an important process in lowering some metal concentrations to acceptable levels, particularly heavily metal laden AMD.

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Sulphate reducing bacteria require the presence of SO₄²⁻, suitable concentrations of low-molecular weight carbon compounds as an energy source, and the absence of oxidizing agents, such as O₂, Fe³⁺ and Mn⁴⁺. These conditions are commonly satisfied in treatment systems that receive AMD and are constructed with an organic substrate, such as a compost material. High concentrations of SO₄²⁻ (> 500 mg/L) are characteristic of contaminated AMD. The O₂ demand of organic substrates causes the development of anoxic conditions and an absence of oxidized forms of Fe or Mn. The low molecular-weight compounds that SRB utilise (lactate, acetate) are common end-products of microbial fermentation processes in anoxic environments. These sulphate reducing and fermentative bacteria are more active above pH 5. However, they can be very active in drainages with lower pH levels, due to the presence of near-neutral pH microenvironments. These microenvironments allow the SRB to become

established, and because they generate alkalinity, these microenvironments are increased.

2.4.1.6: Permeable reactive barriers

Permeable reactive barriers (PRBs) can be classified as chemical or biological passive treatment depending on the reactive material used. PRBs are being used increasingly to treat a wide range of polluted ground waters. Construction of PRBs involves digging of a trench or pit in the flow path of contaminated groundwater, filling the void with reactive materials (a mixture of organic solids or limestone gravel) that are sufficiently permeable to allow unimpeded flow of the groundwater, and landscaping of the disturbed surface. Some reactive barriers are composed of either organic solids or limestone. Alkalinity is generated due to dissolution of limestone or microbiological processes within the PRB and metals are removed as sulphides, hydroxides, and carbonates (Younger et al., 2002).

Passive treatment systems have been developed to treat AMD with only periodic maintenance, which greatly reduces long term costs. However, these systems have some drawbacks. In particular, they use a lot more land space, and most often there is not enough land available to treat large discharges. Where sufficient land is available and the landowners are cooperative, passive systems have generally worked well if the appropriate system is designed based on the chemistry and flow of the individual discharge.

2.4.1.8: Selection of a passive treatment of mine water

The choice of the type of passive treatment depends on; the flow rate and the chemical composition of the mine water. Steps that can be used to select the best treatment method are outlined in Figure 2.4.

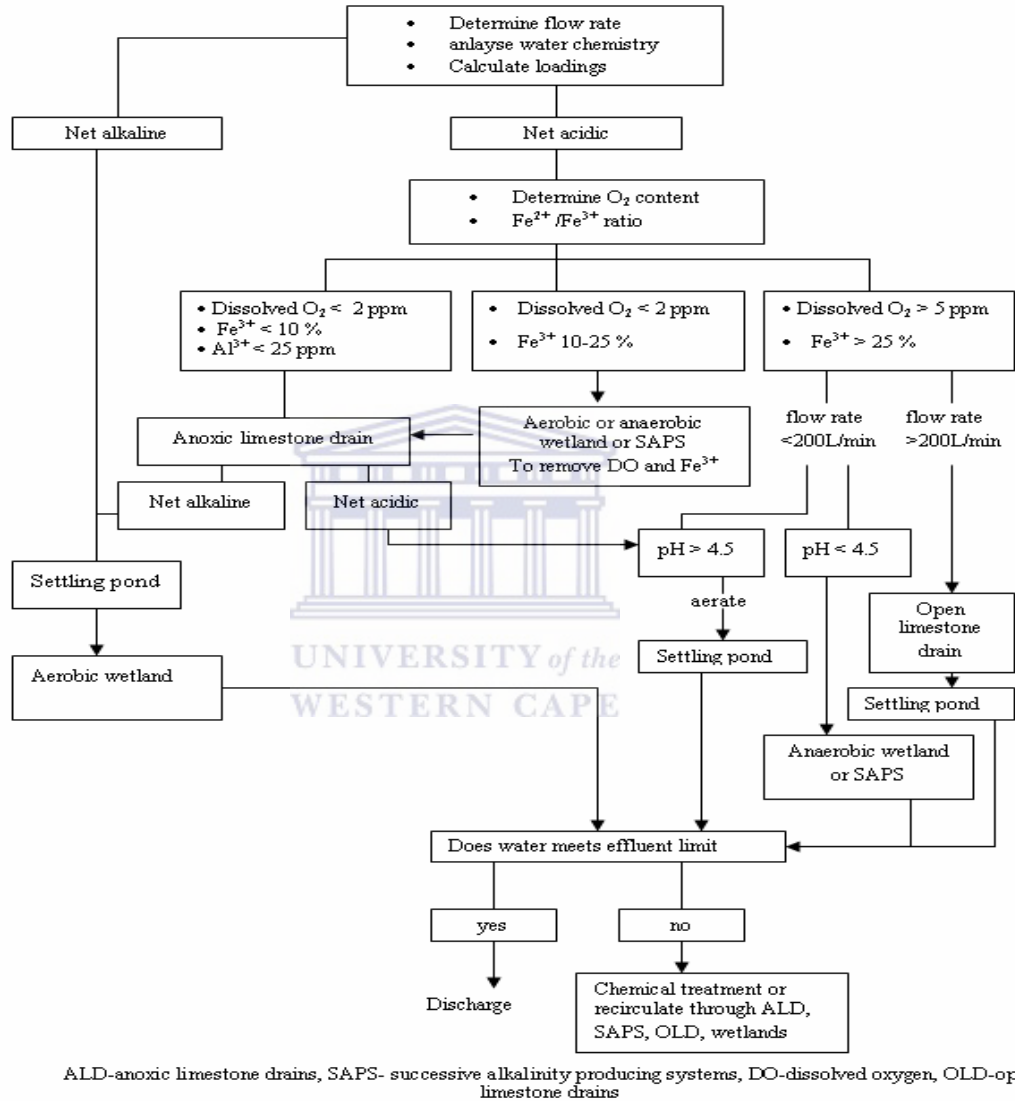


Figure 2.4: Flow chart for selecting a passive AMD treatment system based on water chemistry and flow (Hedin et al., 1994)

2.4.2. Active treatment of mine water

Active treatments of mine water are technologies that improve the water quality of mine water through processes that require continuous inputs of artificial energy, biochemical or chemical reagents (Young et al., 2002). Active treatment methods are recognised by the presence of a water treatment plant that is monitored regularly by a skilled workforce.

The major advantage of active treatment is the capability to handle any changes in mine water quality and quantity, because of the precise process control in response to these changes. Active treatment is also a preferred technique to passive treatment if the land availability is a limiting factor. The major disadvantage of active treatment method is that the brines and sludge that are produced as wastes are more expensive to handle and dispose off. The continuous input of energy, reagents and the need of skilled manpower to run and maintain the treatment plant makes the technique expensive.

Due to vast differences in the chemistry of mine waters and the variety of physical, chemical and biological methods for separating metals from mine water, there is a wide range of treatment technologies that can be applied for mine water treatment. The choice of a suitable treatment technology depends on:

- The mine water quality
- The mine water quantity
- The treated water quality
- Cost of the treatment technique

In reality, there is no technical limit to the quality of the water which can be achieved using current existing techniques, but the cost is the limiting factor. Therefore the selection of a treatment technique comes down to economic-environment cost benefit analysis.

2.4.2.1: Biological treatment

Bioreactors represent an active treatment approach for remediating AMD (Johnson, 2000). These engineered systems have three potential advantages over passive biological remediation in that; their performance is more predictable and readily controlled, they allow heavy metals, such as copper and zinc, present in AMD to be selectively recovered and reused and concentrations of sulphate in processed waters may be significantly lowered.

On the negative side, the construction and operational costs of these systems are considerable. Bioreactors utilise the biogenic production of hydrogen sulphide to generate alkalinity and to remove metals as insoluble sulphides, which is one of the processes that occur in compost bioreactors and PRBs. In as much as the SRB currently used in these reactors are sensitive to even moderate acidity, the systems have to be engineered to protect the microorganisms from direct exposure to the inflowing AMD (Rowley et al., 1997). Raw AMD enters the chemical circuit where it comes into contact with hydrogen sulfide generated in the biological circuit. By careful manipulation of conditions (pH and sulphide concentration), selective separation of a particular metal sulphide is possible; this may then be removed from the partially processed water ahead of further treatment. Some of the treated AMD enters the biological circuit to provide the SO_4^{2-} source in the bioreactor, which contains a mixed culture of SRB. For the process to run optimally, additional alkali may be required beyond that produced by the SRB, in which case, it is added in chemical form.

The process utilises microbiological populations and processes for; conversion of sulphate to sulphide by SRB and precipitation of metal sulphides and conversion of any excess H_2S produced to elemental S, using sulphide-oxidising bacteria.

However, H_2 may substitute hydrocarbon as electron donor for sulphate reduction (Eq. 2.4.16).



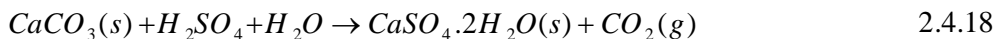
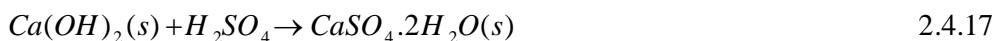
The use of H₂ is advantageous because it is more economical to use for high SO₄²⁻ loadings and results in lesser production of bacterial biomass. Hydrogen may conveniently be formed by cracking CH₃OH or from natural gas. In both cases, CO₂ is also produced, and some SRB are able to fix this as their source of carbon (Johnson and Hallberg, 2005).

2.4.2.2: Chemical treatment

Chemical treatment of mine waters involves the use of alkalis such as lime, limestone, ammonia and sodium hydroxide to neutralize acid mine water. Alkali treatment plants prefer limestone because it is cheaper than the other chemicals. The alkali raises the pH of the water with subsequent precipitation of metals as hydroxides. Different metal hydroxides precipitate at different pH values. Fe³⁺, Al³⁺, Mn²⁺ and Mg²⁺ precipitate at pH values 3, 6, 9 and 11 respectively. Barium salts such as Ba(OH)₂, BaS and BaCO₃ are also used to treat mine water specifically for SO₄²⁻ precipitation.

A. LIME/LIMESTONE

Treatment of mine water using lime and limestone reduce the concentration of SO₄²⁻ in the form of gypsum and due to co precipitation with or adsorption on metal hydroxides.



All the metals are removed to below the allowed effluent limit but SO₄²⁻ is usually above the required DWAF limit of 500 ppm because gypsum is partially soluble in water. Solubility of gypsum ranges from 1500 ppm to 2000 ppm depending on the composition and ionic strength of the solution. Gypsum precipitation is reduced in the presence of Mg²⁺, Na⁺ and K⁺ ions. An integrated limestone/lime process was developed for reducing SO₄²⁻ to less than 1200 ppm (Geldenhuys et al., 2001). This process involves the addition of lime to pH greater than 11 to precipitate out Mg(OH)₂ thereby enhancing the formation of gypsum (Figure 2.5). The stages involved in the integrated limestone/lime are:

Stage 1

Limestone neutralization raises the pH to circumneutrality resulting in precipitation of gypsum and heavy metals and CO₂ production.

Stage 2

Lime treatment to raise the pH to 12 for Mg(OH)₂ precipitation and enhanced gypsum precipitation.

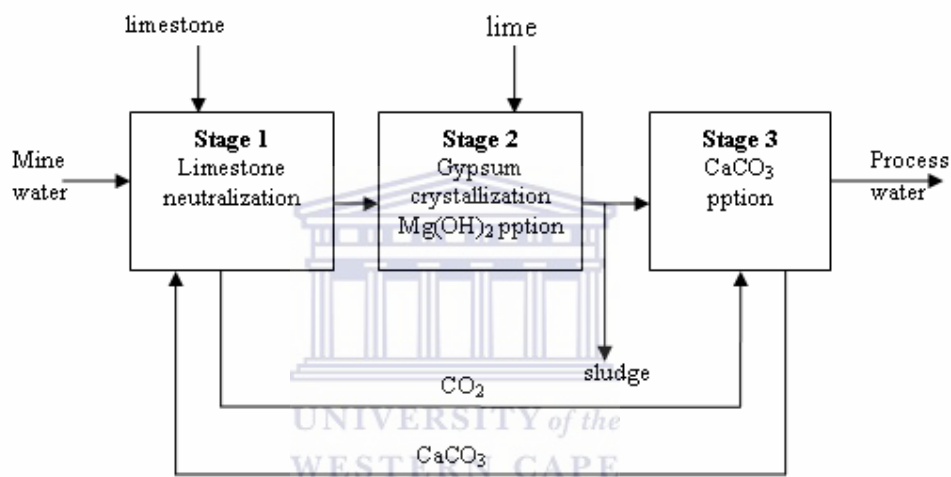


Figure 2.5: Schematic diagram of the integrated lime/limestone mine water treatment (Geldenhuis et al., 2001).

Stage 3

Adjustment of pH with CO₂ produced in stage 1 with concurrent precipitation of CaCO₃. The CaCO₃ produced is relatively pure and can be recycled and used to treat incoming mine water in the first step.

The advantage of this process is that the SO₄²⁻ concentration is reduced to below the saturation level of gypsum of 1200 ppm. The process neutralises the acidity

and metals are removed to below the allowed DWAF effluent limits. The process is said to be capable of eliminating the scaling and corrosion problems during water reuse in the mine and is suitable the water produced is for irrigation. The process can be used as a cost effective pretreatment process where SO_4^{2-} concentration in effluent water should be less than 500 ppm.

The major setback of this treatment method is that the sludge produced is voluminous (final water content of 95 %) and is difficult and expensive to handle. This process can be handled by recycling the low density sludge (Figure 2.6) (Bosman, 1983). The recycled sludge provides nuclei for hydroxides precipitation. This produces a high density sludge that is less voluminous with water content of 80 % before dewatering and filter pressing.

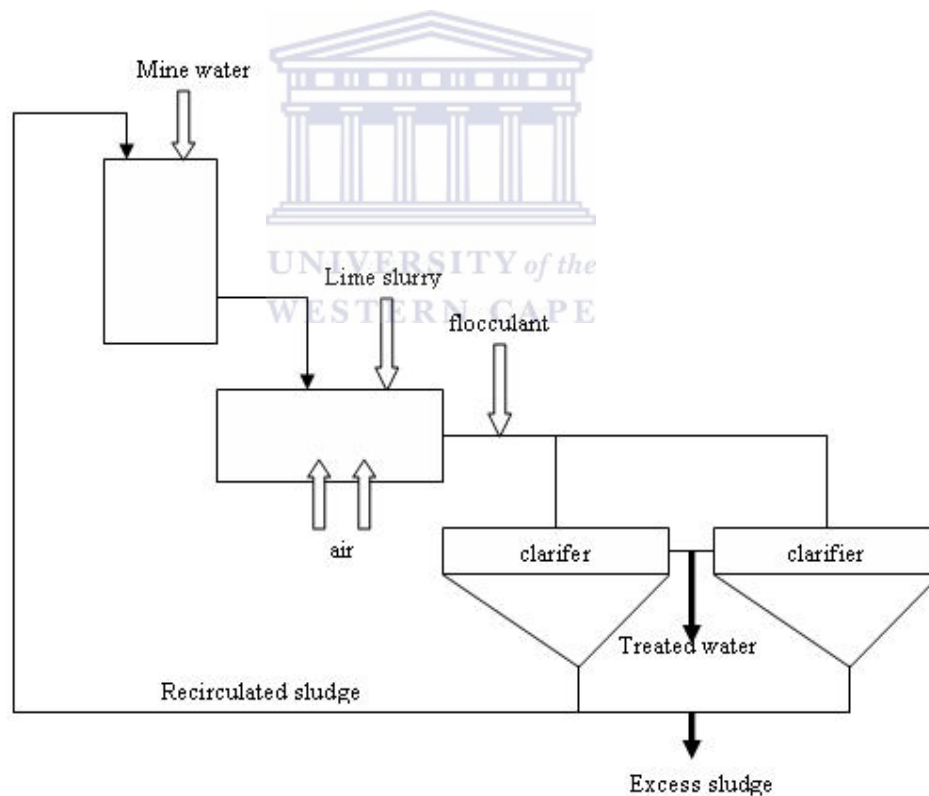


Figure 2.6: Flow diagram of high density sludge mine water treatment plant (Coulton et al., 2003).

B. SAVMIN PROCESS

The SAVIMN process uses the precipitation processes in successive stages to remove dissolved SO_4^{2-} and metals from mine water (Fig 2.7) (Smit, 1999).

Stage 1

Lime is added to raise the pH to values greater than 11. This allows the precipitating of metal hydroxides. The metal hydroxides are removed and the water that remains is supersaturated with respect to gypsum.

Stage 2

The supersaturated solution is seeded with gypsum to catalyse the precipitation of gypsum. The precipitated gypsum is removed from the water and the water from this stage is now saturated with respect to gypsum and the SO_4^{2-} concentration is still above the required limit of 500 ppm.

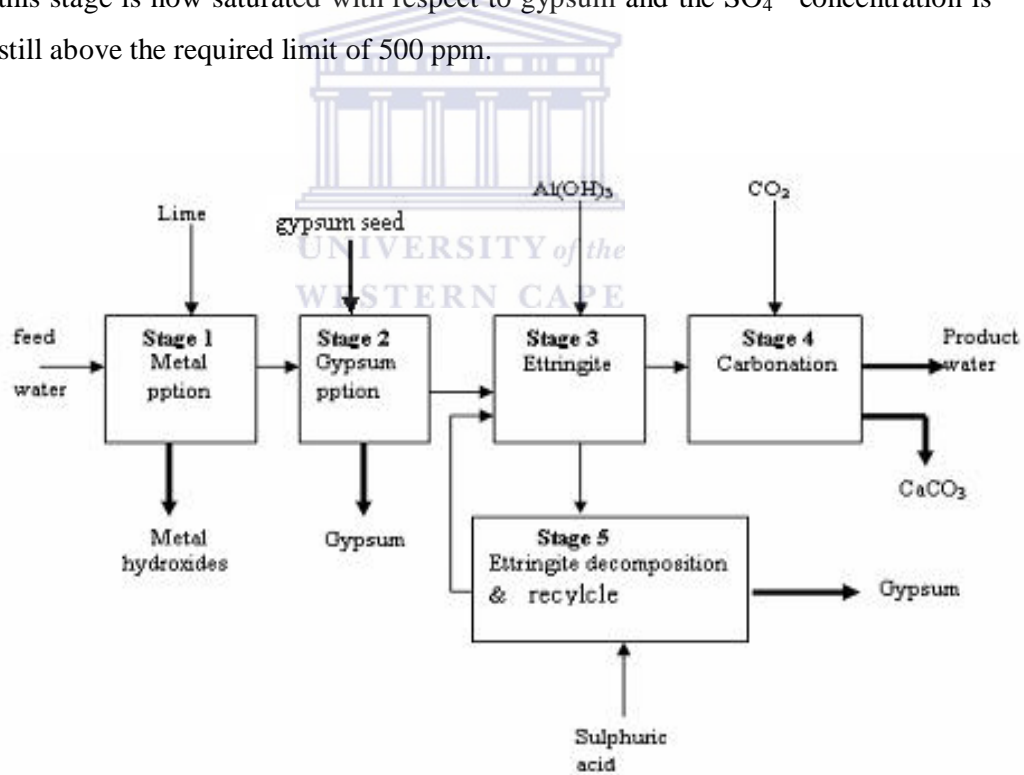
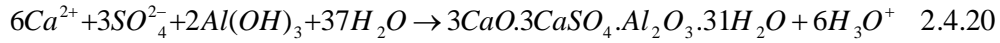


Figure 2.7: Flow diagram of the SAVIMN process (Smit, 1999).

Stage 3

Aluminum hydroxide is added to the water which is saturated with respect to gypsum. This results in precipitation of ettringite ($3CaO \cdot 3CaSO_4 \cdot Al_2O_3 \cdot 31H_2O$) via equation 2.4.20.



Stage 4

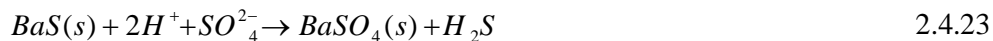
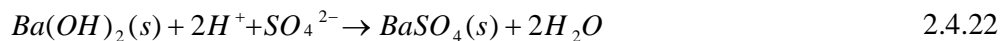
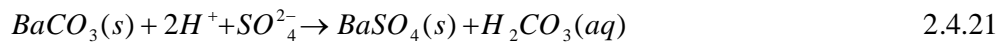
The water from stage 3 (pH 12 and dissolved $SO_4^{2-} < 200$ ppm) is treated with CO_2 . This results in $CaCO_3$ precipitation which is relatively pure. The water produced has a pH of 8 and contains dissolved $SO_4^{2-} < 200$ ppm.

Stage 5

Ettringite is decomposed by addition of sulphuric acid to regenerate $Al(OH)_3$. The $Al(OH)_3$ is recycled and used again in stage 3. The remaining water after removing $Al(OH)_3$ is seeded with gypsum to catalyse the precipitation of gypsum since the solution is still saturated with respect to gypsum. The resultant water is saturated with respect to gypsum and is returned back to stage 3 for ettringite precipitation. The product water from this process contains SO_4^{2-} below 200 ppm and the metal content is below the required effluent limit.

C. BARIUM SALTS TREATMENT

Barite ($BaSO_4$) is a highly insoluble mineral ($K_{sp} \sim 1 \times 10^{-10}$). Introducing sufficient amounts of Ba^{2+} ions into SO_4^{2-} rich waters results in removal of SO_4^{2-} to below 200 ppm. The common sources of Ba^{2+} are $BaCO_3$, $Ba(OH)_2$ and BaS . Sulphates are removed according to equations (Bosman et al., 1990; Hlabela et al., 2007).



BaCO₃ treatment will not remove SO₄²⁻ that were associated with Mg²⁺. This means Mg²⁺ should be removed from the water before Ba²⁺ can be added. This is achieved by addition of an alkali to increase the pH to 11 for Mg(OH)₂ precipitation before Ba²⁺ treatment. The presence of Ca²⁺ increases the dissolution of BaCO₃ (Eq.2.4.24) by precipitation of CaCO₃ (Hlabela et al., 2007).



This means that presence of Ca²⁺ will enhance SO₄²⁻ removal since more Ba²⁺ will come into solution. The dissolution of BaCO₃ is negatively affected by alkalinity thereby reducing the efficiency of using BaCO₃ to remove SO₄²⁻ (Hlabela et al., 2007).

BaS and Ba(OH)₂ treatment is capable of increasing the pH to above 11, since the treatment generates alkalinity (Eqs 2.4.20 and 2.4.21) thereby precipitating Mg(OH)₂. Treatment of mine water using BaS and Ba(OH)₂ does not require alkali treatment prior to addition of Ba salts. Metals in the mine water will react with H₂S produced in reaction 2.4.23 to produce metal sulphides precipitates. (Adlem, 1997; Maree et al., 1989). If the metal cations present in the raw water are not equivalent to the H₂S produced, then the H₂S needs to be removed before discharging the water (Hlabela et al., 2007) to avoid release into atmosphere since it is poisonous.

The major disadvantage of Ba²⁺ treatment of mine water is the cost of the salts. In addition H₂S produced by BaS is a toxic gas that needs to be removed and any failure to remove all of the gas will be fatal. The product water should have Ba concentration of less than 0.7 ppm because Ba is a toxic element (WHO, 2008).

While the chemical treatment works well to raise pH and to precipitate the metals, the treatment plants are very expensive to operate and maintain. Also the disposal of the toxic metal-laden sludge is a very big environmental problem.

2.4.2.3: Membrane treatment

Membrane systems remove contaminants by selectively allowing only certain ions to pass through the pores of the membranes by size exclusion (reverse osmosis, nanofiltration, ultrafiltration and microfiltration). Membrane systems that use a combination of size exclusion and electric charge to remove contaminants from water are called electro dialysis. Membrane treatment can be classified as secondary a processes for treatment of mine water. This is because these systems require pretreatment of mine water to remove suspended solids to reduce fouling of membranes.

Microfiltration is the purification of water by passing it through membranes with pore size $\geq 0.1 \mu\text{m}$ and $< 0.45 \mu\text{m}$. Removal of bacteria is achieved but viruses, colloids, colour and solutes remain in the water.

Ultrafiltration involves passing contaminated water through membranes of size $\geq 0.01 \mu\text{m}$ and $< 0.1 \mu\text{m}$. The treated water is free from colloids and microorganisms, but still contains solutes. Ultrafiltration and microfiltration can be used as pretreatment options for nanofiltration and reverse osmosis (RO) treatment of mine water to produce drinking water.

Nanofiltration uses pressure gradient to separate ions through a porous membrane. The pores on nanofiltration membranes are $\geq 0.001 \mu\text{m}$ and $< 0.01 \mu\text{m}$. Nanofiltration is capable of separating bigger divalent anions such as SO_4^{2-} and organic molecules from water and monovalent small cations ions (Kentish and Stevens, 2001).

Reverse osmosis is a pressure driven membrane process in which the solution is transferred through a semi-permeable membrane (pore size $< 0.001 \mu\text{m}$). During this process a substantially high pressure difference across the membrane is necessary to overcome the osmotic pressure difference between the salt free permeate and the saline reject solution (brine). The smaller water molecules are literally pushed through the semi-permeable membrane, while the larger solute

species are retained. This process is the “reverse” of natural osmosis, which involves water diffusion from a dilute to concentrated region through a semi-permeable membrane. The principle by which these membranes choose or reject ions, are based on size and electrical charge (Kentish and Stevens, 2001; Matsuura, 2001). Although perceived as an economically feasible desalination process for specialized applications however, RO and ultrafiltration are yet to overcome certain drawbacks which include the following (Del Pino and Durham, 1999):

- Extremely high operating pressures are required to overcome osmotic pressure gradients leading to substantial increase in energy consumption, and the fact that such plant installations and operation are relatively costly, makes this an exceedingly expensive treatment option.
- Another major problem is the membrane susceptibility to fouling by suspended solids, colloidal material, or certain dissolved ions in the feed water. The implications of fouling are irreversible membrane damage, reduced flux rates and increased capital and operating costs.
- One critical issue for the successful application of RO is pre-treatment. Pretreatment has to ensure that the quality of the effluent fed to the RO membranes is consistently high to avoid variability in the feed water quality and needless to say, pre-treatment on its own has high costs attached to it.
- The basic principle on which RO operates is size exclusion and selectivity for specific metal ions is restricted and as such limits the scope of the process.

Nanofiltration operating costs are lower compared to RO. This is because of increased permeability of nanofiltration membrane due to bigger pore size than RO membranes.

Electro dialysis (ED) is an electrochemical separation process which involves the selective migration of aqueous ions through ion selective membranes as a result of an applied electrical potential difference. An ED system consists of two

oppositely charged electrodes, a cathode and anode, with a number of compartments in-between. These compartments are separated by alternative cation and anion exchange membranes, filled with polluted water (Figure 2.8). The advent of an electrical potential difference, combined with electrochemical reactions, which includes reduction of water at the cathode and oxidation at the anode impel the ions through the membranes (Valerdi-Perez et al., 2001).

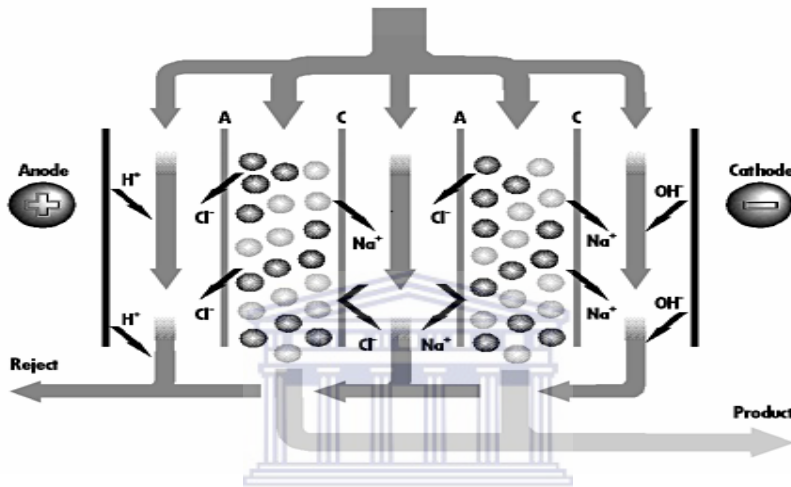


Figure 2.8: Schematic diagram of electro dialysis treatment cell.

The transport rate and direction of each ion depends on its charge, mobility, solution conductivity, relative concentrations and applied voltage. Appropriately then, under the influence of an applied direct current field, ions are forced to migrate to the appropriate electrode, which involves anions migrating through the anion exchange membrane into the adjacent compartment toward the anode, while movement of the cations will be toward the cathode. The ions that are transported out of the feed stream are collected in a brine stream and as such in ED systems, two main streams flowing in parallel to the membrane stack can be observed; one being progressively desalted which is referred to as the product stream, while the other main stream is the salt rich stream (brine).

To enhance the efficiency of ED systems by reducing membrane fouling, the polarity reversal process referred to as electro dialysis reversal (EDR) was developed. This involves the periodic reversal of the polarity of the electrodes,

resulting in the reversal of the direction of ion movement within the membrane stack. The dilute stream then becomes the concentrate stream and vice versa. EDR uses the technique of regularly reversing the polarity of the electrodes, thereby freeing accumulated ions in the membrane surface. Reversing the polarity of electrodes breaks up and flushing out scale and other deposits from the cells (Del Pino and Durham, 1999), which could shorten membrane life by fouling. Consequently the EDR treatment system has reduced sensitivity to scaling and fouling compared to normal ED treatment systems.

The ED/EDR plant operation efficiency increases with an increase in feed water temperature and consequently at a typical plant, a preheating stage, which raises the temperature of the feed water to approximately 35°C immediately prior to the ED/EDR is included (Schoeman and Steyn, 2001). The increased energy input arising from the heating process evidently adds to the capital and process costs. To maintain a constant feed temperature, a boiler plant generates steam, which is injected into the feed water after the plate exchangers and before the ED/EDR. This steam injection ensures that the constant feed water temperature of approximately 35°C is maintained (Schoeman and Steyn, 2001).

The presence of contaminants including suspended solids, high molecular weight dissolved solids, organic compounds and colloids in the feed water may give rise to membrane fouling resulting in irreversible membrane damage. Therefore feed water pre-treatment also exerts a pivotal role in ED/EDR process treatment performance, by trying to ensure that the quality of the water fed to the ED/EDR membranes are consistently high. In order to maintain optimum performance of ED/EDR systems, membrane stacks need to be cleaned intermittently to remove scale and other surface foulants (Del Pino and Durham, 1999). Normal cleaning is usually done by a cleaning-in-place (CIP) system, which utilizes special cleaning solutions that are circulated through the membrane stack; however, the membrane stack needs to be periodically disassembled, cleaned and reassembled at regular intervals for effective removal of scalants and other potential surface foulants (Schoeman and Steyn, 2001).

The major disadvantage of ED/EDR systems, as is the case in all other membrane systems, is that membranes have a limited lifetime before fouling or failure of adhesive bonds necessitates replacement. The costs of periodic replacement are an expensive expedient and needs to be included in any analysis of their economic viability (Kentish and Stevens, 2001). Since approximately 50 % of the total dissolved solids (TDS) can be removed per pass, the ED/EDR process is limited to feed water with maximum TDS value of 3000 ppm. The water to the ED/EDR needs to adhere to specific guidelines pertaining to pH, organic constituents, turbidity and other characteristics. The system is equipped with pH adjustment chemicals (normally acid, e.g. H_2SO_4), as well as imbedded cartridge filters to alleviate source water contamination and as such, adds to the operating costs.

2.4.2.4: Ion exchange

The process of ion exchange can be defined as the reversible interchange of a charged ion (cation or anion) for a similarly charged ion, between a solid material (the ion exchanger) and the surrounding liquid, in which there is no permanent change in the structure of the solid (Kitchener, 1957). Ion exchange resembles sorption, in that in both cases, a dissolved species is taken up by a solid; however, the characteristic difference between the two phenomena is that ion exchange, unlike sorption, is a stoichiometric process where every ion which is removed from the solution is replaced by an equivalent amount of another species of the same sign. In sorption, on the other hand, a solute is taken up without being replaced by another species. Although the distinction between the two phenomena seems clear-cut, in practice however, virtually every ion-exchange process is accompanied by electrolyte sorption or desorption and most of the common sorbents such as activated carbon, alumina, etc. can act, in turn, as ion exchangers.

The unique characteristic properties of ion exchangers can be attributed to a distinctive feature in their structure. They consist of a framework, held together by chemical bonds or lattice energy and the framework carries a positive or negative electric surplus charge, which is compensated by ions of opposite sign, also

referred to as counter-ions (Kitchener, 1957). The counter-ions are mobile thus able to move within the framework and can be replaced by other ions of the same sign (counter ions). However, electro-neutrality must be preserved, i.e., the electric surplus charge of the ion exchanger must be compensated at any time by a stoichiometrically equivalent number of counter-ions within the pores. A counter-ion can subsequently leave the framework, only when, simultaneously, another ion enters and takes over the task of contributing its share to the compensation of the framework charge (Kitchener, 1957).

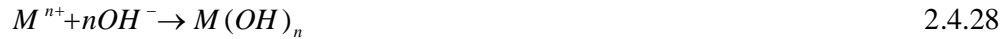
2.4.3. Fly ash treatment of mine water

AMD remediation can be very costly and difficult to achieve due to the high costs of chemicals and storage of high volumes of sludge produced during chemical treatment. Therefore, alternative low cost liming substitutes are constantly being sought. Such substitutes should be readily available, economically feasible and produce less problematic sludge. Coal fly ash has been used for soil reclamation, asphalt shingle production, quarry-fill and sludge stabilization, but mostly is disposed as landfill.

Due to the shortage of landfill sites and stricter environmental regulations, new innovative ways to recycle this coal combustion by-product should be quickly developed. Some of the innovative ways that have been studied include mine water treatment (Gitari et al., 2006, Gitari et al., 2008, Petrik et al., 2003; Klink, 2003) and zeolite synthesis (Moreno et al., 2001; Somerset et al., 2005, Somerset et al., 2008 and R'ios et al., 2008; Wingenfelder et al., 2005). Studies have also shown that addition of FA to AMD results in acid neutralisation, metal retention and therefore, the improvement of the leachate quality (Gitari et al., 2006; Klink, 2003; P'erez-L'opez et al., 2007).

FA is capable of neutralising AMD and precipitating metals and SO_4^{2-} as hydroxides and gypsum respectively. This is because FA contains free lime that leaches out when mixed with mine water (Gitari et al., 2006).





where, M^{n+} is the metal contaminants in the mine water

Researchers have found out that treatment of acid mine water which is rich in Fe and Al results in removal of metals to below detection limit while sulphates can be removed to equilibrium saturation point of ~ 2000 ppm. Preliminary investigation in our laboratory has found that using FA to treat circumneutral mine water, which is Fe and Al free to pH < 10 results in insignificant sulphate removal. This study is therefore directed at the understanding of the mechanism of SO_4^{2-} from circumneutral mine water and AMD.

In the next chapter, all the experimental procedures applied to achieve the goals of this study are explained. The trends of the elements in the water are going to be analysed using inductively couple plasma-mass spectrometry (ICP-MS), inductively couple plasma-atomic emission spectrometry (ICP-AES) and ion chromatography (IC). The changes that occur in FA during of mine water treatment are identified by x-ray diffraction (XRD) and x-ray fluorescence (XRF) spectroscopy with help of PHREEQC thermodynamic geochemical modelling.

CHAPTER 3 : METHODOLOGY

3.1: INTRODUCTION

This chapter explains the choice of the study area and outlines the procedures that were carried out during the process of acquiring data in this study. Step by step outline of how the SO_4^{2-} concentration was being reduced from the mine water was explained thoroughly in this section. It also outlines the analytical techniques and the experimental steps that were carried out.

3.2: STUDY AREA

Coal FA and mine water are two wastes produced by Hendrina coal combustion power plant and Middleburg coal mine in Mpumalanga province respectively (Figure 3.1). The Middleburg coal mine was chosen because it is close to Hendrina power station and the site was never studied in terms of mine water treatment with FA.

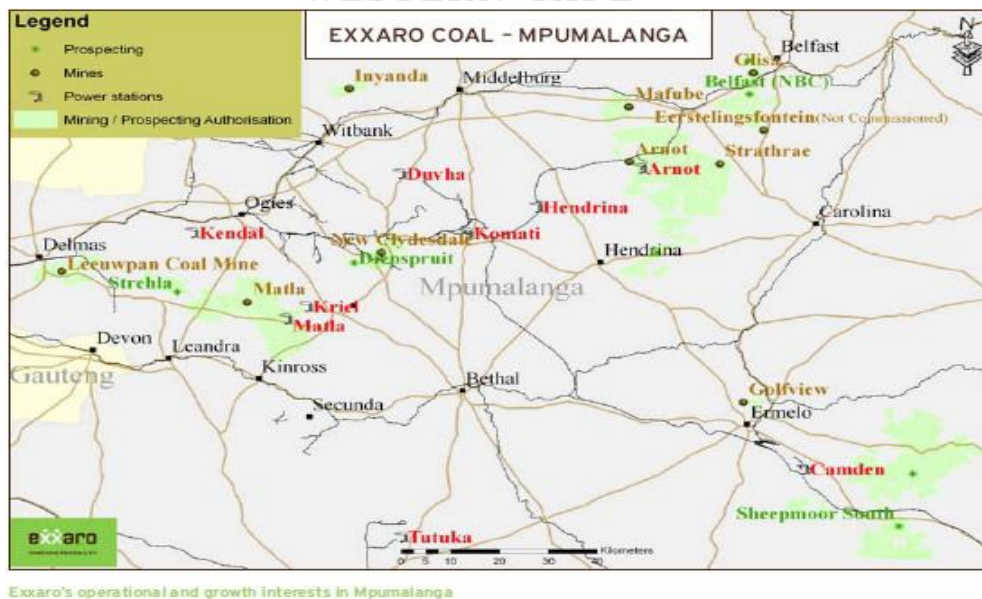


Figure 3.1: Location of the study area where CMW and FA samples were collected (Exxaro, 2007).

In order for these two industries to go a step further to achieve zero effluent discharge this research tried to view these two environmental liabilities as valuable raw materials to produce water that could be used for domestic and irrigation purposes. This seems likely because FA contains CaO that can be exploited to precipitate out SO_4^{2-} as gypsum and ettringite from CMW. The choice of the mine was based on the close proximity of the power station. This will make the treatment economically feasible.

3.3: MATERIALS.

3.3.1: Sampling

This study used two waste materials to ameliorate each other in a bid to achieve zero effluent discharge in the mines and coal fired power stations. These waste materials are FA and mine water collected from Hendrina power station and Middleburg coal mine in the Mpumalanga province (Figure 3.1).

The water was filtered through a 0.45 μm pore membrane filter paper using manual pumping device. The filtered samples were divided into two portions for cation and anion analysis. The cation samples were preserved with 3 drops of concentrated HNO_3 for approximately 100 ml of sample. Both cation and anion samples were preserved at 4 °C until analysis for anions using ion chromatography (IC) and cations using inductively-coupled plasma-mass spectroscopy (ICP-MS) and inductively-coupled plasma-atomic emission spectroscopy (ICP-AES).

Fresh FA was collected directly from the hoppers of one of the nearby Hendrina coal power station. Samples of FA were sealed in plastic bags free from air to avoid the reaction of CaO in the FA with CO_2 forming calcite therefore reducing

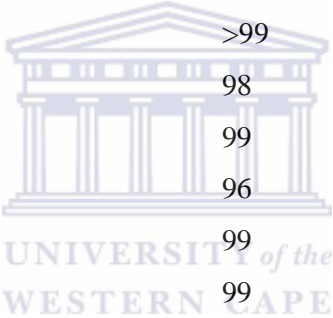
the CaO content. The FA samples were analysed using XRD and XRF for mineralogy and elemental composition respectively.

3.3.2: Chemicals

The chemicals used in this experiment were obtained from KIMIX chemical company and their respective purities are shown in Table 3.1.

Table 3.1: Purities of chemicals used in this study

Chemical formula	Purity (%)
MgSO ₄ .7H ₂ O	99.5
CaSO ₄	99
KNO ₃	99
NaCl	>99
MnCl ₂ .4H ₂ O	98
Al(OH) ₃	99
FeSO ₄ .7H ₂ O	96
Al ₂ (SO ₄) ₃ .18H ₂ O	99
CaSO ₄ .2H ₂ O	99



3.4: METHODS

This section details the methods applied to study the degree of removal of SO₄²⁻ by FA addition to mine water. This is followed by the methods to study the addition of gypsum seed and Al(OH)₃ to remove SO₄²⁻ to below the DWAF limit for potable water. Each experiment was done in triplicate to verify reproducibility of the results. The mixing done in all the experiments was done using the overhead stirrer at 500 rpm.

3.4.1: SIMULATION OF MINE WATER

This study was conducted using simulated mine water to avoid the change in composition of the original water during storage and because of the logistical challenges. Three types of mine waters were simulated; circumneutral mine water (SCMW), Fe only containing AMD (Fe-AMD) and Al only containing AMD (Al-AMD). The waters were simulated based on the chemical analysis of the original mine waters collected in the field. Fe-AMD and Al-AMD were simulated in order to study the effect of Fe and Al on SO_4^{2-} separately.

A. SIMULATION OF CIRCUMNEUTRAL MINE WATER

The SCMW was produced by dissolving the following salts in ultra pure water (1000 ml); $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (8.622 g), CaSO_4 (1.698 g), KNO_3 (0.09 g), NaCl (0.076g) and $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.097 g). The mixture was stirred thoroughly until all the salts dissolved and pH and EC were measured. The simulated mine water was analysed for cations using ICP-MS and ICP-AES and anions using IC to confirm the exact concentration. In the simulation of the mine water, concentration less than 2 ppm in the original Middleburg CMW were ignored and therefore the SCMW was simulated in such a way that it contained the following elements; Mg, Ca, K, Na, Na, Mn, SO_4^{2-} , Cl^- and NO_3^- .

B. SIMULATION OF Fe-AMD

AMD containing Fe was simulated by dissolving the following quantities of salts in 500 ml of ultra pure water; $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (4.978 g), CaSO_4 (0.2545 g), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (1.014 g), KNO_3 (0.045 g), NaCl (0.038 g) and MnCl_2 (0.0485 g). The mixture was stirred thoroughly until all the salts dissolved and pH and EC were measured. The water analysed to confirm the elemental composition using ICP-MS, ICP-AES and IC. Fe-AMD was simulated in such a way that it contained the same elements as in SCMW except Fe. This allowed the study of the effect of Fe on SO_4^{2-} removal from mine water.

C. SIMULATION OF Al-AMD

AMD containing Al was simulated by dissolving the following quantities of salts; $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ (2.3139g), CaSO_4 (0.2545 g), $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$ (1.014 g), KNO_3 (0.045 g), NaCl (0.038 g) and MnCl_2 (0.0485 g) in 500 ml of ultra pure water. The mixture was acidified with 5M H_2SO_4 (1.5 ml) to make up the SO_4^{2-} concentration to 4500 ppm and to for the pH to be less than 3 to prevent precipitation of $\text{Al}(\text{OH})_3$ before reacting with FA. The mixture thoroughly mixed together to make sure all the salts were dissolved and the pH and EC were noted. The water was analysed to confirm the elemental composition using ICP-MS, ICP-AES and IC. Al-AMD was simulated in such a way that it contained the same elements as in SCMW except Al. This allowed the study of the effect of Al on SO_4^{2-} removal from mine water.

The AMDs were simulated in such a way that they contained approximately the same elements as the SCMW used in this study except Fe and Al. The Fe and Al were added such that the ratio of concentration of $\text{Fe}:\text{SO}_4^{2-}$ and $\text{Al}:\text{SO}_4^{2-}$ were 2:1 and 12:1 respectively. These ratios were selected based on the composition of typical AMD in South Africa. Since the concentration of SO_4^{2-} in CMW was approximately 4500 ppm, 312 ppm and 2000 ppm of Al and Fe were added to the simulated mine waters to achieve the required $\text{Fe}:\text{SO}_4^{2-}$ and $\text{Al}:\text{SO}_4^{2-}$ ratios.

3.4.2: Effect of the final pH

This set of experiments was conducted in order to establish the effect of the final pH on SO_4^{2-} removal. SCMW water prepared as specified in section 3.3.1a was mixed with FA in the solid/liquid (L/S) ratio 2:1 to different final pH values (Table 3.2). After reaching the desired pH the mixtures were filtered through a 0.45 μm nucleopore membrane filter paper and analysed for anions and cations using IC and ICP-MS.

Table 3.2: Conditions applied in the treatment of SCMW to different final pH

Experiment	Volume of mine water (ml)	Mass of FA (g)	Final pH
3.3.2a	200	100.2	9.88
3.3.2b	200	98.98	10.21
3.3.2c	200	100.04	11.77
3.3.2d	200	100.04	12.34

3.4.3: Effect of the initial pH

Three experiments were carried out by varying the starting pH of the mine water. In the first experiment simulated circumneutral mine water of pH 6.85 was treated with FA to a pH of 12.35. Aliquot samples were collected at pH 8.98, 9.85 and 12.34. The samples were filtered through 0.45 μm nucleopore membrane filter paper. The product water was analysed for cation and anion concentrations.

In the second experiment, simulated circumneutral mine water was first acidified to pH 3.66 with 0.02 mol/L H_2SO_4 (4 ml) and then treated with FA to a final pH of 12.04. Aliquot samples were collected at pH 7.55, 9.11 and 12.04. The samples were filtered through 0.45 μm nucleopore membrane filter paper. The product water was analysed for cation and anion concentrations.

In the third experiment simulated circumneutral mine water was first acidified to pH 2.3 with 0.2 mol/L H_2SO_4 (10 ml) and treated to pH 12.12 with FA. Aliquot samples were collected at pH 6.45, 9.85 and 12.14. The samples were filtered through 0.45 μm nucleopore membrane filter paper. The product water was analysed for cation and anion concentrations.

In all the three experiments the CMW:FA used was 2:1. All these three experiments were done in triplicates in order to verify the reproducibility of the results.

3.4.4: Effect of the amount of FA

The following set of experiments was done in order to establish the effect of FA on SO_4^{2-} removal. Simulated circumneutral mine water (pH 6.85) was mixed with different amounts of FA for 24 hrs (Table 3.3). After the experiment the mixtures were filtered through a 0.45 μm nucleopore filter paper and the filtrate analysed for anions by IC and cations ICP-MS and ICP-AES.

Table 3.3: Different amounts of FA mixed with SCMW

Experiment	Volume of mine water (ml)	Mass of FA (g)	Ratio
3.3.4a	200	100.05	2:1
3.3.4b	200	66.68	3:1
3.3.4c	200	50.04	4:1
3.3.4d	200	40.03	5:1

For each ratio the experiment was repeated three times for verification of the reproducibility of the results.



3.4.5: Effect of Fe and Al

Previous studies have shown that treating Fe and Al rich AMD with FA to pH 9 resulted in 70 to 80 % SO_4^{2-} removal (Gitari et al., 2006). Initial treatment of circumneutral mine water with FA to pH 9 resulted in less than 10 % SO_4^{2-} removal (Madzivire et al., 2008). This motivated the idea of evaluating the effect of Fe and Al on SO_4^{2-} removal.

The study to establish the effect of Fe and Al upon SO_4^{2-} removal was done in two stages:

1. Navigation AMD was used as the source of Fe and Al by mixing it with SCMW. The mixtures were treated with Hendrina FA to various pH end points and process waters compositions analysed and compared.

2. Simulated CMW, Al-AMD and Fe-AMD (as described in 3.3.1) were treated with FA to the various pH end points and the process waters compositions analysed and compared.

3.4.5.1: Navigation AMD as the source of Fe and Al

Navigation coal mine AMD which is rich in Fe and Al was used as a source of Fe and Al in these experiments. The SCMW and Navigation AMD were mixed as shown in Table 3.4.

Table 3.4: Proportions of SCMW and Navigation AMD mixed

Ratio of SCMW:AMD	Volume of SCMW (ml)	Volume of Navigation AMD (ml)
1:0	1000	0
1:1	500	500
2:1	667	333
3:1	750	250

The mixtures were thoroughly mixed together with an overhead stirrer for 60 mins. After 60 mins the mixtures were treated as follows:

1. For the 1:0 mixture which was 100 % SCMW (300 ml) was reacted with Hendrina FA (150 g) and aliquot samples were collected at pH 8.9, 9.88, 10.96, 11.77 and 12.35.
2. For the 1:1 mixture (300 ml) was reacted with Hendrina FA (150 g) and aliquot samples were collected at pH 4.57, 5.94, 8.34, 9.96 and 10.21.
3. The 2:1 mixture (300 ml) was reacted with Hendrina FA (150 g) and aliquot samples were collected at pH 6.26, 8.98, 9.97 and 12.31.
4. Lastly, the 3:1 mixture was reacted with Hendrina FA (150 g) and aliquot samples were collected at pH 6.15, 8.44, 10, 10.36 and 11.78.

The aliquot samples were filtered through 0.45 µm nucleopore membrane filter paper. The filtrate was analysed for cation by ICP-MS and ICP-AES and anions using IC. The possible mineral phases that precipitate at each pH end point were predicted by PHREEQC geochemical modeling.

3.4.5.2: Effect of Fe or Al on sulphate removal

Simulated CMW, Fe-AMD and Al-AMD as outlined in section 3.3.1 were used in the following experiments:

1. SCMW (300 ml) was reacted with Hendrina FA (150 g) and aliquot samples were collected at pH 9.88, 10.21, 11.77 and 12.34.
2. Fe-AMD (300 ml) was reacted with Hendrina FA (150 g) and aliquot samples were collected at pH 9.54, 10.2, 11.8 and 12.12.
3. Al-AMD (300 ml) was reacted with Hendrina FA (150 g) and aliquot samples were collected at pH 9.46, 10.3, 11.5 and 12.

The aliquot samples were filtered through 0.45 μm nucleopore membrane filter paper. The filtrate was analysed for cation by ICP-MS and ICP-AES and anions using IC. The possible mineral phases that precipitate at each pH end point were predicted by PHREEQC geochemical modeling.

3.4.6: Alkalinity and acidity determination

Alkalinity of mine water used in experiments was determined to gain an understanding of the acid neutralising potential. This parameter is very important for cation/anion balance in PHREEQC geochemical modeling. The alkalinity was determined by titrating circumneutral mine water (20 ml) with 0.1 M HCl to an end point of pH 4 (Eaton et al., 1995). The alkalinity was calculated as follows:

$$\text{ppm}(\text{HCO}_3^-) = \frac{1000 \times 61.02 \times V(\text{acid}) \times [\text{HCl}]}{V(\text{sample})} \text{ where, } V = \text{ml and } [] = \text{mol/L.}$$

Acidity was determined by titrating AMD (20 ml) sample that was pretreated with H_2O_2 with 0.1 M NaOH to an end point of 8.3. Pretreatment was done by adding 5 drops of H_2O_2 to the sample followed by heating for 5 mins and left to cool before titration. The acidity was calculated as follows:

$$\text{acidity}(\text{ppmCaCO}_3) = \frac{V(\text{NaOH}) \times [\text{NaOH}] \times 1000}{V(\text{sample})}, \text{ where } V = \text{ml and } [] = \text{mol/L.}$$

3.5: STEPWISE REMOVAL OF SULPHATES

Treatment of mine water with Hendrina FA has shown that SO_4^{2-} concentration can be reduced to between 1000-1400 ppm, which is above the required limit for domestic and industrial use category 4 of 0-400 ppm and 0-500 ppm respectively (DWAF, 1996; WISA, 2009). Smit and Sibilski (2003) have treated Stilfontein Gold mine water to meet the SO_4^{2-} requirements for domestic and industrial use by using lime followed by addition of $\text{Al}(\text{OH})_3$. The following experiments were motivated by the work of Smit and Sibilski, replacing lime with Hendrina FA.

3.5.1: Effect of gypsum seeding

The following experiments were performed to establish if it was possible to enhance SO_4^{2-} removal by introducing gypsum seeds after treatment of mine water with FA to pH 12. This initiates gypsum precipitation as the gypsum seed acts as nucleus sites for gypsum growth. The following steps were carried out in order to evaluate the effect of gypsum seeding on SO_4^{2-} removal:

1. SCMW (150 ml) was treated with FA (50 g) to pH 12.12.
2. SCMW (150 ml) was treated with FA (50 g) to pH 12.12 and gypsum (0.03 g) was added.
3. SCMW (150 ml) was treated with FA (50 g) to pH 12.12 and gypsum (0.06 g) was added.

After the above treatment of mine water the mixtures were filtered through 0.45 μm nucleopore membrane filter paper and analysed for elemental composition using ICP-MS, ICP-AES and IC.

3.5.2: Effect of gypsum seeding and $\text{Al}(\text{OH})_3$

SCMW (600 ml) as prepared in section 3.3.1 was first treated with Hendrina FA to pH greater than 12. The solid to liquid ratios used were 3:1 and 2:1 since these were the ratios that successfully raised the pH to greater than 12 (section 3.3.4). After the mixture reached a pH of greater than 12, gypsum seed (0.12 g) followed

by $\text{Al}(\text{OH})_3$ (0.4498 g) was added to mine water. The amount of gypsum seed added was based on results of the optimization performed in experiments as set out in the previous section 3.4.1. The optimum gypsum seed was 0.03 g for 150 ml of mine water for which translates to 0.12 g for 600 ml. The amount of $\text{Al}(\text{OH})_3$ that was added was calculated from the maximum amount of SO_4^{2-} that remained after treating mine water with FA using the solid/liquid ratio of 3:1 which is approximately 1400 ppm. The stoichiometry equivalent required to remove all 1400 ppm (0.015 M) of SO_4^{2-} from 600 ml of mine water with $\text{Al}(\text{OH})_3$ is 0.4498 g (Eq.2.4.20).

The lag time after adding gypsum but before adding $\text{Al}(\text{OH})_3$ was 75 mins. After adding $\text{Al}(\text{OH})_3$ aliquots were collected at 15, 60, 240, 720 and 1440 mins. The aliquots were filtered through a 0.45 μm nucleopore membrane filter paper and analyzed for anions by IC and for cations using ICP-MS AND ICP-AES.

3.5.3: Effect of $\text{Al}(\text{OH})_3$

Simulated CMW (600 ml) as prepared in section 3.3.1 was first treated with Hendrina FA to pH greater than 12. The two solid to liquid ratios used were 3:1 and 2:1. After the pH reached values greater than 12, $\text{Al}(\text{OH})_3$ (0.4498 g) was added to the SCMW/FA mixture. After adding $\text{Al}(\text{OH})_3$ aliquots were collected at 15, 60, 240, 720 and 1440 mins. The aliquots were filtered through a 0.45 μm nucleopore membrane filter paper and analysed for anions by IC and for cations by ICP-MS and ICP-AES.

3.6: pH REDUCTION OF THE PROCESS WATER

From the results obtained in the preceding experimental work it was found that the mine water treated by addition of Hendrina FA, followed by addition of $\text{Al}(\text{OH})_3$ conforms to the DWAF effluent limit except for the pH. The pH of the water was raised to 12, which was much higher than the required limit of 6-9

(DWAF, 1996, WHO, 2008). Carbonation of the alkaline process water was performed in order to reduce the pH to less than 9.

Process water (100 ml after filtration to remove FA) recovered after the treatment of mine water as described in section 3.4.3 was put in a 450 ml sealed reactor and connected to a CO₂ source. The valve was opened and the pressure of the reactor increased to 275.79 KPa with CO₂. After reaching this pressure the valve was closed and the water was stirred at 210 rpm for 10 mins at room temperature of 25 °C. After 10 mins the pressure dropped from 275.79 KPa to 206.842 KPa. The water was collected and the pH was measured. The white precipitates that formed were identified using FT-IR and the spectrum obtained was compared with that of pure CaCO₃.

3.7: ANALYTICAL TECHNIQUES

This section summarises the different instrumental techniques were used to elucidate the elemental and mineral composition of the water and solid residues before and after conducting different experiments as described in section 3.1 to 3.5.

3.7.1: pH meter

Hanna HI 991301 portable pH/EC/TDS/temperature pH meter was used to measure the progress of experiment by measuring pH, EC and TDS of the water. Before using this pH meter it was calibrated for pH using fresh buffers of pH 4 and 7 or 10.01 depending on the pH range being measured. EC was calibrated using an EC calibration solution with a conductivity of 12.88 ms/m.

3.7.2: Ion chromatography (IC)

Ion chromatography (IC) was used to analyse the changes in anion concentration during treatment of mine water with Hendrina FA. The samples were filtered through 0.45 μm nucleopore membrane filter paper and preserved at 4 °C until analysis was conducted. A Dionex DX-120 Ion Chromatograph with a AS40 automated sampler, ASRS- 300 suppresser, AS14 analytical column, AG14 guard column and a conductivity detector was used for the analysis. The eluant used was a mixture of 3.5 mM NaHCO_3 and 1.0 mM Na_2CO_3 .

3.7.3: Inductively coupled plasma (ICP)

Cation concentration was analysed using inductively coupled plasma atomic emission (ICP-AES) and mass spectrometry (ICP-MS) to follow the changes in the composition of mine water during treatment. Trace cations were analysed using Agilent 7500CE ICP-MS using a High Matrix Introduction (HMI) accessory and He as collision gas. Major cations were analysed using a Varian Radial ICP-AES. Both instruments were calibrated before analysis.

3.7.4: X-ray diffraction spectroscopy (XRD)

Qualitative XRD was performed to evaluate any mineralogical changes between the fresh Hendrina FA and the solid residues after mixing with mine water. This was performed using a Philips X-ray diffractometer and Cu-K_α radiation with a PW3011 (Miniprop) detector. The instrument settings are as shown in Table 3.6.

Table 3.5: XRD machine operating parameters

Radiation source	Cu-K α
Radiation wavelength (λ)	1.541
Voltage	40 kV
Current	25 mA
2 θ range	4° < 2 θ < 65°
Step size	0.02
Anti scatter slit	1°

The mineral phases were identified by search and match technique with the powder diffraction file data. This identification was complemented with Joint Committee of Powder Diffraction Standards (JCPDS) files for inorganic compounds.

3.7.5: X-ray fluorescence spectroscopy (XRF)

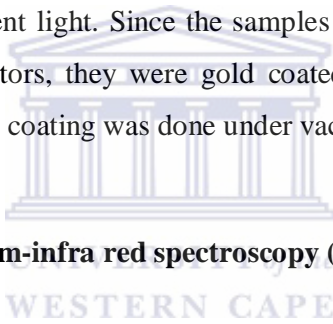
XRF was performed on fresh Hendrina FA and on solid residues recovered after treatment of SCMW to identify the elemental changes that occurred when FA was mixed with mine water. Preparation of samples for XRF analysis was done by mixing 9 g of FA or solid residues with 2 g of binder. The binder used is made up of 10 % C-wax and 90 % EMU powder. The mixture was then milled thoroughly and molded by pelletizing at a pressure of 15 tons for 1 minute using Dickie and Stockler binder. Samples were placed in a furnace at a temperature of 1000 °C for 45 minutes to measure loss on ignition (LOI).

The elemental composition of FA and solid residues were determined using a Philips PW1480 X-ray spectrometer. The spectrometer was fitted with Cr-tube and five analyzing crystals (LIF200, LIF220, GE, PE and PX). A combination of gas-flow proportional counter and scintillating detectors were used. The gas-flow proportional detector used P10 gas (mixture of 90 % Ar and 10 % CH₄). Major elements were analysed on a fixed glass bead at a voltage of 40 kV and current of 50 mA. Trace elements were analyzed on briquette tube at a voltage of 50 kV and

40 mA. Matrix effects were corrected by application of the theoretical alpha factors and measured line overlap factors to the raw intensities measured with SuperQ Philips software.

3.7.6: Scanning electron microscope (SEM)

Hendrina FA and solid residues from the SCMW treatment with FA followed by gypsum seeding and addition of $\text{Al}(\text{OH})_3$ were analysed using a HITACHI X-650 Scanning Electron Microanalyzer. The samples were prepared by fixing the samples on aluminum stubs using carbon adhesive. The carbon adhesive was attached to the top part of the aluminum stub and then the sample was sprinkled on the carbon adhesive with great precaution to avoid forming a thick layer that would absorb the incident light. Since the samples that were analysed were poor electromagnetic conductors, they were gold coated using argon gas on Sputter Coater S150B. The gold coating was done under vacuum.



3.7.7: Fourier transform-infra red spectroscopy (FT-IR)

Solid residues obtained during the carbonation of the process water to reduce the pH were analyzed using Fourier transform-Infra red (FT-IR) spectroscopy. The spectrum of the solid residue was compared with a pure CaCO_3 sample. A Perkin Elmer Spectrum 100 FT-IR spectrometer was used for the analysis. The resolution was set at 4 cm^{-1} .

3.7.8: Geochemical modelling

3.7.8.1: Aq.QA

Mine water classification was done using the Aq.QA software. This software classifies mine water according to the abundance of the cations (Mg, Ca, K, Na, etc) and anions (SO_4^{2-} , Cl, HCO_3^-) present in the water. The programme generates the water type depending on these abundances. The software generates a graphical representation of the

input data in the form of Piper diagrams, Stiff, Radial and pie plots. The type of plot depends on what you want to show or explain.

3.7.8.2: PHREEQC modelling

XRD identified crystalline mineral phases and PHREEQC geochemical modeling was done in order to predict the minerals that may precipitate from a solution during the treatment under different conditions. PHREEQC for windows geochemical modeling software (Parkhurst and Appelo, 1999) and WATEQ4F database were used to calculate saturation indices (SI) at different final pH values. The WATEQ4F database was edited to include the thermodynamic parameters of ettringite as calculated by Perkins and Palmer (1999). All the Fe concentration was assumed to be Fe³⁺ thus redox reactions were eliminated from the modeling equilibrium calculation. The redox potential ($\rho\varepsilon = 4$) was used for all the equilibrium calculation. The SI was calculated as follows:

$SI = \log \frac{IAP}{K_{sp}}$, where IAP is the ion activity product and K_{sp} is the solubility product.

If the $SI \geq 0$ then that particular mineral is supersaturated or saturated and is likely to precipitate. If the $SI \leq 0$ the mineral phase is under saturated and will not precipitate (Appelo and Postma, 2007).

CHAPTER 4 : RESULTS AND DISCUSSION

4.1: INTRODUCTION

In this chapter the results obtained from the experimental work conducted as explained in the previous chapter are presented and discussed. This chapter is focused on explaining the following parameters: the effect of the final pH achieved during treatment of coal mine water; the effect of the initial pH of the mine water; the effect of the amount of FA; and the effect of Fe and Al in mine water on SO_4^{2-} removal from mine water. The behaviour of other elements such as Fe, Al, Mn, Mg and some of the trace elements during treatment of mine water with FA is highlighted and explained in this chapter.

4.2: CHARACTERIZATION OF FLY ASH

Fresh fly ash (FA) used for the neutralisation of mine water was collected from the ash hoppers at Hendrina power station. The FA was characterized by XRD, XRF and SEM using conditions set out in sections 3.7.4, 3.7.5 and 3.7.6. The characterization was done in order to determine the composition of the fresh FA. Comparing the composition of the FA recovered after mixing with mine water with that of fresh FA will help to gain an understanding of the chemical reactions that took place during treatment of mine water with FA.

SEM images showed that Hendrina FA is typically composed of irregular and numerous spherical shaped particles having an average diameter of less than 10 μm (Figure 4.1).

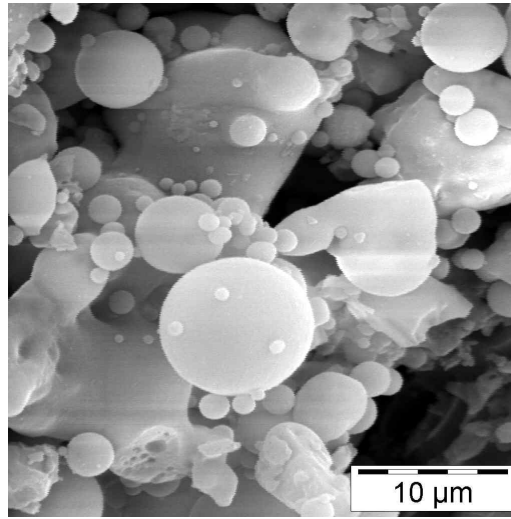


Figure 4.1: Scanning electron microscope of Hendrina FA (x 2000 magnification).

FA composition was analysed using XRD and the results obtained are as depicted in Figure 4.2. Hendrina FA was found to be a heterogeneous material composed of crystalline phases; mullite ($3\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$), quartz (SiO_2), hematite (Fe_2O_3) and lime (CaO).

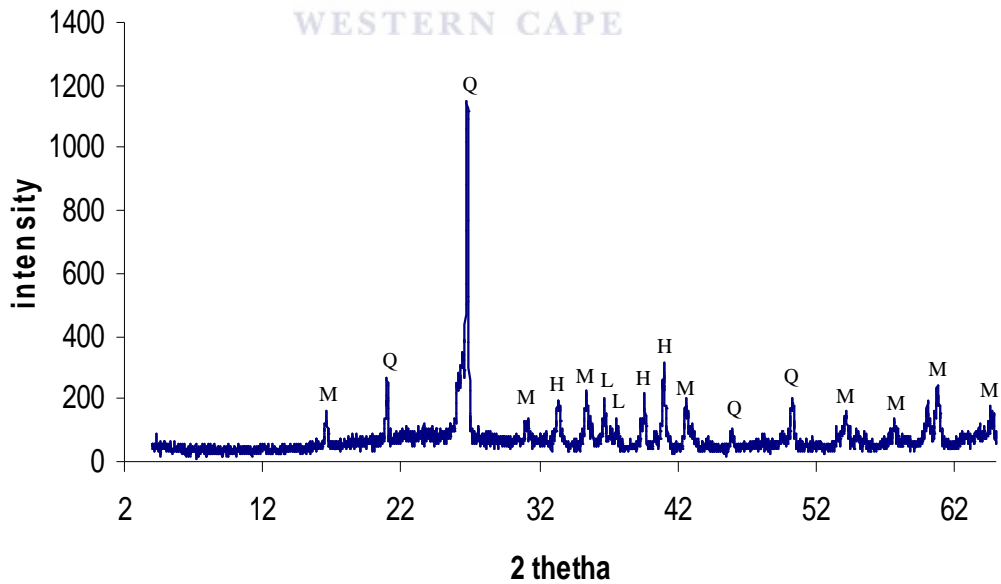


Figure 4.2: XRD spectrum for Hendrina FA (M-mullite, Q-quartz, H hematite and L-lime)

The presence of these minerals in FA was as a result of the thermal transformation during the combustion process of minerals found in the parent coal. Clay minerals such as kaolinite and illite were transformed to mullite, hematite was a product of oxidation of pyrite and marcasite, lime was formed due to the oxidation of clays and the quartz phase remained unchanged in the combustion cycle (Mattigod et al., 1990; Martinez-Tarazona and Spears, 1996).

The elemental composition of Hendrina FA was determined using XRF and the results are shown in Table 4.1.

Table 4.1: Elemental composition of Hendrina FA

Major elements		Minor elements	
species	% w/w composition	Element	Concentration (ppm)
SiO ₂	54.01 ± 0.28	Sr	1265.68 ± 8.43
Al ₂ O ₃	29.01 ± 0.13	Zr	806.41 ± 2.57
Fe ₂ O ₃	3.99 ± 0.07	V	380.91 ± 1.00
MnO	0.04 ± 0.001	Ce	274.69 ± 6.32
MgO	1.12 ± 0.03	Ba	219.69 ± 7.06
CaO	4.63 ± 0.09	Pb	111.58 ± 3.17
Na ₂ O	0.14 ± 0.01	Zn	101.37 ± 2.61
K ₂ O	0.78 ± 0.01	Y	84.82 ± 2.25
P ₂ O ₅	0.54 ± 0.02	Cu	73.66 ± 1.90
TiO ₂	1.79 ± 0.03	Ni	69.38 ± 2.42
SO ₃	0.24 ± 0.01	Rb	45.34 ± 0.29
Loss of ignition	3.70 ± 0.53	Nb	35.58 ± 2.94
Total	99.99	Co	34.51 ± 3.19
		Mo	6.44 ± 0.358
		As	3.04 ± 0.93

Number of samples analyzed = 4, results reported as mean ± SD

From the XRF data, Hendrina FA is a ferroaluminosilicate because it is made up of mainly Fe, Al and Si. Hendrina FA can be classified as class F using the American Society for Testing and Measurement (ASTM C618) classification which states that the sum of; SiO₂ + Al₂O₃ + Fe₂O₃ > 70 % for class F FA. Class F FA is formed during the combustion of either bituminous or anthracitic type of coal (Mattigod et al., 1990).

Trace elements found in Hendrina FA by XRF are shown in Table 4.2.1. The concentration of the trace elements in Hendrina FA is orders of magnitude greater than the concentration usually found in coal (Martinez-Tarazona and Spears, 1996). This is because coal is made up of about 60-70% combustible material and 20-40 % incombustible inorganic material (Pinetown et al., 2007). These incombustible materials include the trace elements that get concentrated during the combustion cycle since the combustible material is burnt away during the process.

4.3: CHARACTERIZATION OF MINE WATER

The mine waters used in this study were characterized for elemental composition, alkalinity and acidity. Comparing the composition of the mine water after treatment with Hendrina FA, of known composition (section 4.2) helped to gain an understanding of the chemical reactions that bring about the changes observed.

The characteristics of Middleburg and Navigation mine waters are shown in Table 4.2. Mine water from Middleburg coal mine has a circumneutral pH and the chemical composition is mainly Ca, Mg and SO_4^{2-} . It also contains substantial amounts of Mn. Navigation coal mine water is acidic and contains substantial amounts of Fe, Al and Mn. The SO_4^{2-} content is far much greater than Middleburg coal mine water. The acidity of Navigation mine water was found to be much greater than that of Middleburg mine water. This is because of the high concentration of Fe, Al and Mn (which produce protons during the formation of their respective hydroxides) in Navigation mine water compared to Middleburg mine water (Younger et al., 2002). The reactions in which protons are formed are as follows:



Table 4.2: Composition of water from Middleburg and Navigation coal mines

	Middleburg coal mine water	Navigation coal mine water
element	concentration (ppm)	concentration (ppm)
pH	6.50 ± 0.49	2.48 ± 0.06
EC (ms/m)	5.02 ± 0.16	13.98 ± 0.20
Acidity	0	14958
alkalinity	106.78	0
Ca	537.55 ± 2.87	598.73 ± 16.87
Mg	861.77 ± 15.51	398.90 ± 33.28
K	29.19 ± 0.014	34.16 ± 1.4
Mn	24.96 ± 0.085	88.22 ± 7.27
Na	20.12 ± 0.036	70.48 ± 5.33
Fe	0.07 ± 0.0062	8158.20 ± 42.13
Al	0.016 ± 0.00071	473.95 ± 12
Sr	1.81 ± 0.033	1.02 ± 0.000072
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 ± 0.000035	ND
SO ₄ ²⁻	4603 ± 28.28	42 862 ± 92.19
Cl	115 ± 8.49	9.80 ± 0.26
NO ₃ ⁻	35.69 ± 0.014	8.01 ± 0.13
PO ₄ ³⁻	1.55 ± 0.071	167 ± 18.21
F	0.79 ± 0.014	1.75 ± 0.0028

Number of samples analyzed = 3, results reported as mean ± SD ND: not detected, concentrations of elements are ppm except pH and EC.

The fluid properties obtained using the Aq.QA software (Figure 4.3) shows that the Middleburg and Navigation mine waters are of Mg-SO₄²⁻ and Fe-SO₄²⁻ types

respectively. The conductivity of Navigation mine water is orders of magnitude higher than that of Middleburg mine water. This is because Navigation mine water contains an abundance of dissolved salts in comparison with Middleburg mine water which is much less contaminated. On the other hand Middleburg mine water has more hardness than Navigation mine water because of the high concentration of Ca and Mg ions. Total hardness is proportional to the concentration of Ca and Mg and is calculated as follows (DWAF, 1996):

$$\text{Total hardness ppm}(\text{CaCO}_3) = 2.497 \times \text{ppm}(\text{Ca}) + 4.118 \times \text{ppm}(\text{Mg})$$

Fluid Properties

Middleburg Water Type Mg-SO ₄		Navigation Water Type Fe-SO ₄	
Dissolved Solids	3.36 mg/L Measured	Dissolved Solids	7.6772 mg/L Measured
Density	0.99703 g/cm ³ Calculated	Density	0.99704 g/cm ³ Calculated
Conductivity	0.61 μmho/cm Measured	Conductivity	139.8 μmho/cm Measured
Hardness (as CaCO₃)		Hardness (as CaCO₃)	
Total	4899.8 mg/kg 4885.3 mg/L Calculated	Total	3137.7 mg/kg 3128.4 mg/L Calculated

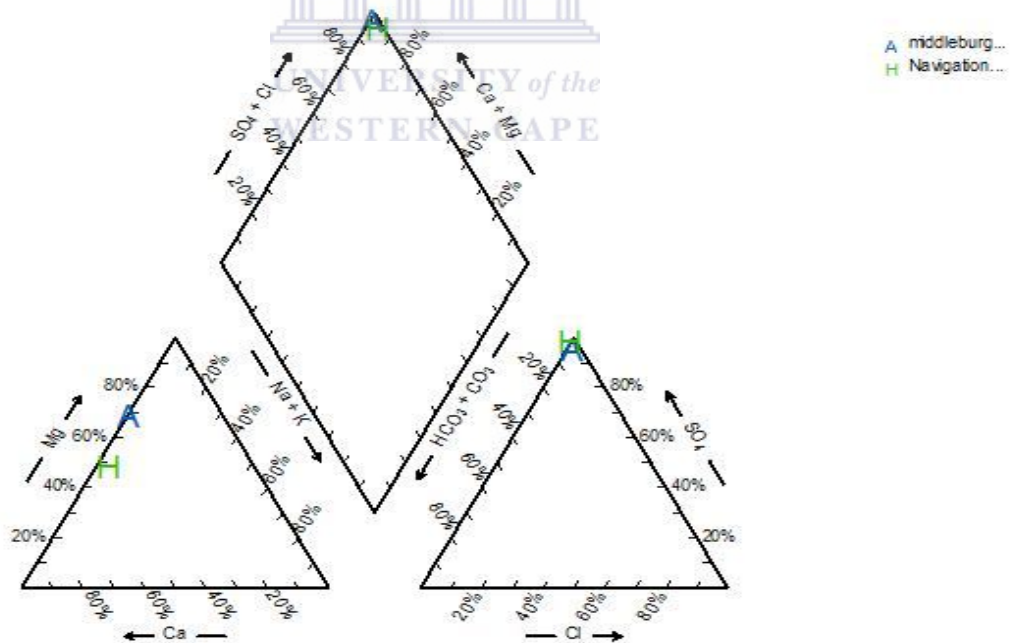
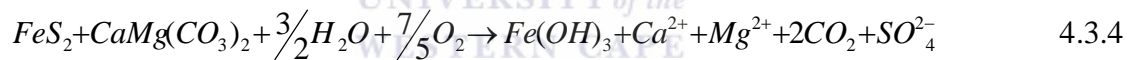


Figure 4.3: Piper diagram showing the % distribution of major cations and anions of Navigation and Middleburg coal mine waters modelled using Rockware Aq.QA software.

The type of water generated in a mine depends on the geology of the bedrock in the coal mine. Middleburg mine is situated in a dolomitic/pyritic geology while Navigation coal mine is found in pyritic dominated geology. Navigation coal mine water is highly acidic as a result of oxidation of pyrite and dolomite weathering. Navigation mine water has substantial amounts of Ca and Mg because of the dolomite composition of the surrounding rocks, but the pyrite phase is far more abundant than the dolomite phase resulting in AMD formation. The alkalinity produced during weathering of dolomite is not sufficient to neutralise the acidity generated by pyrite oxidation (Section 2.3.1).

Middleburg mine water results from the oxidation of the pyrite associated with the coal followed by dolomite dissolution resulting in CMW. At the circumneutral pH Al and Fe precipitate out as hydroxides (Uhlman et al., 2004; Jenke and Gordon, 1983). In addition the weathering of dolomite causes elevated concentrations of Ca and Mg resulting in high value of total water hardness obtained by Aq.Qa software (Eq 4.3.4).



Some of the SO_4^{2-} may be removed from the mine water due to precipitation of gypsum over time. More SO_4^{2-} is also removed through precipitation of complexes of oxyhydroxysulphate phases such as alunite ($KAl_3(SO_4)_2(OH)_6$), basaluminite ($Al_4(OH)_{10}SO_4$), jurbanite ($AlOHSO_4$), jarosite-ss ($K_{0.77}Na_{0.03}H_{0.2}Fe_3(SO_4)_2(OH)_6$), jarosite-K ($KFe_3(SO_4)_2(OH)_6$), jarosite-Na ($NaFe_3(SO_4)_2(OH)_6$) and jarosite-H ($H_3OFe_3(SO_4)_2(OH)_6$) (Seth and Ghazi, 1997).

The composition of the simulated mine water (SCMW) used in this study was formulated (section 3.4.1) to be comparable to the real mine water in many aspects as presented in Table 4.3. Simulated AMD containing Fe and Al (Fe-AMD and Al-AMD) separately were also prepared (Table 4.3.2). Simulated AMD was made so that the

SO₄²⁻ composition approximates the amount in CMW and the Fe:SO₄²⁻ and Al:SO₄²⁻ in the ratio of 2:1 and 12:1 respectively. This was done in order to have similar ratios as those typically found in South African AMD waters (Gitari et al., 2006; Gitari et al., 2008).

Table 4.3: Composition of simulated AMD containing Fe (Fe-AMD), simulated AMD containing Al (Al-AMD) and SCMW

	Fe-AMD	Al-AMD	SCMW
pH	2.49 ± 0.01	1.54 ± 0.03	6.57 ± 0.021
EC(ms/m)	6.43 ± 0.11	14.56 ± 1.02	5.61 ± 0.013
Ca	140.17 ± 3.15	138.27 ± 2.42	572.98 ± 1.201
Mg	207.21 ± 4.53	213.01 ± 5.72	846.98 ± 12.15
K	38.14 ± 0.47	40.05 ± 0.31	34.16 ± 0.034
Mn	30.21 ± 2.18	29.12 ± 1.73	27.09 ± 1.47
Na	30.64 ± 2.12	35.77 ± 1.91	23.66 ± 0.23
Fe	1795 ± 156	3.50 ± 0.01	0.86 ± 0.0036
Al	0.28 ± 0.03	384.21 ± 12.78	0.13 ± 0.00021
Sr	0.54 ± 0.02	0.50 ± 0.003	1.37 ± 0.03
Co	0.13 ± 0.003	ND	ND
Ni	0.67 ± 0.004	ND	ND
Zn	7.45 ± 0.061	0.36 ± 0.0012	ND
B	0.19 ± 0.001	0.056 ±	ND
Mo	0.0025 ± 0.0003	0.031 ± 0.0013	ND
Ba	0.030 ± 0.002	0.023 ± 0.0032	ND
SO ₄ ²⁻	4598.31 ± 21.15	4655.24 ± 16.73	4623 ± 11.13
Cl ⁻	85.24 ± 4.64	82.62 ± 2.57	82.28 ± 0.814
NO ₃ ⁻	46.18 ± 3.21	48.24 ± 1.12	43.4 ± 0.1508

ND: not detected, concentrations of elements are in ppm except pH and EC
 SCMW: simulated circumneutral mine water

SCMW contained more Ca and Mg than Fe-AMD and Al-AMD because the low masses of CaSO₄ and MgSO₄·7H₂O were added in order for the SO₄²⁻ concentration to be equal. The pH of the Fe-AMD was 2.49. This could be due to the oxidation of Fe²⁺

to Fe^{3+} and subsequent precipitation of some of Fe^{3+} as $\text{Fe}(\text{OH})_3$ that generated protons (Eqs. 2.3.2 and 2.3.3). Precipitation of some of the Fe as $\text{Fe}(\text{OH})_3$ resulted in the concentration of Fe (1795 ppm) being less than the expected 2000 ppm (Table 4.3.2). The pH of Al-AMD was 1.54 because of the 1.5 ml of 5M H_2SO_4 that was added during its preparation to reduce the pH of the water to prevent $\text{Al}(\text{OH})_3$ precipitation before the experiment (section 3.4.1).

4.4: EFFECT OF THE FINAL pH

The experiment was conducted to evaluate the effect of the final pH on SO_4^{2-} removal. Simulated CMW was treated with Hendrina FA (L/S=2:1) to different final pH values as described in section 3.4.2. Treatment of SCMW with Hendrina FA to pH 8.98, 9.88, 10.21, 10.96, 11.77 and 12.35 resulted in 6, 19, 37, 45, 63 and 71 % of SO_4^{2-} removed from SCMW respectively (Figure 4.4).

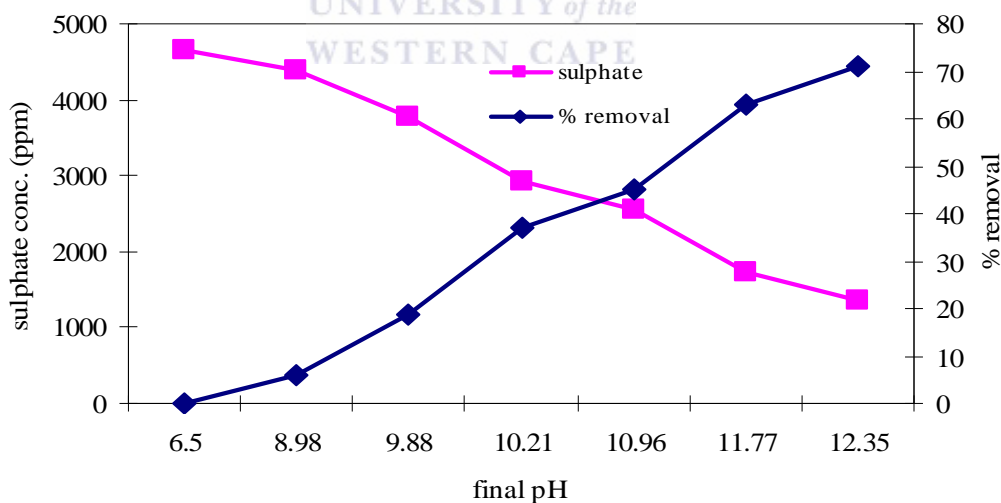


Figure 4.4: Percentage SO_4^{2-} removal and SO_4^{2-} concentration of SCMW treated to various final pH values.

These results in Figure 4.4 show that the amount of SO_4^{2-} removed from the mine water depended on the final pH achieved during treatment of SCMW.

The elemental composition of the solid residues recovered from the reaction at various pH end points were determined using XRF (Table 4.4) in order to compare the solid residues composition with that of fresh FA. Comparing the elemental composition of the fresh Hendrina FA and solid residues shows that % SO_3 increased in the solid residues recovered after the experiments at different final pH end points. This correlates perfectly with the anion results obtained by IC analysis of the process water recovered at each pH end point which showed a decrease in the SO_4^{2-} concentration of the water as the final pH end point was increased (Figure 4.4).

Table 4.4: Elemental composition of Hendrina FA and solid residues recovered at different pH end points

Oxide	Hendrina % w/w	pH 9.88 % w/w	pH 10.21 % w/w	pH 11.77 % w/w	pH 12.34 % w/w
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

LOI: loss on ignition

The XRD spectrum of fresh Hendrina FA was compared to that of the solid residues recovered after the treatment of SCMW with Hendrina FA to pH 12.35 (Figure 4.5). This was done in order to determine whether formation of any new mineral phase was responsible for SO_4^{2-} removal.

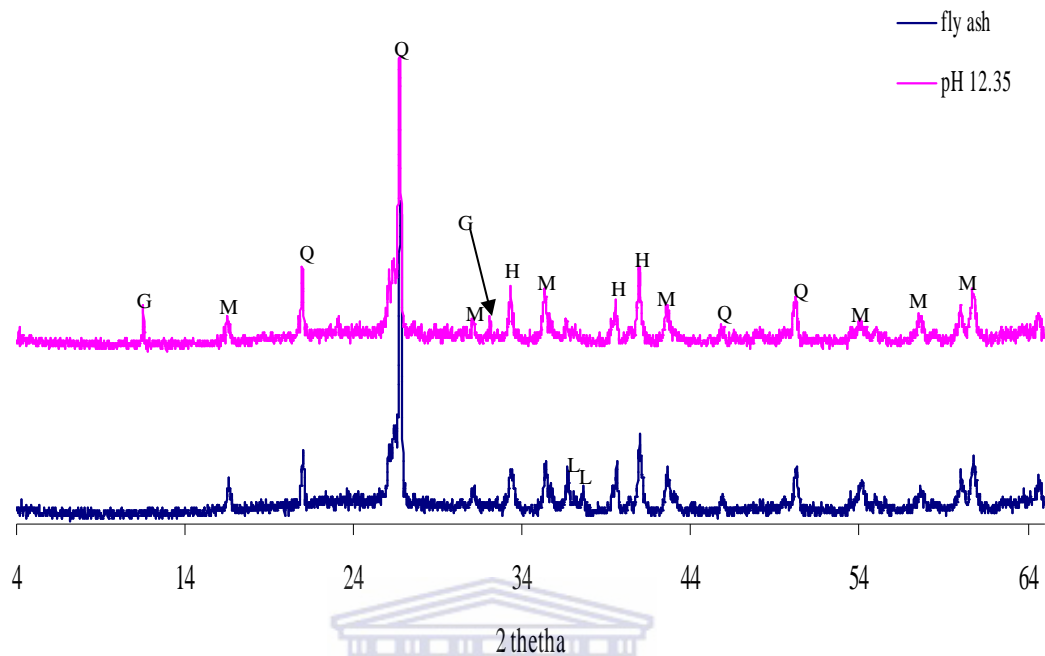


Figure 4.5: XRD spectra of Hendrina FA and solid residues at pH 12.35 (G-gypsum, M-mullite, H-hematite, L-lime and Q-quartz).

The spectrum of the solid residue collected at pH 12.35 showed the development of gypsum phase in the solid residue confirming the increase in the % SO_3 in the solid residue in Table 4.4 and the decrease in the SO_4^{2-} concentration in the treated water.

Changes in the concentration of Ca, Mg and Mn in SCMW were followed by analysing the process water by ICP-AES after treatment with Hendrina FA to various pH end points (Figure 4.6). The results obtained show that Ca concentration increased as the pH end point was increased, while the concentration of Mn and Mg dropped to below the DWAF limit for potable water at pH end point greater than 9 and 11 respectively. The DWAF limit for Mn is 0.05 ppm and for Mg is 30 ppm (DWAF, 1996).

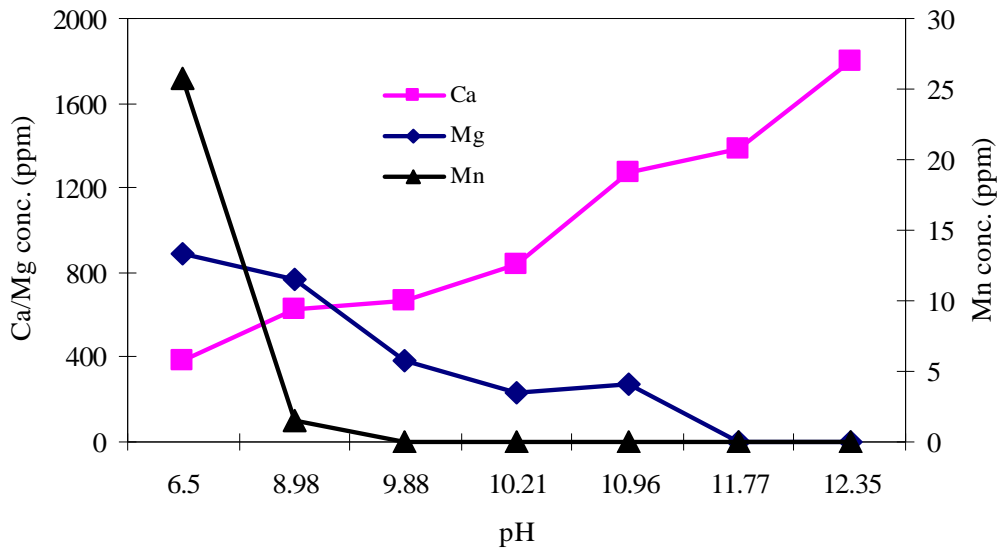


Figure 4.6: Ca, Mg and Mn concentrations at various pH end points during treatment of SCMW with Hendrina FA.

During treatment of SCMW with Hendrina FA to various pH end points the free lime in FA dissolves into solution thereby causing the pH of the water to increase (Eq. 4.4.1). This is shown in the XRD data presented in Figure 4.5 where the lime peaks disappeared from the spectrum of FA and the new gypsum peak appeared in the solid residues recovered at pH 12.35. More lime is leached into the mine water for the pH to increase from 6.5 to 12.35 than for the pH to increase from 6.5 to 8.98. This caused the Ca^{2+} concentration to increase equivalently (Figure 4.4.3), thereby shifting the equilibrium of reaction 4.4.2 to the right according to Le Chatelier's principle, hence more gypsum precipitated and more SO_4^{2-} is removed in the process.



Results obtained in this set of experiments showed that Mn and Mg ions are removed to below DWAF limit for potable water when SCMW is treated to pH 9 and 12 respectively (Fig 4.6). The minerals phases contributing to Mn and Mg removal could not be detected by XRD due to their amorphous nature or due to the dilution by the

prominent peaks of quartz and mullite. PHREEQC modelling was performed on SCMW to calculate the saturation indices (SI) of the mineral phases at different pH end points. If the $SI < 0$ then that particular mineral phase was under saturated could not precipitate at those experimental conditions. If a $SI \geq 0$ then that mineral was saturated or supersaturated and could precipitate at those experimental conditions (Appelo and Postma, 2005).

The SI calculated by PHREEQC showed that Mn bearing mineral phases such as birnessite (MnO_2), bixbyite (Mn_2O_3), hausmannite (Mn_3O_4), manganite ($MnOOH$), nsutite (MnO_2), pyrochroite and $(Mn(OH)_2)$ pyrolusite (MnO_2) could be responsible for Mn removal from SCMW (Figure 4.7). For Mg the mineral phase predicted to form was only brucite ($Mg(OH)_2$) (Figure 4.8).

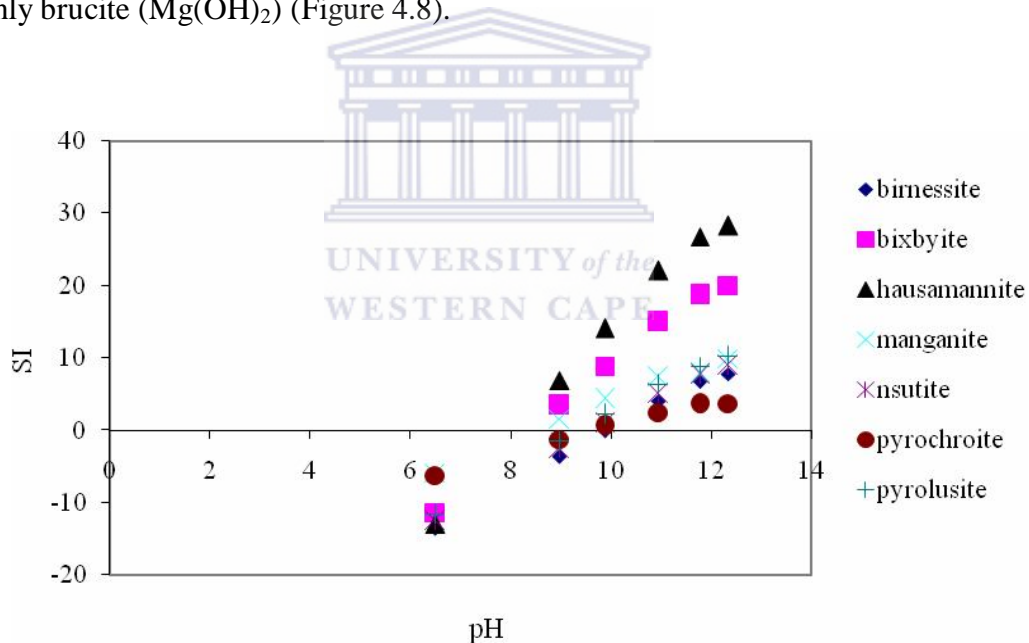


Figure 4.7: SI of Mn bearing mineral phases predicted using PHREEQC geochemical model at various pH end points

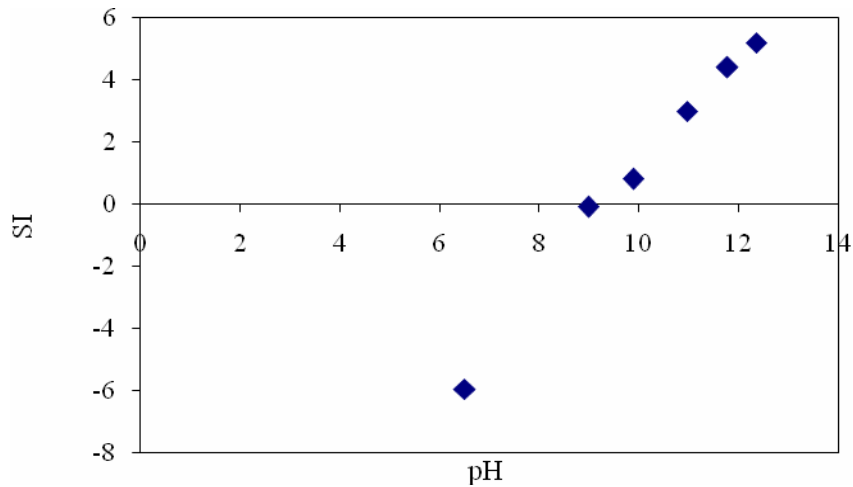


Figure 4.8: SI of brucite calculated using PHREEQC geochemical model at various pH end points

Manganese mineral phases were predicted to start precipitating at pH 8.98 were bixbyite, hausmannite and manganite, while birnissite, nsutite, pyrochroite and pyrolusite were predicted to start precipitating at pH 9.88. The Mg bearing mineral phase brucite was predicted to start precipitating at pH 9.88. This correlates well with the results obtained from ICP-MS as given in Figure 4.6 as there is a sharp decrease of Mn and Mg concentration at pH 6.5-9 and 9-11 respectively corresponding well with the SI predicted by PHREEQC.

4.5: EFFECT OF THE INITIAL pH

The pH of the SCMW was adjusted to pH 2.3 and 3.66 as outlined in section 3.4.3. These two modified mine waters with pH values of 2.3 and 3.66 together with unmodified SCMW were treated to various pH end points using Hendrina FA. The results showed that if the final pH of the process water was the same, the initial pH of

the water has no major effect on the SO_4^{2-} removed during treatment with FA (Figure 4.9).

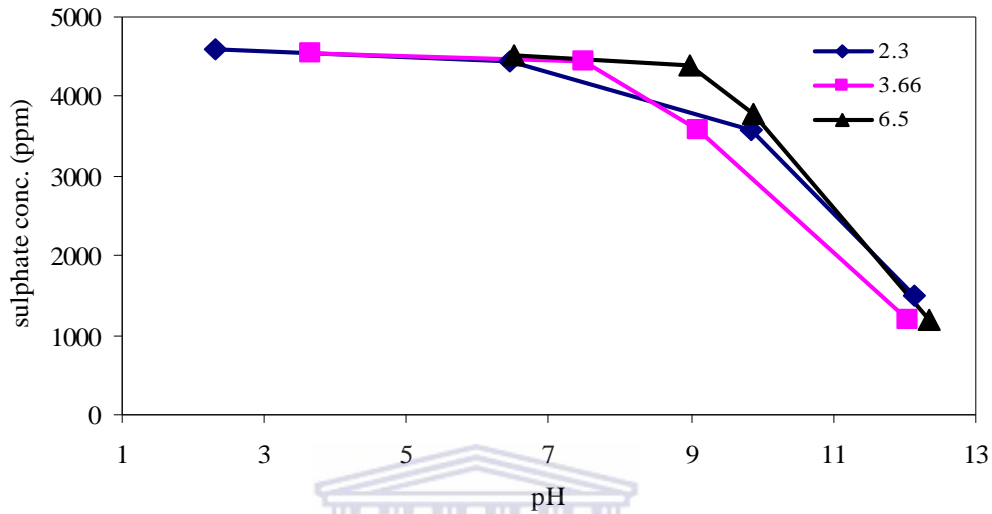


Figure 4.9: SO_4^{2-} concentration of simulated mine waters with different starting pH treated to various pH end points using Hendrina FA.

Theoretically for the pH to increase from 2.3 to 6.5, the concentration of H^+ decreases from $10^{-2.3}$ to $10^{-6.5}$ mol/L by neutralization according to Equation 4.5.1.



This means that 5.013×10^{-3} mol/L of H^+ must be consumed for the pH to increase from 2.3 to 6.5. From the mole ratio in equation 4.5.1, this means 2.506×10^{-3} moles of CaO will react to form 2.506×10^{-3} moles of Ca^{2+} . According to the gypsum formation reaction (Eq.4.4.2) this is the amount of Ca^{2+} that comes into solution from the dissolution of FA and reacts with 2.506×10^{-3} mol/L of SO_4^{2-} to form gypsum. This translates to:

$$2.506 \times 10^{-3} \times 96.06 \times 1000 = 241 \text{ ppm of } \text{SO}_4^{2-} \text{ removed.}$$

Theoretically the percentage SO_4^{2-} removal by starting from pH 2.3 rather than 6.5 is:

$$\frac{241}{4597} \times 100 \approx 5\%$$

The observed percentage removal of SO_4^{2-} when pH was increased from 2.3 to 6.45 was 4 %, which correlates well with the theoretical value.

4.6: EFFECT OF THE AMOUNT OF FA

Simulated circumneutral mine water (SCMW) was mixed with different amounts of Hendrina FA for 24 hrs as outlined in section 3.4.4. When large amount of FA was added to SCMW more SO_4^{2-} was removed as shown in Figure 4.10 and Figure 4.11. The SO_4^{2-} concentration was reduced from 4655 ppm to 2099, 1850, 1385 and 1185 ppm when SCMW:FA ratios of 5:1, 4:1, 3:1 and 2:1 were used respectively.

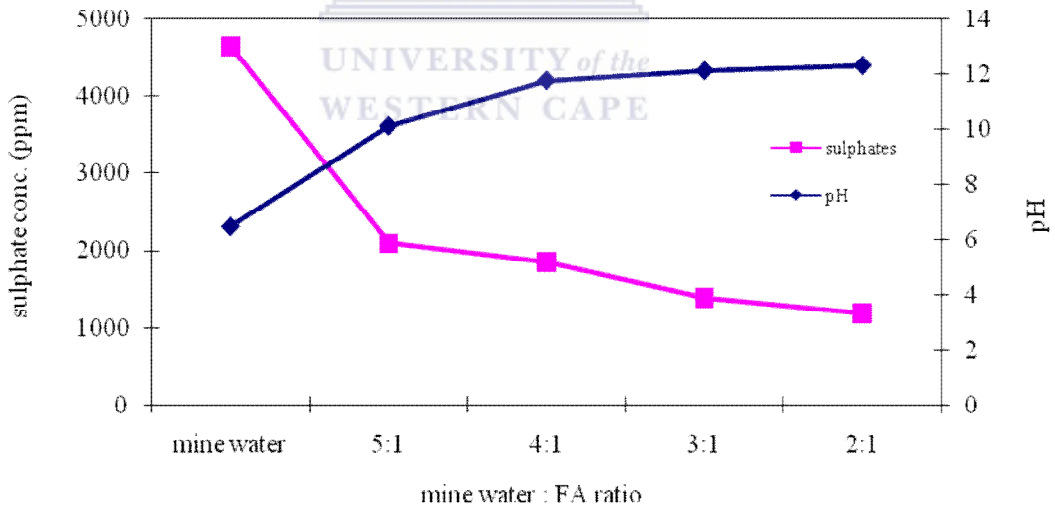


Figure 4.10: SO_4^{2-} concentration and final pH after treatment of SCMW with different amounts of Hendrina FA for 24 hrs.

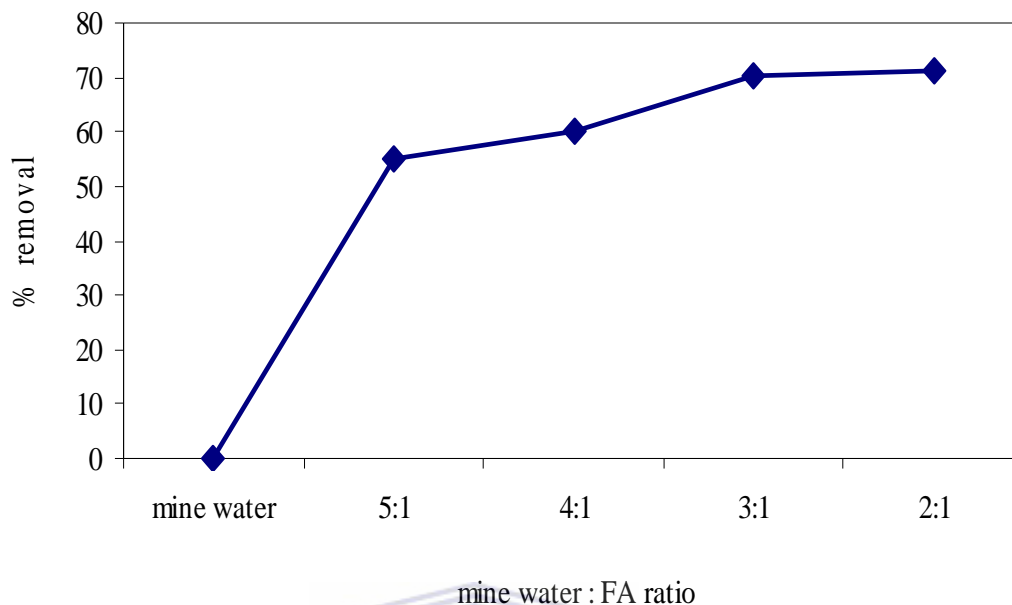


Figure 4.11: % SO_4^{2-} removal when different amounts of Hendrina FA were reacted with SCMW for 24 hrs.

For 5:1 ratio of SCMW:FA, 55 % SO_4^{2-} removal was attained while for 2:1 ratio 71 % SO_4^{2-} removal was attained (Figure 4.11). The maximum attained pH was a function of the amount of FA added (Figure 4.10). The maximum attained pH for ratios 5:1, 4:1, 3:1 and 2:1 were 10.13, 11.77, 12.12 and 12.31 respectively. This is because as more FA was added more CaO was available to neutralise the SCMW and hence more Ca^{2+} ions to cause equation 4.4.2 to shift to the right according to Le Chatelier's principle and hence more SO_4^{2-} could be removed as gypsum (Figure 4.5).

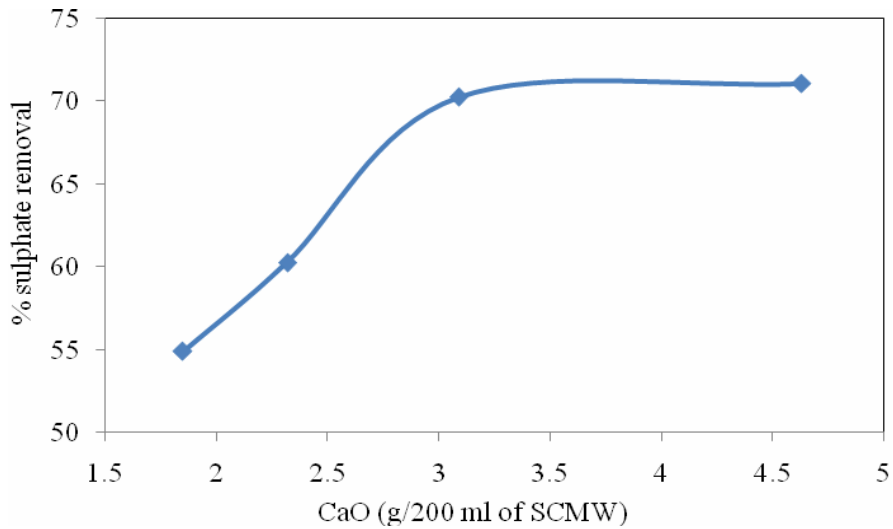


Figure 4.12: % sulphate removal as function of the amount of lime added in form of Hendrina FA.

From the results obtained, it can be concluded that the amount of FA added to the mine water has a great effect on the amount of SO_4^{2-} that can be removed from the water. The SO_4^{2-} removal from SCMW was directly related to the dissolution of available free CaO on the FA particles up to 3.09 g of CaO per 200 ml of SCMW thereafter the removal was constant (Figure 4.12). The mass of available free CaO was calculated using the % w/w of CaO (Table 4.4) from the mass of Hendrina FA added for each SCMW:FA ratio. The optimum ratio for treatment of SCMW with Hendrina FA was found to be approximately 3:1 which resulted in 70 % SO_4^{2-} removal. Adding more FA (2:1 ratio) resulted in 71 % SO_4^{2-} removal which is 1 % greater than the 3:1 ratio.

4.7: EFFECT OF Fe AND Al

The following set of experiments was done in order to compare the chemistry of the treatment of Al and Fe AMD rich with treatment of SCMW which is Fe and Al free with FA. The first set of experiments was done using Navigation AMD as the source of Fe and Al added to SCMW. The two waters, SCMW and Navigation AMD were

mixed together in four different ways (SCMW:AMD); 1:0, 1:1, 2:1 and 3:1 as outlined in section 3.4.5.1

The second set of experiments was done with three different simulated mine waters; SCMW, Fe-AMD and Al-AMD. The preparation of these solutions was described in section 3.4.1 and the compositions of the solutions are presented in Table 4.3. All the three simulated mine waters had approximately the same starting concentration of SO_4^{2-} in order to draw a conclusive understanding of the first set of experiments which started with different concentrations of SO_4^{2-} depending on the ratio of SCMW and Navigation AMD.

4.7.1: Navigation as the source of Fe and Al

The 1:0, 1:1, 2:1 and 3:1 SCMW and Navigation AMD mixtures had pH values of 6.5, 2.3, 2.65 and 2.63 before adding FA respectively. The mixtures were treated with Hendrina FA as outlined in section 3.4.5.1 and the pH profiles over time of different mixtures are as shown in Figure 4.13.

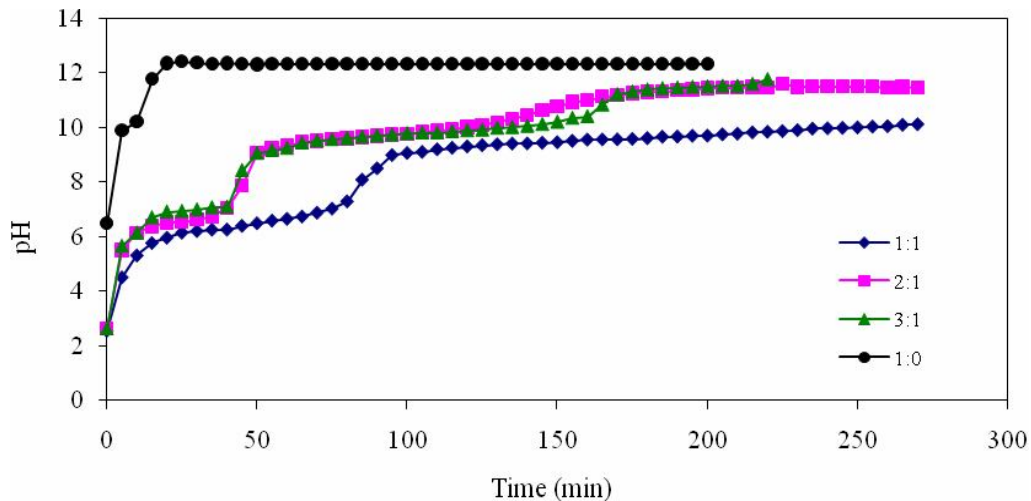


Figure 4.13: pH profiles during treatment of different SCMW:AMD ratios with Hendrina FA.

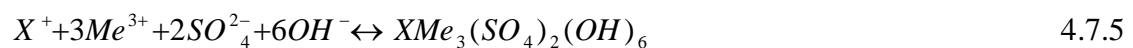
As Figure 4.13 shows, the treatment of SCMW with Hendrina FA resulted in a rapid change in pH from 6.5 to 12.35 with a slight buffering plateau at pH 10, which was not as pronounced compared to SCMW/AMD treatment profiles. The buffering plateau at pH 10 is ascribed to the hydrolysis of Mn^{2+} (Eq.4.4.71) and oxidation and precipitation of Mn^{2+} (Eq.4.7.2) (Younger et al., 2002). The Mn^{2+} concentration is higher in SCMW/AMD mixtures than in SCMW resulting in a more pronounced buffer plateau at pH 10.



The profiles for the 3:1, 2:1 and 1:1 mixtures show gradual changes in pH with multiple buffering plateaus. Presence of Fe and Al introduced into SCMW from AMD caused pH buffering at pH 6-6.5. The buffering at pH 6 is caused by the hydrolysis reactions (Eq 4.7.3 to 4.7.4). The precipitation of $Fe(OH)_3$, $Fe(OH)_2$ and $Al(OH)_3$ occurs at pH 4-7 (Uhlman et al, 2004 and Jenke and Gordon, 1983).



The precipitation of oxyhydroxysulphates consumes alkalinity thereby causing pH buffering according to equation 4.7.5, 4.7.6 and 4.7.7. The precipitation of the oxyhydroxysulphates occurs at pH 4-9 (Younger et al., 2002).



where X can be K , Na or H_3O^+ and Me is either Al or Fe .



Sulphate removal as function of pH for different SCMW:AMD mixtures is shown in Figure 4.14.

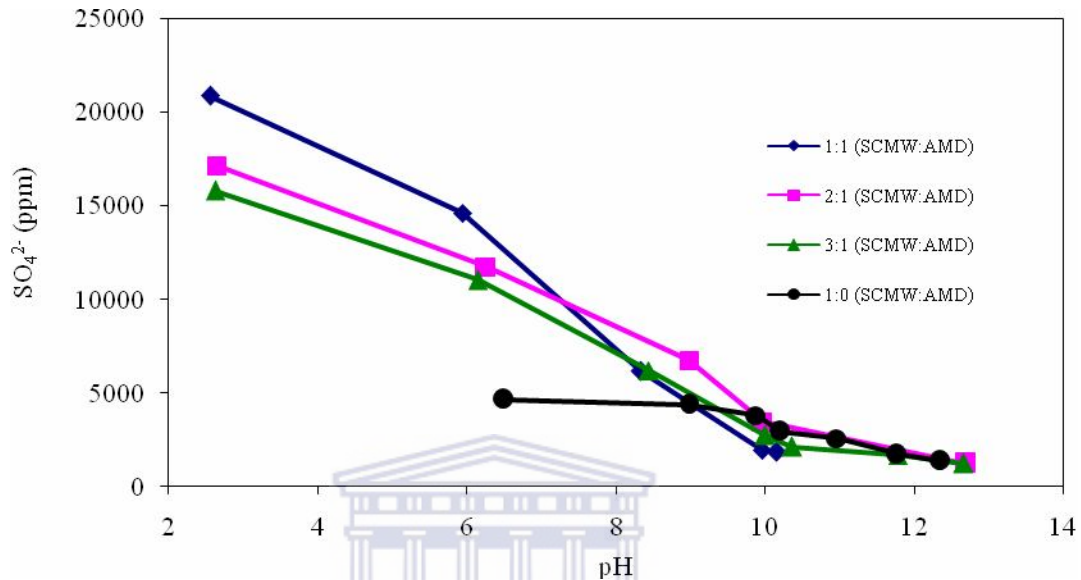


Figure 4.14: SO₄²⁻ concentration during treatment SCMW and different SCMW:AMD ratios with Hendrina FA.

Sulphate concentration for the SCMW (1:0 mixture) was reduced from 4655 ppm to 4381 ppm when SCMW was treated with Hendrina FA to pH 10, which is approximately 19 % SO₄²⁻ removal. In the case of the mixtures; the SO₄²⁻ concentration of 3:1 SCMW:AMD mixture was reduced from 15797 ppm to 2731 ppm, for 2:1 SCMW:AMD mixture the SO₄²⁻ concentration was reduced from 17142 ppm to 2435 ppm and for the 1:1 mixture the SO₄²⁻ concentration was reduced from 20870 to 1970 ppm when the mixtures were treated with Hendrina FA to pH 10. This translates to 82, 85 and 91 % SO₄²⁻ removal when 3:1, 2:1 and 1:1 mixtures respectively were treated with Hendrina FA to pH 10. It can be concluded that the presence of Fe and Al in mine water enhanced SO₄²⁻ removal.

The small SO₄²⁻ removal observed for SCMW (1:0 mixture) when treated with Hendrina FA to pH 10 was because the pH rise only required a very small amount of

CaO to be released from Hendrina FA due to the absence of Fe and Al to buffer the sharp rise in pH. This means that only a small concentration of Ca^{2+} will be available for gypsum precipitation.

In the case of 3:1, 2:1 and 1:1 SCMW:AMD mixtures more CaO was released from Hendrina FA and consumed in the neutralisation reaction with subsequent release of Ca^{2+} to counter the buffering effect of Al and Fe. The released Ca^{2+} reacted with SO_4^{2-} to form gypsum. The ratio 1:1 had increased buffering effect than 2:1, while 2:1 ratio had higher buffering effect than 3:1 because of the higher concentration of Fe and Al. In addition because of the Al and Fe added in the SCMW:AMD, the precipitation of Al and Fe (oxy)hydroxides and oxyhydroxysulphates tend to adsorb or incorporate SO_4^{2-} leading to increased SO_4^{2-} removal (Seth and Ghazi, 1997).

The possible SO_4^{2-} mineral phases at various pH were modelled using PHREEQC thermodynamic geochemical model and the results are shown in Figure 4.15. The saturation indices (SI) obtained by PHREEQC geochemical modelling predicted the following SO_4^{2-} bearing mineral phases; alunite ($\text{KAl}_3(\text{SO}_4)_2(\text{OH})_6$), anhydrite (CaSO_4), barite (BaSO_4), basaluminite ($\text{Al}_4(\text{OH})_{10}\text{SO}_4$), jurbanite (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 (SrSO_4) and gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) to be precipitating at various pH values (Figure 4.15).

Saturation indices of different SO_4^{2-} bearing mineral for SCMW at different pH values (Figure 4.15a) shows that gypsum, barite, celestite, anhydrite and ettringite are the only mineral phases that could precipitate out SO_4^{2-} when SCMW was mixed with FA. The amount of SO_4^{2-} that could be removed as ettringite, barite and celestite were very insignificant since the concentration of Al, Ba, and Sr were very low in SCMW meaning that gypsum was the main mineral controlling SO_4^{2-} removal from SCMW.

Saturation indices calculated for the 3:1, 2:1 and 1:1 SCMW:AMD mixtures (Figure 4.15b-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 SO_4^{2-} removal. All the oxyhydroxysulphates are super saturated at pH 4-10 except ettringite. Above pH 10 they become under saturated. This explains why the 3:1, 2:1 and 1:1 SCMW:AMD mixtures tend to precipitate out more SO_4^{2-} compared to SCMW when pH was only raised to below 10.



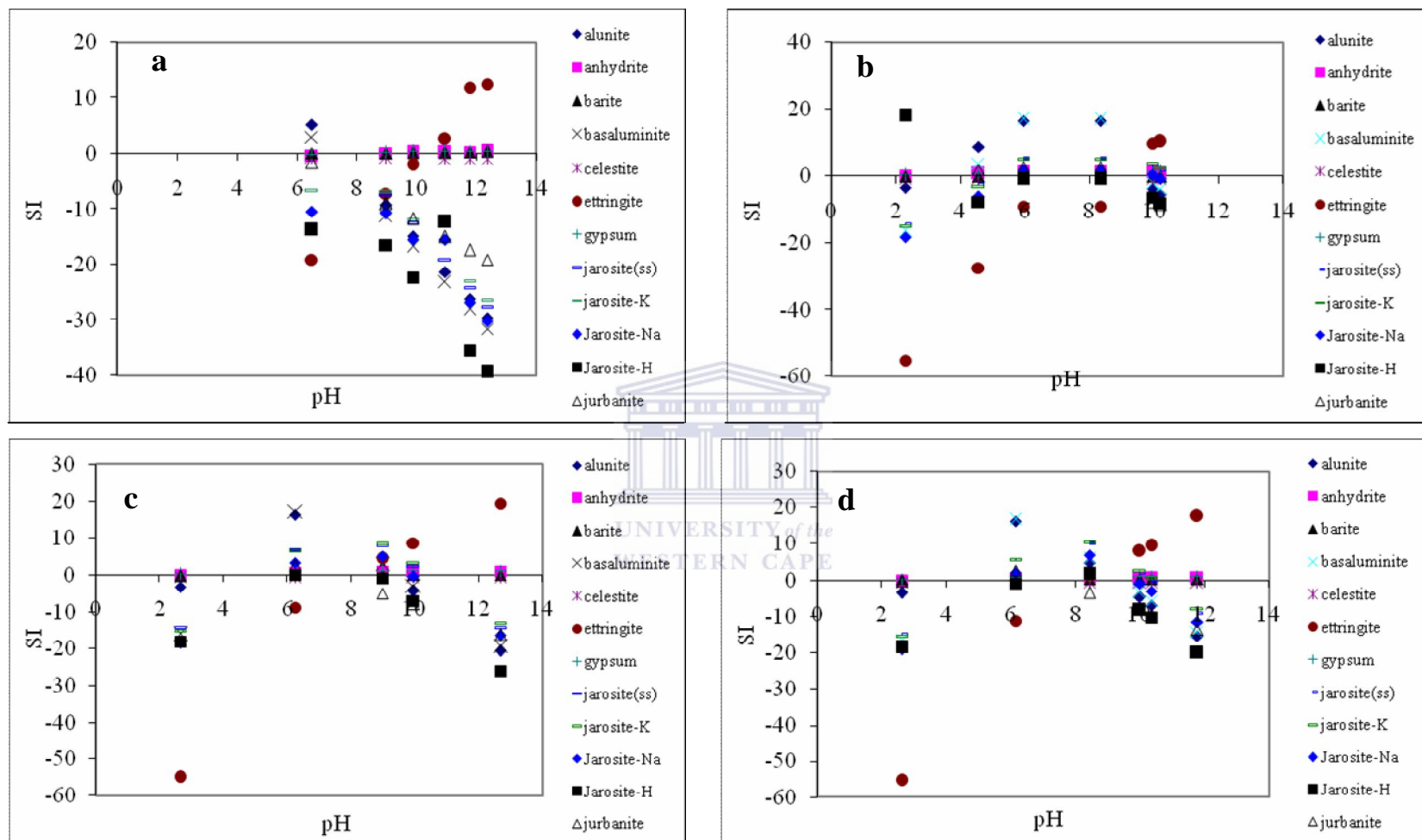


Figure 4.15: Saturation indices of SO_4^{2-} minerals at different final pH for treatment of SCMW (a) and SCMW:AMD mixtures (b-1:1, c-2:1 and d-3:1) with Hendrina FA.

The presence of Fe and Al ions generates acidity (H^+ ions) when Al and Fe (oxy) hydroxides precipitate according to equations 4.7.3 and 4.7.4. Precipitation of oxyhydroxysulphates consumes alkalinity as shown in equations 4.7.5, 4.7.6 and 4.7.7 (Younger et al., 2002). The acidity generated by hydrolysis reaction during 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 SO_4^{2-} to form gypsum leading to removal of SO_4^{2-} . Precipitation of Al, Fe (oxy)hydroxides and oxyhydroxysulphates in addition to gypsum precipitation contribute to more SO_4^{2-} removal through adsorption and structural incorporation of SO_4^{2-} .

Treatment of SCMW and all the mixtures to higher pH levels beyond pH 10 shows similar trends of SO_4^{2-} removal for SCMW:AMD mixtures (Figure 4.14). This is because the SO_4^{2-} phases that are supersaturated above pH 10, hence responsible for SO_4^{2-} removal are; barite, ettringite, gypsum and anhydrite for all the SCMW and SCMW:AMD mixtures.

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Treatment of SCMW (1:0 ratio) and SCMW:AMD mixtures with Hendrina FA results in Ca^{2+} ions leaching from the FA into solution (Figure 4.16). Generally increasing the pH of the mine water using Hendrina FA resulted in increased Ca^{2+} concentration for all the solutions. This was because of the dissolution of free CaO from the FA particles. The increase in Ca concentration suggests that the leaching rate over the time of the experiment of CaO from Hendrina FA is faster than the rate of gypsum precipitation, resulting in the gradual increase in the Ca concentration.

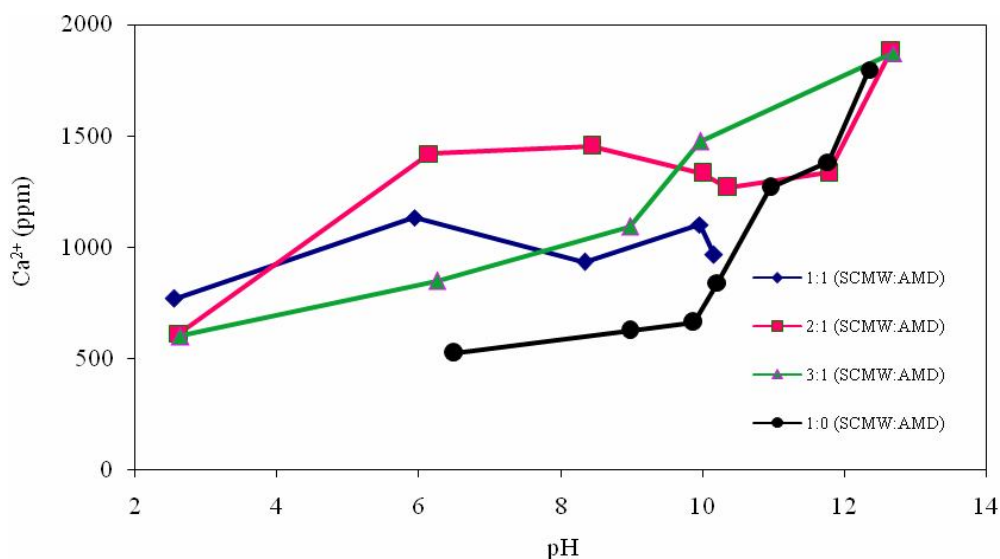


Figure 4.16: Ca concentration at various pH values during treatment of SCMW and different SCMW:AMD ratios with Hendrina FA.

The trend of the Ca concentration as pH was increased to 10 was different for each SCMW:AMD mixture. The 1:1 and 2:1 SCMW:AMD mixtures containing more SO_4^{2-} , Fe, Al and Mn than the 3:1 and 1:0 SCMW:AMD mixtures showed an increase of the Ca concentration between pH 2-6, and a decrease between pH 6-9 and an increase again between pH 8-10, with a decrease again at pH 10 again. The decrease in Ca concentration occurred at the buffering pH plateaus in the pH trend graphs (Figure 4.13). The buffering of the pH caused by the presence of high concentrations of Fe, Al and Mn (Figure 4.13), caused the pH to increase slowly while the high SO_4^{2-} concentration caused the rate of gypsum precipitation to be greater than the rate of change of pH. The trends for the 3:1 and 1:0 mixtures for the Ca concentration showed a gradual increase when pH was increased to 10. The buffering effect of Fe, Al and Mn was small because of the lower concentration of Fe, Al and Mn and hence the rate of gypsum precipitation was higher than the pH increase.

The Ca concentration trends for the 2:1, 3:1 and 1:0 from pH 10 to 12 showed a rapid increase in Ca concentration because Fe, Al and Mn have precipitated out and the buffering effect was only through precipitation of brucite ($\text{Mg}(\text{OH})_2$). For

the 1:1 mixture the Ca concentration slightly decreased at pH10 and the pH could not be increased beyond 10.21, suggesting that the free CaO in Hendrina FA was exhausted by the high acidity of the mixture due to the high concentration of Fe, Al and Mn.

Treatment of SCMW and SCMW:AMD mixtures with Hendrina FA results in approximately 100 % removal of Mg from 600-800 ppm to 0.3 ppm. The degree of removal depended 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 from Hendrina FA, at pH 9 Mg starts precipitating rapidly and eventually precipitating to below 0.3 ppm at pH greater than 10 (Figure 4.17).

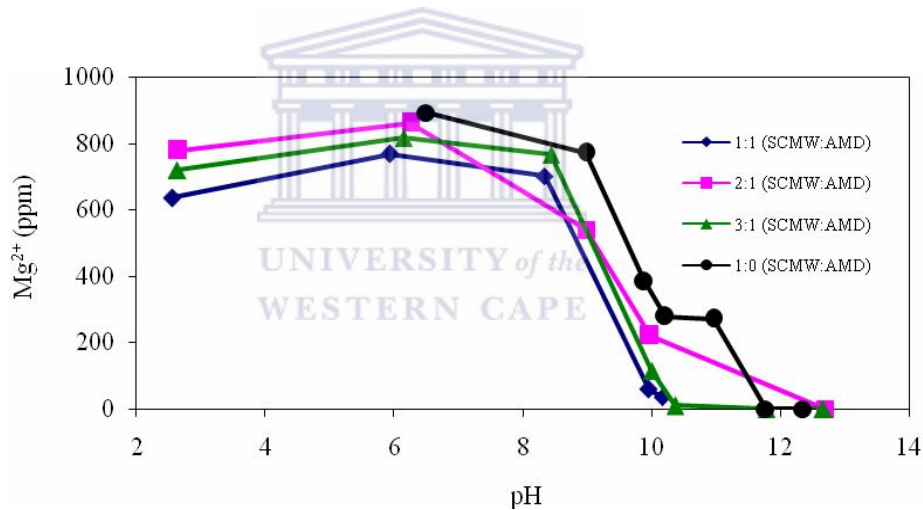


Figure 4.17: Mg concentration during treatment to various pH values of SCMW and different SCMW:AMD ratio with Hendrina FA.

PHREEQC geochemical modeling predicts that Mg would start to precipitate at pH greater than 8 (Figure 4.18) as brucite ($Mg(OH)_2$). SI show that $Mg(OH)_2$ is saturated when the pH is approximately 8.5. At pH above 10, $Mg(OH)_2$ is supersaturated, consequently the Mg concentration decreased to below 0.3 ppm due to the formation of $Mg(OH)_2$. This is below the required DWAF limit for domestic water use of 0-30 ppm (DWAF, 1996).

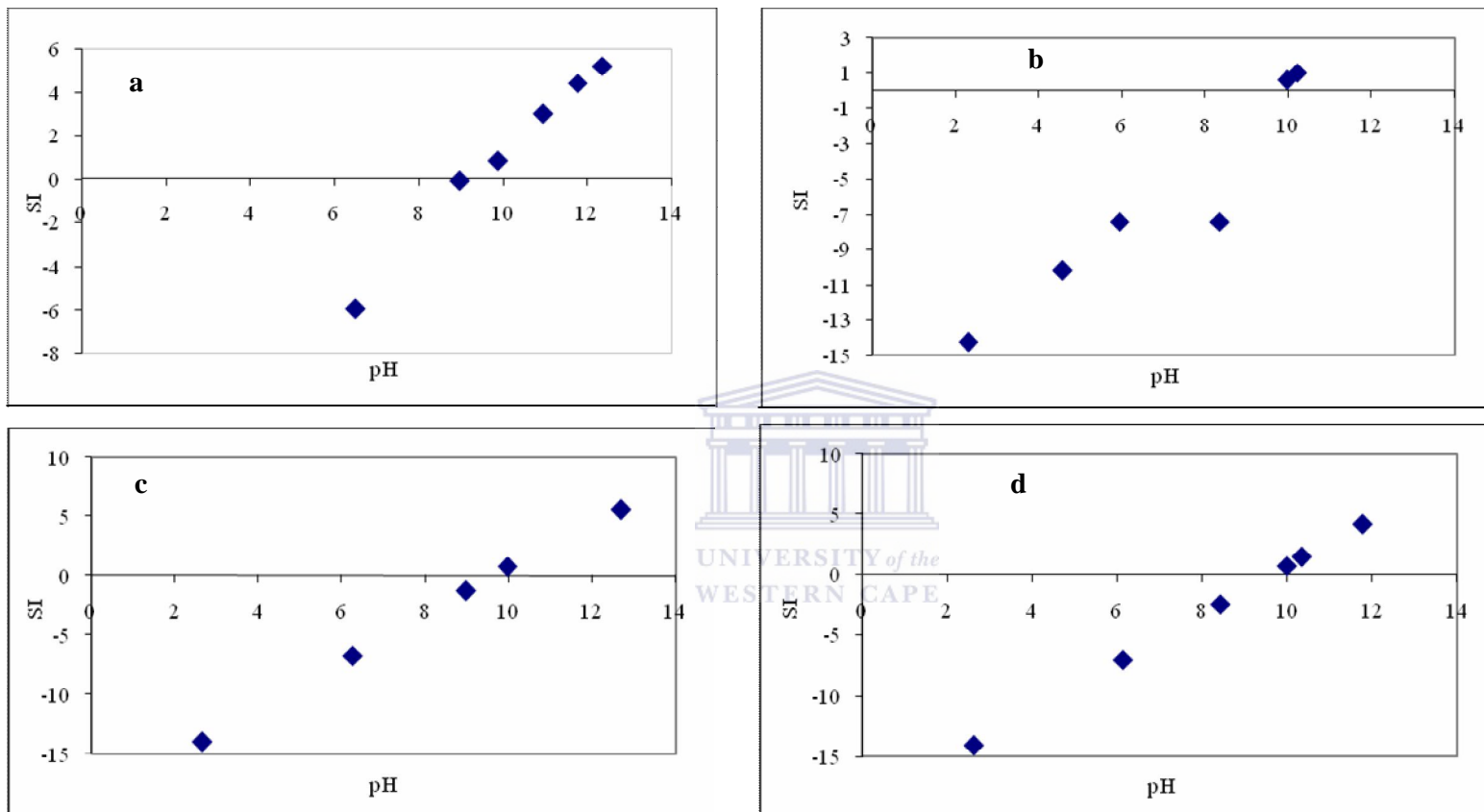


Figure 4.18: Saturation indices of brucite at different final pH end points during treatment of SCMW (a) and SCMW:AMD mixtures (b-1:1, c-2:1 and d-3:1) with Hendrina FA.

Results obtained when SCMW and SCMW:AMD mixtures were treated with Hendrina FA show that Mn is also removed from between 40-70 ppm to below 0.04 ppm (Figure 4.19) when the pH was higher than 8. This level was within the required DWAF limit domestic use of 0-0.05 ppm of Mn for potable water (DWAF, 1996).

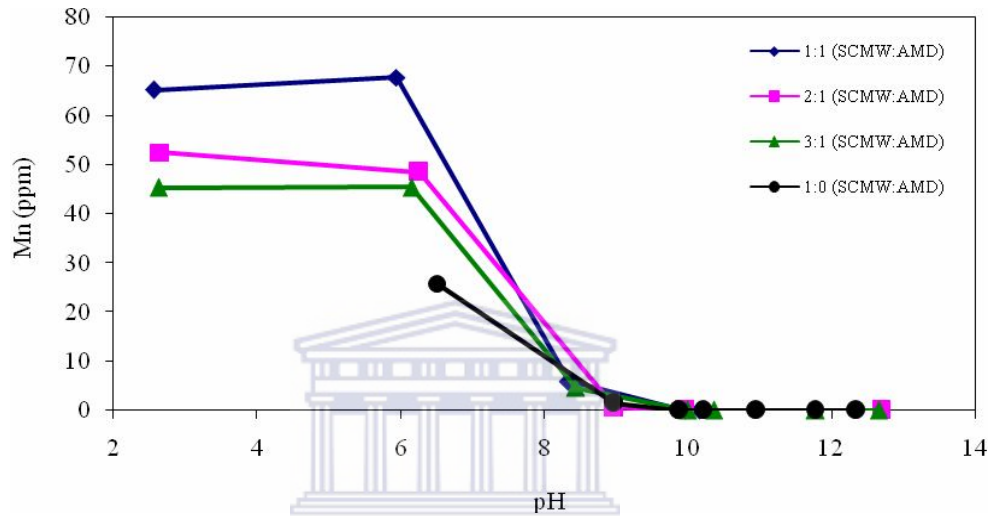


Figure 4.19: Mn concentration during treatment of SCMW and different SCMW:AMD ratio with Hendrina FA to various pH end points

Saturation indices obtained using PHREEQC showed that Mn bearing mineral phases start precipitating at pH greater than 8 (Figure 4.20) as birnessite (MnO_2), bixbyite (Mn_2O_3), hausmannite (Mn_3O_4), manganite ($MnOOH$), nsutite (MnO_2), pyrochroite ($Mn(OH)_2$) and pyrolusite (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.

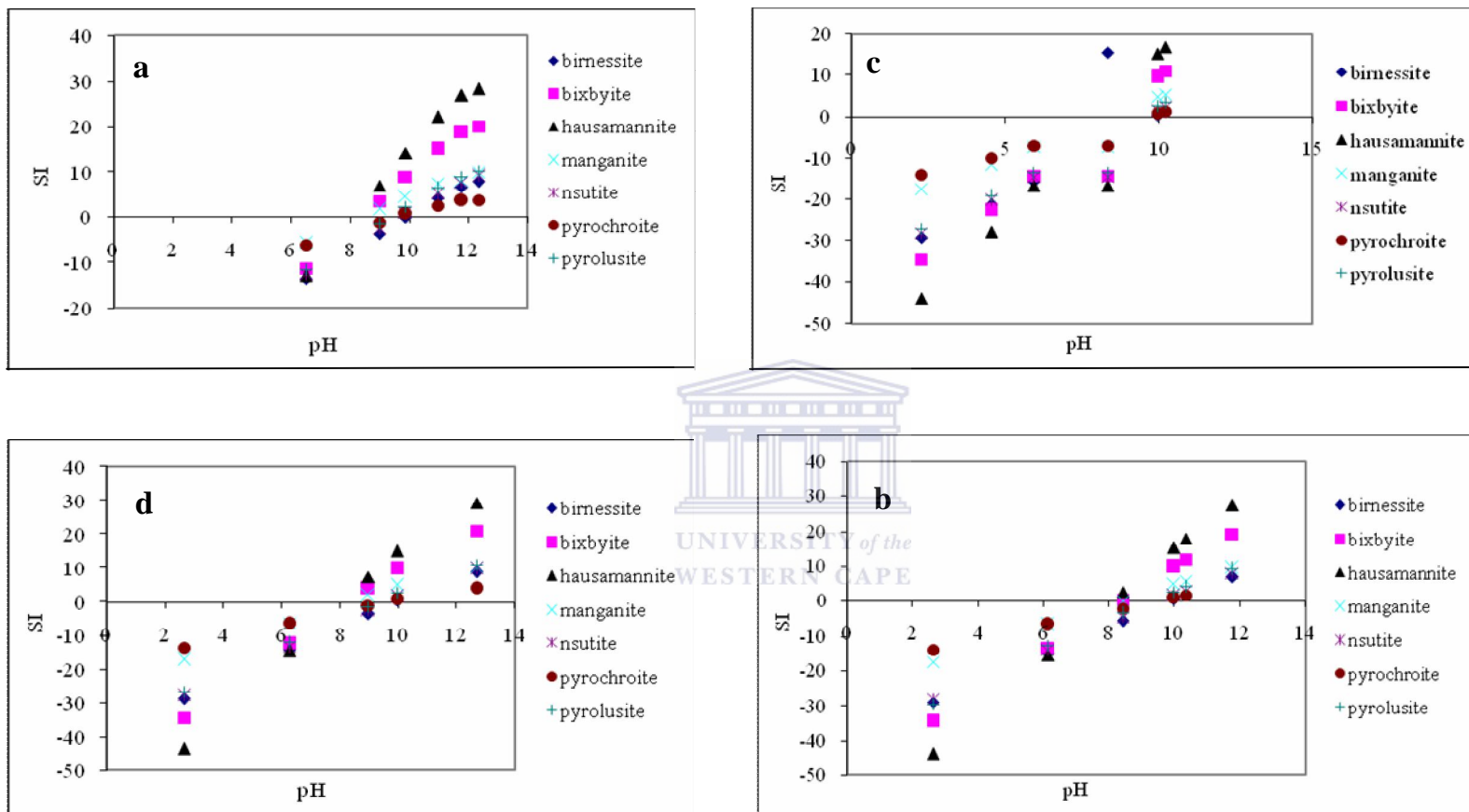


Figure 4.20: Saturation indices of Mn bearing minerals at different final pH end points during treatment of SCMW (a), SCMW:AMD mixtures (b-1:1, c-2:1 and d-3:1) with Hendrina FA

When 3:1, 2:1 and 1:1 SCMW:AMD mixtures were treated with Hendrina FA to various pH end points the Al concentration was reduced from between 124-228 ppm to as low as 48 ppm when the pH was raised to 6. The Al concentration further decreased to below 0.04 ppm when the pH was raised to 9 (Figure 4.21). This was within the required DWAF limit for domestic water use of 0-0.15 ppm Al (DWAF, 1996). The trend for the SCMW (1:0 mixture) was not included in Figure 4.21 because the Al concentration is almost zero in SCMW.

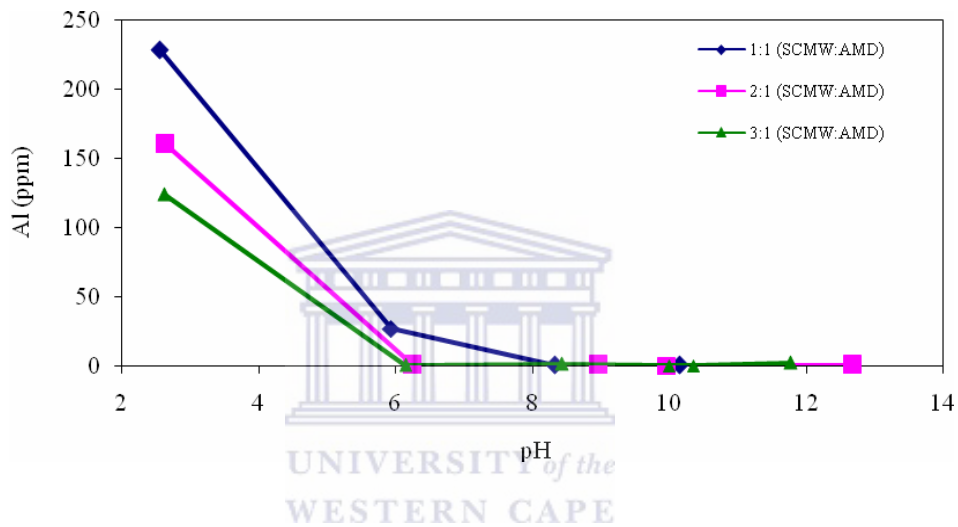


Figure 4.21: Al concentration during treatment of SCMW:AMD mixtures to various pH end points with Hendrina FA.

The SI indices were calculated for Al bearing mineral phases using PHREEQC geochemical model (Figure 4.22). 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 (AlOOH), diaspore (AlOOH), ettringite, jurbanite (AlOHSO_4) and gibbsite ($\text{Al}(\text{OH})_3$) could precipitate out when mine water was treated with FA (Figure 4.7.10). Amorphous $\text{Al}(\text{OH})_3$, alunite, basaluminite and jurbanite are supersaturated between pH 4-9, while boehmite, diaspore and gibbsite are supersaturated at pH greater than 4. Ettringite is supersaturated at pH greater than 10.

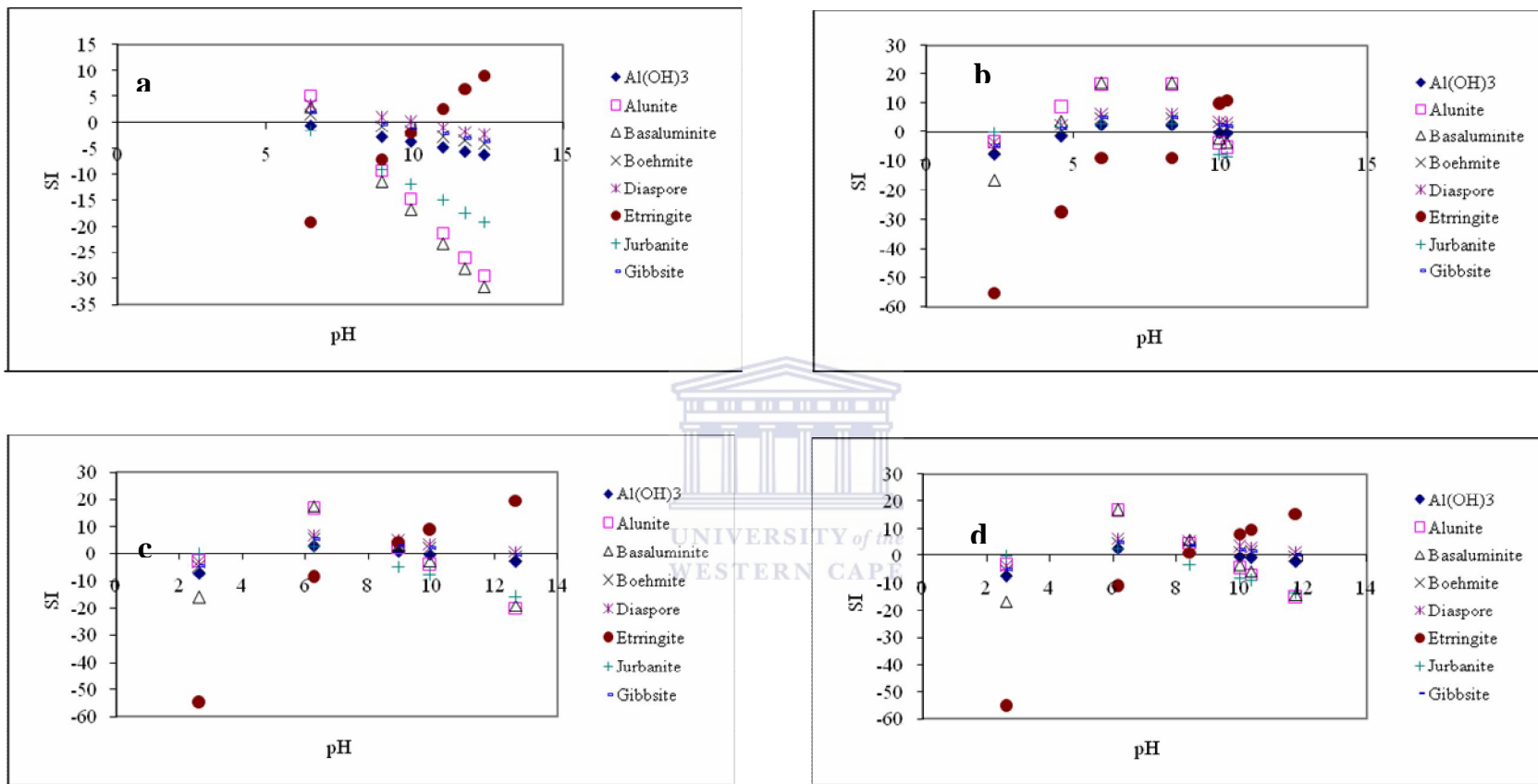


Figure 4.22: Saturation indices of Al bearing minerals at different end points during treatment of SCMW (a) and SCMW:AMD mixtures (b-1:1, c-2:1 and d-3:1) with Hendrina FA

Treatment of 3:1, 2:1 and 1:1 SCMW:AMD mixtures with Hendrina FA have shown that the Fe concentration was reduced from between 2202-5108 ppm to between 0.03-0.05 ppm when pH was raised to 9. This is within the required DWAF domestic water use of 0-0.1 ppm (DWAF, 1996). Fe starts precipitating from the solutions at pH greater than 5 when FA was mixed with the SCMW:AMD mixtures (Figure 4.23). The profile for the SCMW (1:0 mixture) is not included because the Fe concentration is almost zero in SCMW.

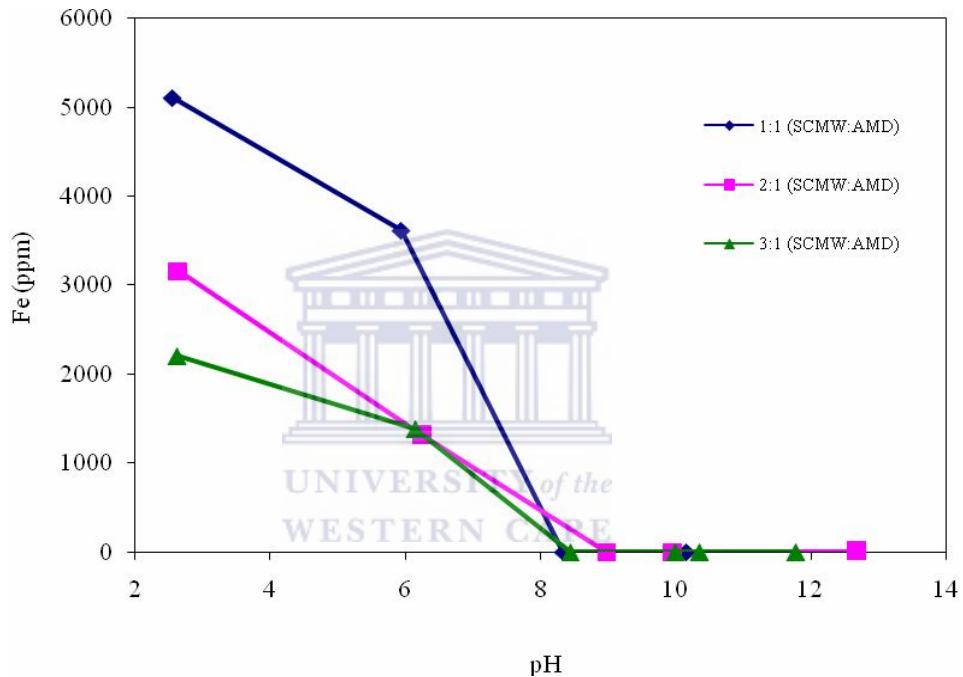


Figure 4.23: Fe concentration during treatment of different SCMW:AMD mixtures to various pH end points with Hendrina FA

The SI indices were calculated for Fe bearing mineral phases using PHREEQC model (Figure 4.24). Calculated SI showed that Fe hydroxides, oxyhydroxides and oxyhydroxysulphate mineral phases started precipitating at pH 5 (Figure 4.24). The minerals controlling Fe removal according to the model are $\text{Fe}(\text{OH})_{2.7}\text{Cl}_{0.3}$, amorphous $\text{Fe}(\text{OH})_3$, $\text{Fe}_3(\text{OH})_8$, goethite (FeOOH), hematite (Fe_2O_3), maghematite (Fe_2O_3), magenetite (Fe_3O_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 4-10.



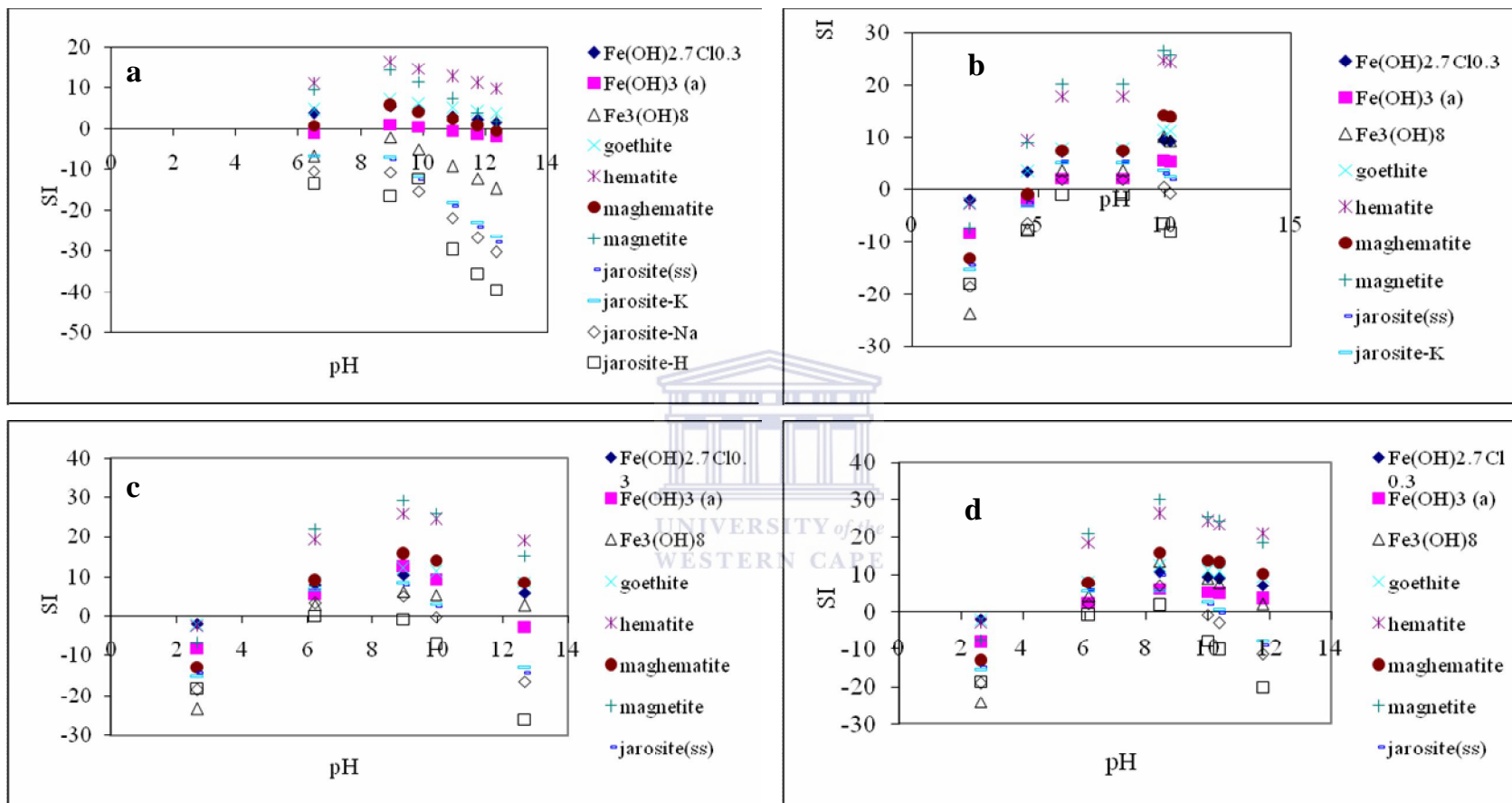


Figure 4.24: Saturation indices of Fe mineral phases at different pH end points during treatment of SCMW (a) and SCMW:AMD mixtures (b-1:1, c-2:1 and d-3:1) with Hendrina FA

4.7.2: Effect of Fe and Al separately

Simulated CMW, Fe-AMD and Al-AMD waters were prepared as outlined in section 3.4.1. SCMW, Fe-AMD and Al-AMD were treated with Hendrina FA to various pH end points as described in section 3.4.5.2. Results from the analysis of the waters by ICP-AES and IC before and after treatment with Hendrina FA to various pH end points are shown in Tables 4.5, 4.6 and 4.7. The three simulated mine waters contained approximately the same concentration of SO_4^{2-} and differ in the concentration of Fe and Al. The SCMW had a starting pH of 6.55, while Fe-AMD and Al-AMD had pH of 2.49 and 1.54 respectively. The Fe-AMD and Al-AMD had a starting pH less than 3 because they were acidified to prevent precipitation of Fe and Al hydroxides before mixing with Hendrina FA.

The SO_4^{2-} concentration was reduced from 4655 ppm to 1502 ppm for SCMW, from 4598 ppm to 1466 ppm for Fe-AMD and 4698 ppm to 1540 ppm for Al-AMD when the pH was increased to 12 by Hendrina FA.

Table 4.5: Elemental composition of SCMW during treatment with Hendrina FA to various final pH end points

Time (min)	0	3	7	14	30
pH	6.55	9.88	10.21	11.77	12.14
Ca	525	625	662	841	1259
Mg	892	384	230	0.38	0.04
K	36	52	65	51	51
Na	30	47	47	44	41
Mn	26	0	0	0	0
Fe	0.03	0.01	0.01	0.02	0.1
Al	0.05	0.05	0.06	0.03	0.02
SO_4^{2-}	4655	3776	2937	1720	1502
Cl^-	80	79	66	73	77
NO_3^-	43	42	36	37	41

Table 4.6: Elemental composition of Fe-AMD during treatment with Hendrina FA to various final pH end points

Time (min)	0	25	30	40	90
pH	2.49	9.54	10.2	11.8	12.12
Ca	140	792	895	1058	1127
Mg	207	92	0.38	0.19	0.06
K	52	56	59	62	65
Na	94	95	99	100	100
Mn	43	0	0	0	0
Fe	1795	0.05	0.05	0.07	0.03
Al	0.3	0.03	0.02	0.01	0.02
SO ₄ ²⁻	4598	2419	2219	1609	1466
Cl ⁻	85.24	89	130	131.5	129
NO ₃ ⁻	46.18	47	43	49	49

Table 4.7: Elemental composition of Al-AMD during treatment with Hendrina FA to various final pH end points

Time (min)	0	10	25	40	80
pH	1.54	9.46	10.3	11.5	12
Ca	138	582	797	858	1261
Mg	213	103	54	0.29	0.01
K	40	53	51	52	55
Na	36	43	51	51	51
Mn	29	0.03	0.01	0	0
Fe	3.49	0.03	0.1	0.04	0.02
Al	384	0.06	0.06	0.02	0.05
SO ₄ ²⁻	4698	2857	2266	2110	1540
Cl ⁻	83	86	89	91	95
NO ₃ ⁻	48	46	48	48	50

The results in Tables 4.5, 4.6 and 4.7 shows that the presence of Fe or Al buffered the pH in the mine water solution compared to SCMW by itself during treatment with Hendrina FA. It took only 7 mins for the pH to increase to values greater than 10 for SCMW. For Fe-AMD it took 30 mins, while for Al-AMD it took 25 mins for pH to increase to greater than 10 showing that Al introduced more buffering than Fe. At pH \approx 10 the SO₄²⁻ removal for SCMW, Al-AMD and Fe-AMD was approximately 18 %, 38 % and 47 % respectively (Figure 4.25). The Fe or Al addition enhanced SO₄²⁻ removal when the pH of the mine water was increased up to pH 10 with Hendrina FA. At pH \approx 12 the percentage SO₄²⁻

removal for all the samples is approximately 66 % for all the simulated mine waters.

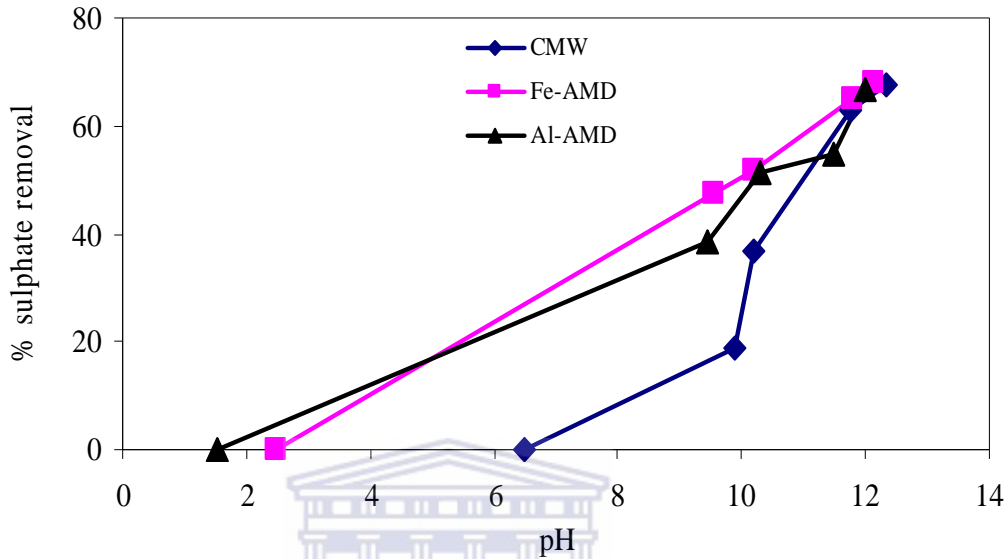


Figure 4.25: % SO_4^{2-} removal at different final pH of SCMW, Fe-AMD and Al-AMD after treatment with Hendrina FA.

The enhanced SO_4^{2-} removal at pH below 10 caused by the presence of Fe and Al was because of the buffering effect of Fe and Al which caused more CaO dissolution when Fe-AMD and Al-AMD were treated with Hendrina FA for pH to increase to 10. As more Ca^{2+} came into solution more SO_4^{2-} were precipitated as gypsum. In addition precipitated Al and Fe oxyhydroxides adsorb SO_4^{2-} on their surfaces (Seth and Gazhi, 1997) and precipitation of Fe and Al oxyhydroxysulphates (Figure 4.26 and 4.27) enhanced SO_4^{2-} removal for Fe-AMD and Al-AMD samples as PHREEQC modelling showed particularly at pH 10. In the case of SCMW the SO_4^{2-} removal is controlled by gypsum and anhydrite only since the concentration of Al, Sr and Ba was very low to remove significant concentration of SO_4^{2-} (Figure 4.15a).

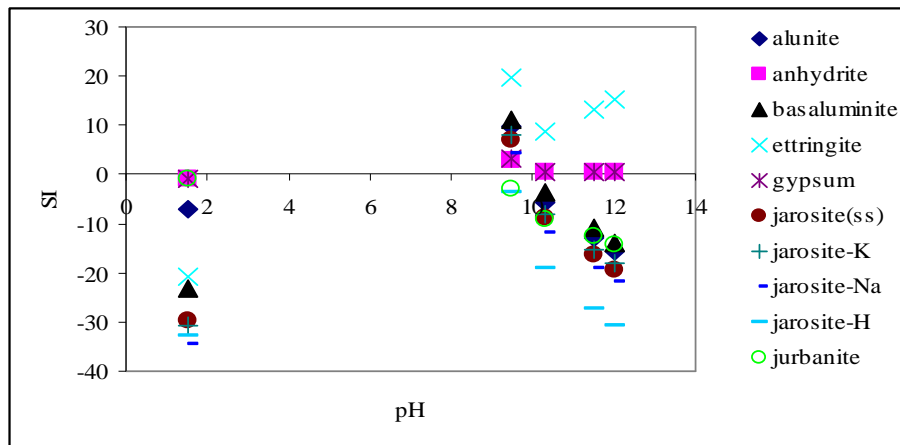


Figure 4.26: Saturation indices of SO_4^{2-} bearing mineral phases for Al-AMD at different pH values

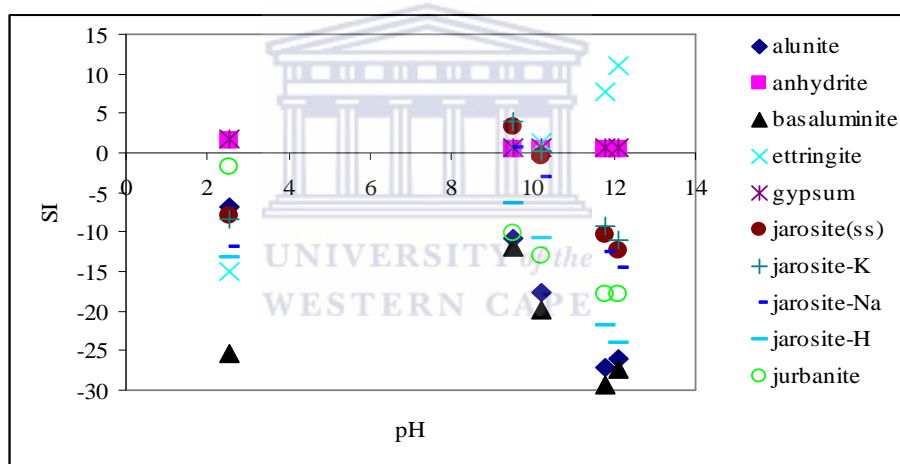


Figure 4.27: Saturation indices of SO_4^{2-} bearing mineral phases for Fe-AMD at different pH values.

Treatment of SCMW, Fe-AMD and Al-AMD with FA to pH greater than 10 resulted in similar removal trends for SO_4^{2-} . This was because the SO_4^{2-} removal was controlled by the same mineral phases (ettringite, anhydrite and gypsum) above a pH of 10. This was confirmed by PHREEQC modelling (Figure 4.26 and 4.27).

4.8: STEPWISE REMOVAL OF SULPHATES

Treatment of mine water with Hendrina FA could reduce SO_4^{2-} concentration from 4655 ppm to between 1000-1500 ppm which was not yet within DWAF limit for potable water. Further optimization of SO_4^{2-} removal by gypsum seeding and addition of amorphous $\text{Al}(\text{OH})_3$ was therefore evaluated. The procedures followed are set out in section 3.5. The results obtained are presented in sections 4.8.1 to 4.8.3.

4.8.1: Effect of gypsum seeding

Treatment of SCMW with Hendrina FA in the ratio 3:1 to pH greater than 12 resulted in a decrease in SO_4^{2-} concentration from 4655 ppm to 1385 ppm as shown in Figure 28. When 0.03 and 0.06 g of gypsum seed were added at this stage the SO_4^{2-} concentration decreased further to 1190 and 1257 ppm respectively (Figure 4.28).

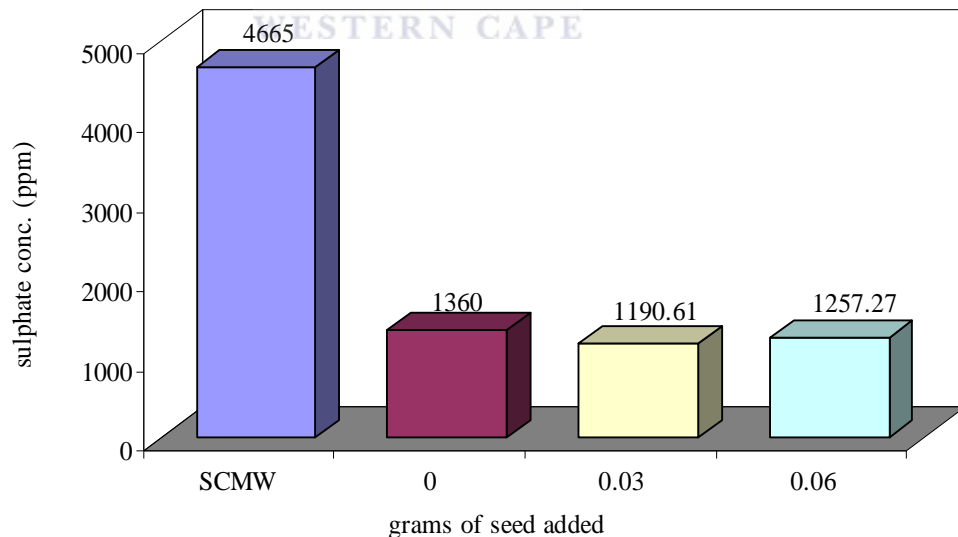


Figure 4.28: SO_4^{2-} concentration of simulated SCMW before and after treatment to pH greater 12 followed by addition of different amounts of seed.

Introduction of gypsum seed in the SCMW and FA slurry resulted in a small additional decrease in SO_4^{2-} concentration because gypsum seed particles provide the surfaces on which metastable gypsum crystals can grow (Smit and Sibilski, 2003).

4.8.2: Effect of gypsum seeding and $\text{Al}(\text{OH})_3$.

In the SAVMIN process where CaO was used to attain a high pH and SO_4^{2-} removal through gypsum precipitation, $\text{Al}(\text{OH})_3$ was added after the liming and gypsum seeding steps to further precipitate out the SO_4^{2-} as ettringite to below 200 ppm (Smit, 199; Smit and Sibilski, 2003). In this case, the same approach was investigated using Hendrina FA instead of CaO to adjust the pH and to remove SO_4^{2-} through gypsum precipitation.

Gypsum seeding and $\text{Al}(\text{OH})_3$ addition was performed as the gypsum seeding by itself did not achieve the target water quality in the process water as set out in section 3.4.2. After adjusting the pH of SCMW (600 ml) to above 12 with Hendrina FA using a SCMW:FA ratio of 3:1, gypsum seed (0.12 g) and $\text{Al}(\text{OH})_3$ (0.4498 g) were added and this additional step showed that SO_4^{2-} concentration could be reduced from 1470 ppm to 545 ppm (Figure 4.29). For the solid to liquid ratio of 2:1 the SO_4^{2-} concentration decreased from 1220 ppm to 504 ppm (Figure 4.29) after gypsum seeding and addition of $\text{Al}(\text{OH})_3$. This is due to the removal of SO_4^{2-} through precipitation of ettringite (Eq. 4.8.2):



Ettringite precipitation generates acidity but the pH range of stability of ettringite of 11.5-12.5 (Myneni et al., 1998) was maintained during the experiment due to the presence of FA in the mixture.

The optimum time observed for maximum SO_4^{2-} removal to be attained when the 2:1 SCMW and FA slurry was seeded with gypsum followed by addition of

$\text{Al}(\text{OH})_3$ was 240 mins, whereas for the 3:1 ratio the best removal was observed at 60 mins after addition of $\text{Al}(\text{OH})_3$ (Figure 4.29). The optimum ratio of SCMW:FA that can be used to remove SO_4^{2-} through ettringite precipitation was found to be 3:1.

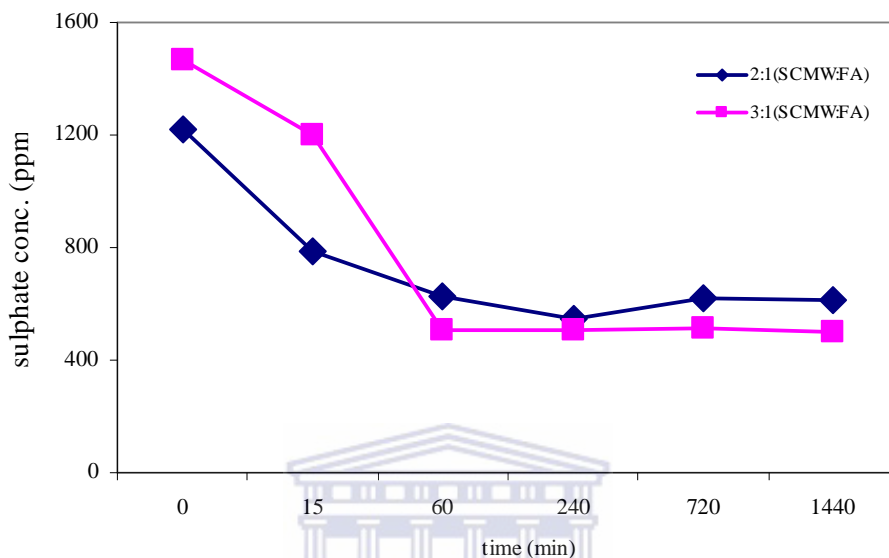


Figure 4.29: SO_4^{2-} concentration in the process water after addition of gypsum seed and $\text{Al}(\text{OH})_3$ at different times for SCMW:FA ratios 2:1 and 3:1 (pH>12).

The solid residues (for the 3:1 SCMW:FA) obtained after gypsum seeding and 60 mins after addition of $\text{Al}(\text{OH})_3$ (termed SR2) were dried and analysed using XRF and the elemental composition was compared with that of solid residues after mixing FA and SCMW to pH greater 12 (SR1) and fresh Hendrina FA. From the XRF results obtained for the solid residues, the % weight of SO_3 increased in the solid residues (Table 4.8). This indicated that the SO_4^{2-} sink was the FA residue. The % weight of SO_3 was greater in the case of SR2 compared to SR1.

Table 4.8: Chemical composition of FA and SR analysed using XRF

Major Oxides	% w/w (FA)	% w/w (SR1)	% w/w (SR2)
SiO ₂	54.01 ± 0.28	53.16 ± 0.18	54.13 ± 0.37
Al ₂ O ₃	29.01 ± 0.14	26.17 ± 0.21	25.94 ± 0.17
CaO	4.63 ± 0.09	4.61 ± 0.10	4.97 ± 0.13
Fe ₂ O ₃	3.99 ± 0.07	4.3 ± 0.06	4.66 ± 0.07
TiO ₂	1.79 ± 0.03	1.45 ± 0.04	1.44 ± 0.06
MgO	1.12 ± 0.03	1.93 ± 0.03	1.9 ± 0.06
K ₂ O	0.78 ± 0.01	0.76 ± 0.01	0.78 ± 0.01
P ₂ O ₅	0.54 ± 0.02	0.55 ± 0.03	0.55 ± 0.12
SO₃	0.24 ± 0.01	0.65 ± 0.04	0.89 ± 0.04
Na ₂ O	0.14 ± 0.01	0.04 ± 0.001	0.01 ± 0.0002
MnO	0.038 ± 0.001	0.06 ± 0.001	0.06 ± 0.001
LOI	3.7 ± 0.54	4.73 ± 0.24	3.92 ± 0.35
Total	99.99 ± 0.13	99.28 ± 0.08	99.60 ± 0.10

LOI (loss on ignition), FA (fly ash) SR1 (solid residue obtained after mixing FA with mine water to pH 12.35 and SR2 (solid residue obtained after mixing FA to pH 12.35 and then gypsum seeding and Al(OH)₃ addition).

The % weight of MgO and MnO are higher in the SR1 and SR2 than in FA (Table 4.8). This correlated well with the decrease in Mg and Mn concentration in the SCMW when pH was increased to pH above 11 (Figures 4.6). PHREEQC geochemical modelling have proved that Mn start precipitating at pH 8 (Figure 4.7) and Mg start precipitating at as brucite at pH 9 (Figure 4.8).

The morphological structures of the FA and the solid residues were analysed using SEM. From the images obtained the morphology of the solid residues after addition of Al(OH)₃ shows the presence of rod shaped and needle shaped structures characteristic of gypsum and ettringite respectively (Figure 4.30).

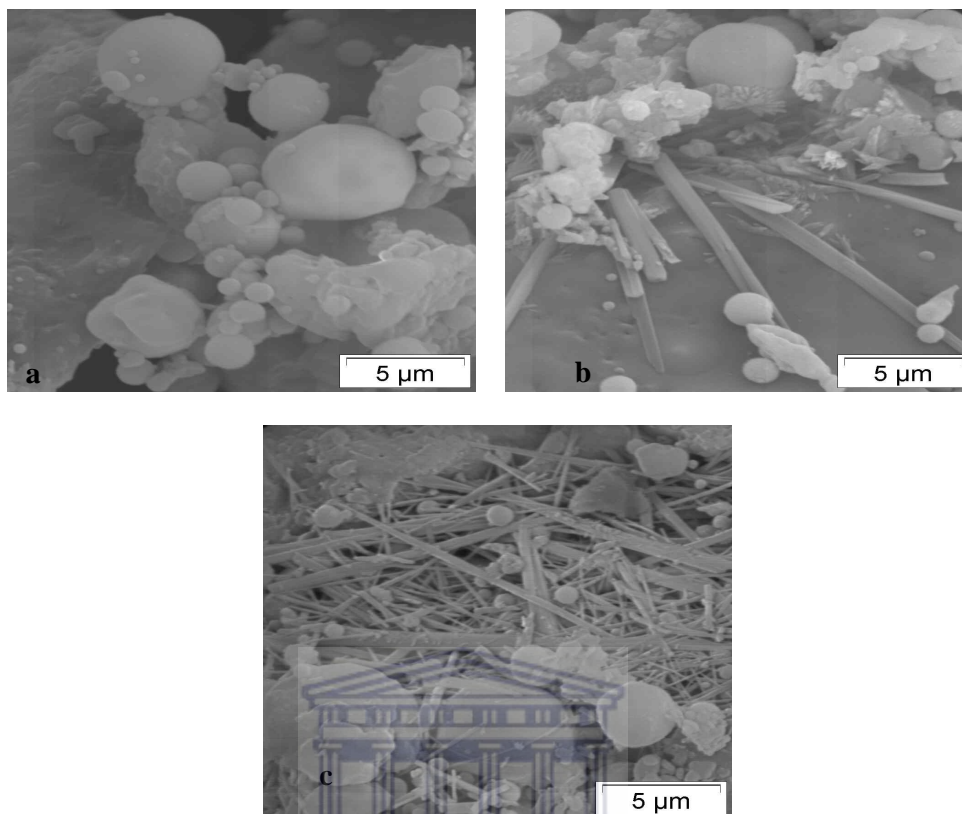


Figure 4.30: Scanning electron microscope images of Hendrina FA (a), SR1 (b) and SR2 (c) (x 5000 magnification)

SEM images obtained show that FA is made of spherical particles of less than 10 μm and irregular shaped particles (Figure 4.30a). A SEM image of SR1 shows the presence of rod shaped crystals characteristic of gypsum (Figure 4.30b). The SEM image for SR2 show the presence of rod shaped (gypsum) and needle shaped characteristic of ettringite (Figure 4.30c). The rod shaped particles were not present in the FA sample but in SR1 supporting that SO_4^{2-} removal after addition of FA could be due to gypsum precipitation. The needle shaped particles were not present in FA and SR1 but only in SR2 and this supported the interpretation that ettringite was the mineral phase that was responsible for further removal of SO_4^{2-} after $\text{Al}(\text{OH})_3$ was added.

4.8.3: Effect of Al(OH)₃.

In order to separately evaluate the role of Al(OH)₃ a further set of experiments was performed as described in section 3.5.3. These experiments were done using SCMW:FA ratios of 2:1 and 3:1 to treat mine water to pH greater than 12 after which Al(OH)₃ was added. Samples were collected and analysed after the addition of Al(OH)₃ at different times. The results obtained showed that addition of Al(OH)₃ only without gypsum seeding resulted in the SO₄²⁻ concentration decreasing from 1961 ppm to 526 ppm for the SCMW:FA ratio of 3:1 and 1513 ppm to 595 ppm for SCMW:FA ratio of 2:1 (Figure 4.31). This again showed that SO₄²⁻ removal through ettringite precipitation was similar for both 3:1 and 2:1 SCMW:FA ratios.

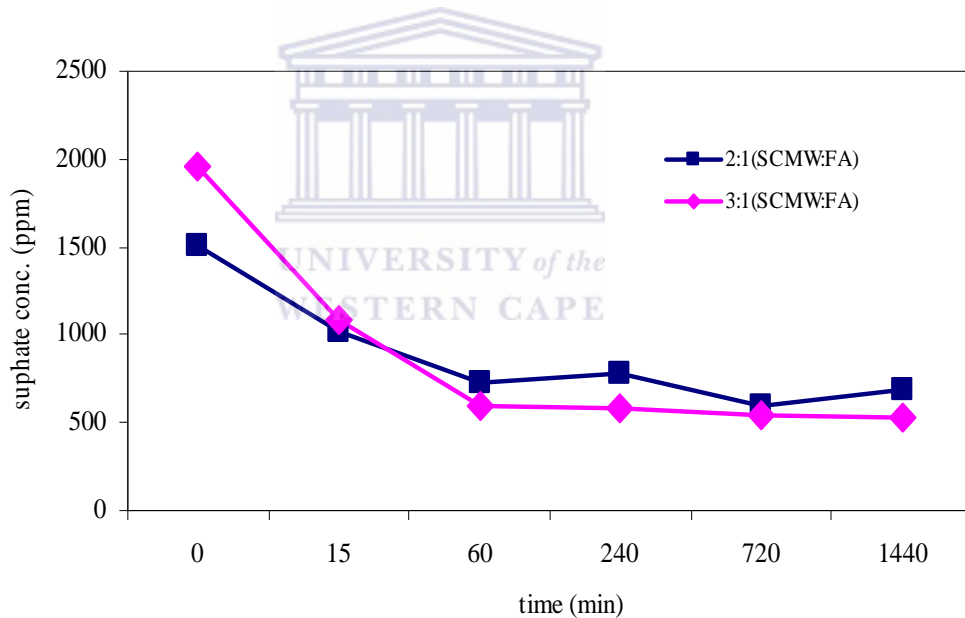


Figure 4.31: SO₄²⁻ concentration in the process water after addition of Al(OH)₃ only at different times for SCMW:FA ratios 2:1 and 3:1 (pH>12).

The results shown in Figure 31 are almost similar to those obtained when the mine water FA slurry was seeded with gypsum followed by addition of Al(OH)₃ (Figure 4.29). These results show that Al(OH)₃ is playing the major role in the removal of the SO₄²⁻ remaining after FA treatment and that the role played by gypsum

seeding was marginal, although gypsum seeding helped to achieve low SO_4^{2-} concentration compared to $\text{Al}(\text{OH})_3$ treatment alone..

The $\text{Al}(\text{OH})_3$ was added according to the stoichiometric calculations based on the ettringite formation reaction (Eq.4.8.2) and was sufficient in theory to remove 1440 ppm of SO_4^{2-} . The SO_4^{2-} concentration removed was between 716-1435 ppm after addition of $\text{Al}(\text{OH})_3$. Higher removal of SO_4^{2-} was observed with the 3:1 ratio compared to the 2:1 ratio, suggesting that the FA added was reacting with $\text{Al}(\text{OH})_3$ to form mineral phases other than ettringite, or was inhibiting $\text{Al}(\text{OH})_3$ availability to react with SO_4^{2-} to form ettringite.

4.9: pH REDUCTION OF THE PROCESS WATER.

Process water from the treatment of SCMW with FA followed by addition $\text{Al}(\text{OH})_3$ had the elemental composition conforming to the DWAF limit for domestic water except the pH which was much higher than the required limit of 6-9 (DWAF, 1996; WHO, 2008). The process water was reacted with CO_2 to reduce pH of the process water as outlined in section 3.6. The experiments were performed in triplicate and the results are tabulated in Table 4.9.

Table 4.9: pH and pressure changes during carbonation of process water

Experiment	Initial pH	Final pH	Initial pressure (KPa)	Final pressure (KPa)
1	11.68	7.82	275.79	206.842
2	11.68	6.64	275.79	206.842
3	11.68	6.72	275.79	206.842

These results showed that the high pH obtained during FA followed by addition $\text{Al}(\text{OH})_3$ treatment of SCMW can be adjusted simply by CO_2 sparging and does not require dosing with chemicals to attain a pH of 7.06 which was within DWAF limits.

The elemental analysis of the water before and after carbonating the process water shows that all other elements remained unchanged except Ca concentration (Table 4.10). Introducing CO₂ into the process water was expected to enhance mineral carbonation as relatively high levels of Ca remained in solution after reacting SCMW with FA and Al(OH)₃ (Table 4.10).

Table 4.10: Major elements composition of process water and carbonated water

Element (ppm)	Process water	Carbonated process water
Ca	2224.13 ± 84.11	126.41 ± 16.58
Mg	0.12 ± 0.01	0.22 ± 0.02
K	19.00 ± 6.04	21.83 ± 1.99
Na	48.35 ± 11.21	58.56 ± 3.94
Mn	0.11 ± 0.01	ND
K	51	51
Na	33	37
SO ₄ ²⁻	544.05 ± 12.02	508.17 ± 15.09
Cl ⁻	70.00 ± 1.41	72.67 ± 3.09
NO ₃ ⁻	31.50 ± 2.12	40.67 ± 2.35

The FT-IR spectrum obtained for the solids collected after carbonation compared closely with the spectrum for a pure CaCO₃ sample (Figure 4.32). The vibrational peaks at wave number 710, 872 and 1400 cm⁻¹ were observed in the both the sample and the pure CaCO₃. These peaks represent the ν₄, ν₂ and ν₃ vibrational modes for CO₃²⁻ respectively (Nyquist et al., 1997).

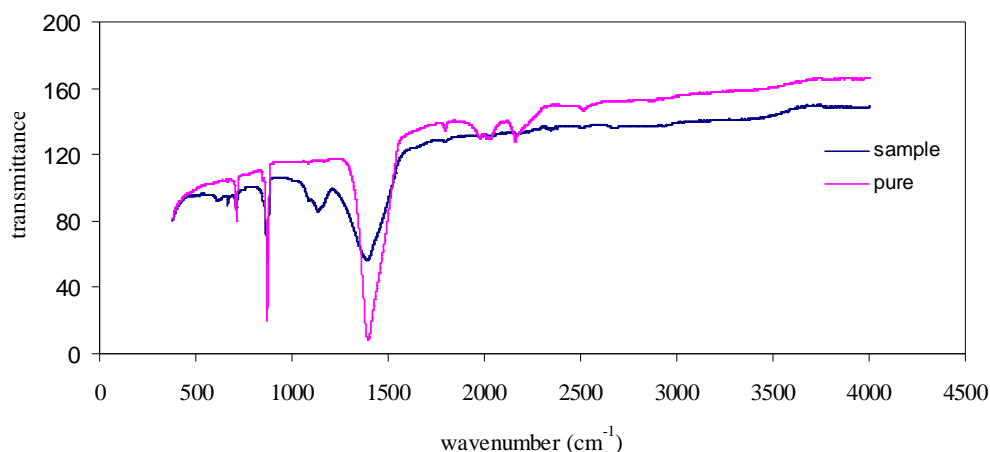
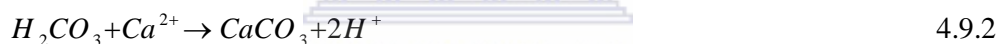


Figure 4.32: FT-IR spectra for pure CaCO_3 and carbonation solid residues of process waters

When CO_2 was introduced into the water it reacted to form H_2CO_3 , which in turn reacted with Ca^{2+} in the process water to form CaCO_3 causing the decrease in Ca concentration observed (Eqs 4.9.1 and 4.9.2.



The H^+ protons generated in equation 4.9.2 caused the pH to decrease when CO_2 was introduced in the process water. The process water was separated from the FA solid residues before carbonation as the lower pH could mobilize any pH sensitive mineral phases such as ettringite.

Carbonation of the process water from FA and $\text{Al}(\text{OH})_3$ treatment resulted in the reduction of the total hardness of the process through CaCO_3 precipitation. Total hardness is calculated from the Ca and Mg concentrations as follows (DWAF, 1996):

$$\text{Total hardness ppm}(\text{CaCO}_3) = 2.497 \times \text{ppm}(\text{Ca}) + 4.118 \times \text{ppm}(\text{Mg})$$

From the concentrations of Ca and Mg from Table 4.10 the total hardness of the process water was reduced from 5553 ppm to 317 ppm, which was 99.94 % reduction of the total hardness of the process water. The effective total hardness

reduction for the original SCMW using the concentrations of Ca and Mg from Table 4.3 was from 4919 ppm to 317 ppm, which translates to 94 % effective total hardness reduction after the SCMW was passed through all the treatment steps undertaken in this study. The total water hardness was still above the required limit of 100 ppm (DWAF, 1996),

When the CO₂ was reacted with process water from FA and Al(OH)₃ treatment for 10 mins the pressure decreased from 275.79 KPa to 206.842 KPa and the pH was reduced from 11.68 to 7.06. From the ideal gas equation ($pV = nRT$) this means:

$$n(\text{CO}_2) = \frac{pV}{RT} \text{ where } n: \text{ number of moles, } p: \text{ pressure (Pa), } R: \text{ ideal gas constant (J.K}^{-1}\text{mol}^{-1}) \text{ and } T: \text{ temperature (K)}$$

$$n(\text{CO}_2) = \frac{68948 \times 0.00035}{8.314 \times 298} = 0.00974 \text{ moles}$$

$$\text{Mass of CO}_2 \text{ used: } m(\text{CO}_2) = nMr$$

$$m(\text{CO}_2) = 0.00974 \text{ mol} \times 44 \text{ g / mol}$$

$$= 0.4286 \text{ g/100 ml of process water}$$

$$= 4.286 \text{ t/ML of process water}$$

Since most coal mines are situated near coal power stations, the source of CO₂ can be the flue gas from the boilers. Hendrina power station emits 11 Mt per annum of CO₂ (Engelbrecht et al., 2004). This enhances the sustainability of this water treatment technique. This will also be another way of reducing CO₂ emissions by Hendrina coal power station and hence reducing atmospheric contamination. About 4.286 t/ML of CO₂ could be expected to be sequestered by mineral carbonation of the process water.

4.10: TRACE ELEMENTS

Apart from the major elements, Hendrina FA was composed of trace elements such as Sr, Zr, V, Ce, Ba, Pb, Y, Zn, Cu, Ni, Rb, Nb, Co, Mo and As (Table 4.1).

The behavior of these elements was studied during the different treatments of mine water applied in this study. Analysis of the trace element concentration of the following product waters was performed by ICP-MS as specified in section 3.63 and the results are presented in Table 4.11:

- (i) the product water after treating mine water with FA,
- (ii) the product water after treating mine water with FA followed by adding $\text{Al}(\text{OH})_3$ and
- (iii) after CO_2 addition for pH regulation.

Table 4.11: Trace element concentration after different treatment stages of simulated circumneutral mine water (SCMW)

Element (ppm)	SCMW	After mixing FA	After mixing $\text{Al}(\text{OH})_3$	After mixing with CO_2	DWAF 1996a	WHO, 2008
pH	6.5	12.35	11.68	7.06	6-9	6.5-8.5
B	ND	2.2	1.8	1.4	0.5	0.5
Ti	0.000067	0.00013	0.000045	ND		
V	0.000049	0.0006	0.00012	0.00017	0.1	
Cr	0.00016	0.031	0.030	0.023	0.05	0.05
Co	ND	ND	ND	ND		
Ni	0.00023	0.000098	0.000096	0.00012		
Cu	0.00054	0.00091	0.000026	ND	1	2
Zn	0.0045	0.0029	0.0012	ND		3
As	0.000051	0.000053	ND	ND		0.01
Se	0.00021	0.0044	0.0029	0.0041	0.05	0.01
Mo	0.00089	0.30	0.3	0.018	0.05	0.07
Cd	ND	ND	ND	ND		
Ba	0.00099	0.048	0.013	0.0093		0.7
Pb	0.000051	0.00028	0.00019	0.000063		0.01
Si	0.026	0.66	0.34	0.26		
Sr	1.66	11.8	12.3	18.79		
K	36	48	51	51	50	
Na	25	32	33	37	100	200
Cl^-	74	76	77	72.67		250
NO_3^-	39	38	33	40.67	200	500

ND: not detected

Table 4.11 showed that after treating SCMW with Hendrina FA to pH 12.35, Ni and Zn were removed from the mine water by approximately 57 and 35 % respectively. Co and Cd were not detected in the mine water and the process waters. Major elements such as K and Na as well as traces such as Ti, V, Cu, As, B, Se, Ba, Pb, Si, Cr, B, Mo and Sr were found to leach from Hendrina FA into mine water, but were still below the required DWAF or WHO limit for domestic use water except Cr, B and Mo which were present after treatment in levels above the domestic limit for potable water (Table 4.11). Cr, B and Mo concentrations were increased from approximately zero to 0.03, 1.8 and 0.3 ppm respectively after treatment of SCMW with Hendrina FA.

After adding $\text{Al}(\text{OH})_3$, the concentration of As, B, Ti, V, Se, Ba and Si were reduced. Arsenic was reduced to below detection limit. Se, B, Ti, Ba and Si were reduced by 34, 45, 65, 80, 73 and 48 % respectively. This is because as ettringite is forming some of these elements such as Se, B and As in the form of their oxyanions are incorporated into its structure in place of SO_4^{2-} (Zhang and Reardon, 2003; Chrysochoou and Dermatas, 2006). There was no significant change of the composition of trace elements after reacting CO_2 with process water to neutralize it after FA and $\text{Al}(\text{OH})_3$ treatment.

Previous work has shown the potential of zeolite adsorbents synthesized from coal FA to remove these toxic elements such as Cr, Mo and B (Somerset et al. 2005, Somerset et al., 2008, Petrik et al., 2006, Moreno et al., 2001). It is thus proposed that these last remaining trace elements should be removed via adsorption with zeolites to make this treatment option viable.

In summary, mine water treatment with FA resulted in SO_4^{2-} removal from between 20000-4500 ppm to between 1000-1500 ppm. Major cations such as Fe, Al, Mn, and Mg were removed to below the DWAF limit for potable water when pH of SCMW was raised to 12 using Hendrina FA. When SCMW was reacted with FA elements such as K, Na, Ti, V, Cu, As, B, Se, Ba, Pb, Si, Cr, B, Mo and Sr leached into the SCMW from Hendrina FA. All other elements leached to

below the acceptable limits except Cr, Mo and B. Further refining of the process water from FA treatment using gypsum seeding and addition of $\text{Al}(\text{OH})_3$ was capable of reducing the concentration of SO_4^{2-} further to levels around 500 ppm which is slightly above the threshold for drinking water requirements of 400 ppm. Gypsum seeding was found to play an insignificant role in refining the process water from FA treatment compared to addition of $\text{Al}(\text{OH})_3$ at pH greater than 12. Process water from FA and $\text{Al}(\text{OH})_3$ treatment was found to be highly alkaline ($\text{pH} > 12$) and with total water hardness of 5553 ppm. Upon carbonation the pH was reduced from 11.68 to 7.06 while the total hardness was reduced by 99.94 % to 317 ppm through CaCO_3 precipitation. The product water from all the treatment steps had all contaminants to below the allowed limits except for Cr, Mo, B and the water hardness which was still in hard category.

A proposed flow diagram is presented in Figure 4.33 showing all the steps that were carried in this study. Included in the flow diagram is a recommended additional step to remove trace elements such as Cr, B and Mo if good quality potable water is required.

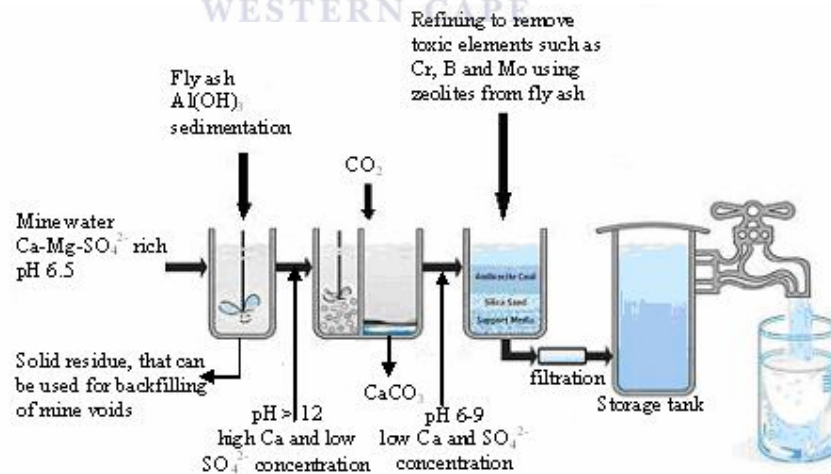


Figure 4.33: A proposed flow diagram for the mine water treatment with a recommended step to remove Cr, Mo and B

CHAPTER 5 : CONCLUSION AND RECOMMENDATIONS

5.1: CONCLUSION

The results from this study have proved that SO_4^{2-} can be removed from Middleburg mine water to 500 ppm which is slightly above the DWAF threshold of 400 ppm for potable water by treating with Hendrina fly ash followed by ettringite precipitation.

This study was carried out with the aim of understanding the mechanism of the removal of SO_4^{2-} from mine waters with Hendrina fly ash by understanding the following: the effect of the amount of fly ash used, the effect of the final pH achieved during treatment, the effect of the initial pH of the mine water and the effect of the composition of the mine water. Also this study involved the application of the ettringite precipitation method to remove SO_4^{2-} to below 500 ppm.

From the results obtained in this study it can be concluded that SO_4^{2-} removal depends on; the amount of FA used, the final pH achieved and the composition of the mine water. The initial pH of the mine water does not play a significant role on SO_4^{2-} removal with only an additional 4 % obtained when the starting pH was 2.3 instead of 6.5. The percentage of SO_4^{2-} removed from simulated circumneutral mine water depended on the amount of Hendrina fly ash added. A ratio of simulated circumneutral mine water to fly ash of 2:1 achieved 71 % SO_4^{2-} removal compared to 55 % achieved with a 5:1 ratio. More fly ash added means more CaO available to leach and react with SO_4^{2-} to form gypsum. The SO_4^{2-} removal from SCMW was directly related to the dissolution of available free CaO on the FA particles up to 3.09 g of CaO per 200 ml of SCMW thereafter the removal was constant.

Sulphate removal was found to depend on the final pH end point achieved during the treatment of simulated circumneutral mine water treatment with Hendrina fly ash. Treatment of simulated circumneutral mine water with Hendrina fly ash to pH 9, 10, 11 and 12 resulted 6, 19, 45 and 71 % SO_4^{2-} removal respectively.

Mine waters of different composition show different mechanisms of SO_4^{2-} removal at different final pH of treatment. Removal of SO_4^{2-} from modified circumneutral mine water by mixing with Navigation coal mine AMD showed that more SO_4^{2-} were removed when pH was increased to 10 (93 %), while 6 % SO_4^{2-} removal was observed when unmodified circumneutral mine water (Fe and Al poor) pH was increased to 10. Navigation coal mine acid mine drainage was used a source of Fe and Al when mixed with circumneutral mine water.

The mechanism for SO_4^{2-} removal from circumneutral mine water depends on gypsum precipitation. The mechanism was different from the way SO_4^{2-} were removed from Fe and Al rich mine water which involves gypsum precipitation in conjunction with Fe and Al oxyhydroxysulphates precipitation. The oxyhydroxysulphates predicted using PHREEQC thermodynamic modelling are jarosites, alunite, basaluminite, jurbanite and ettringite, which were found to precipitate at pH 4-9.

Addition of $\text{Al}(\text{OH})_3$ to simulated circumneutral mine water that have been treated to pH greater than 12 have shown that SO_4^{2-} can be further precipitated out from between 1000-2000 ppm to 500 ppm. Gypsum seeding at pH greater than 12 reduced the SO_4^{2-} concentration by only 200 ppm.

Mine water treatment using FA can successfully remove all major elements such as Fe, Al, Mn and Mg to below the DWAF limit for potable water. Fe and Al were found to be removed at pH 4-7, while Mn and Mg were removed at pH 9 and 11 respectively. Elements such as K, Na, Ti, V, Cu, As, Se, B, Ba, Pb and Si leach from FA during treatment of mine water with FA to levels below the allowed DWAF limits for potable water. Cr, B and Mo leached into the mine water to

0.03, 1.8 and 0.3 ppm respectively after treatment of simulated circumneutral mine water with Hendrina fly ash which was above the DWAF limits for potable water of 0.05 ppm for Cr, 0.5 ppm for B and 0.05 ppm for Mo.

The advantage of using fly ash to treat mine water compared to the use of chemical is that it is cheaper because fly ash is a waste material found close to coal mines producing polluted mine water.

5.2: RECOMMENDATIONS FOR FUTURE WORK

This study has proved that FA can be used to treat mine water to remove most of the contaminants from the Fe-Al rich and Ca-Mg mine waters. The problem lies with the trace elements such as Cr, B and Sr that leach into the water from Hendrina FA. I recommend that if potable water need to be produced in sustainable way zeolites synthesized from FA or solid residues obtained after treating mine water can be used to further refine the water to remove these trace elements.

Also this study needs to be applied to some other mine water such as Na-K rich mine waters to find out if significant SO_4^{2-} removal could be achieved. Also the use of other FA from nearby coal power stations such as Arnot, Duvha, Komati and Kendal need to be evaluated in order to compare the efficiency of these FAs in treatment of Middleburg mine water.

REFERENCES

- Adlem, C.J.L. 1997, "Treatment of sulfate-rich effluents with the barium sulfide process", University of Pretoria, South Africa.
- Adriano, D.C., Page, A.L., Elseewi, A.A., Chang, A.C. & Straughan, I. 1980, "Utilization and disposal of fly ash and other coal residues in terrestrial ecosystems: A review", *Journal of Environmental Quality*, **9**, pp. 333-344.
- Appelo, C.A.J. & Postma, D. 2005, "Geochemistry, groundwater and pollution", 2nd edn, A.A. Balkema Publishers, New York.
- ASTM 1994, "Standard specification for fly ash and raw or calcined natural pozzolan for use as mineral admixture in Portland cement concrete", American Society for Testing and Materials, Pennsylvania.
- Banks, D., Younger, P.L., Arnesen, R.L., Egil R. Iversen, E.R. & Banks, S.B. 1997, "Mine-water chemistry: the good, the bad and the ugly", *Environmental Geology*, **32** (3), pp. 157-174.
- Barson, M.S., Van Niekerk, P.H. & van Rooyen, J.A. 1997, "Overview of Water Resources Availability and Utilization in South Africa", Department of Water Affairs and Forestry, Pretoria.
- Blowes, D.W., Ptacek C J., Jambor, J.L., Weisener C.G. 2003, "The Geochemistry of Acid Mine Drainage" in *Environmental Geochemistry* Elsevier-Pergamon, Oxford, UK, pp. 149-204.
- Blowes, D.W. and Ptacek, C.J. 1994, "Acid-neutralization mechanisms in inactive mine tailings" in Short Course Handbook on Environmental Geochemistry of Sulfide Mine Waste, ed. Jambor, J.L. and Blowes, D.W., 22nd edn, Mineralogical Association of Canada, Nepean, Canada, pp. 271-291.

Bosman, D.J. 1983, "Lime treatment of acid mine water and associated solids/liquid separation", *Water Science and Technology*, **15**, pp. 71-84.

Bosman, D.J., Clayton, J.A., Maree, J.P. & Adlem, C.J.L. 1990, "Removal of sulphates from mine water with sulphide", Proceedings of the Lisbon 90 International Symposium: Acidic Mine Water in Pyritic Environments, Lisbon, Portugal, pp. 16.

Brown, M., Barley, B. and Wood, H. 2002, "Mine water Treatment Technology, Application and Policy", IWA Publishing.

Butler, J.N. 1991, "Carbon Dioxide Equilibria and Their Applications", Chelsea, MI: Lewis Publishers.

Chrysochoou, M. & Dermatas, D. 2006, "Evaluation of ettringite and hydrocalumite formation for heavy metal immobilization: Literature review and experimental study", *Journal of hazardous materials*, **136**(1), pp. 20-33.

Conlon, W.J. 1990, "Chapter 11 Membrane process. Water Quality and Treatment" in A handbook of Community Water Supplies, 4th edn, American Water Works Association, McGraw-Hill Inc., pp. 561-640.

Coulton R., Bullen C., Hallett C. 2003, "The design and optimisation of active mine water treatment plants", *Land Contamination and Reclamation*, **11**(2), pp. 273-279.

Cravotta, C.A., Brady, K.B.C., Smith, M.W. & Beam, R.L. 1990, "Effectiveness of the addition of alkaline materials at surface coal mines in preventing or abating acid mine drainage- Prt 1, Geochemical considerations", Proceedings of the 1990 Mining and Reclamation Conference, ed. W.V. Charleston, West Virginia University, Morgantown, pp. 221-223.

Cravotta, C.A. & Trahan, M.K. 1999, "Limestone drains to increase pH and remove dissolved metals from acidic mine drainage", *Applied Geochemistry*, vol. 14, pp. 581-606.

Davies, B.R., O'keeffe, J.H. & Snaddon, C.D. 1993, "A Synthesis of the Ecological Functioning, Conservation and Management of South African River Ecosystem", Water Research Commission, Pretoria.

Del Pino, M.P. & Durham, B.D. 1999, "Wastewater reuse through dual-membrane processes: opportunities for sustainable water resources", *Desalination*, **124**(1-3) pp. 271-277.

Department of Water Affairs and Forestry 1996, "South African Water Quality Guidelines (second edition), Volume 3: Industrial Use", CSIR Environmental Services, Pretoria, South Africa.

Department of Water Affairs and Forestry 1996, "South African Water Quality Guidelines (second edition), Volume 1: Domestic Use", CSIR Environmental Services, Pretoria, South Africa.

Engelbrecht, A., Golding, A. & Hietkamp, S. 2004, "The potential for sequestration of CO₂ in South Africa", Council for Scientific and Industrial Research, South Africa.

Eskom, 2008, "Annual Report", www.eskom.co.za/annreport08/downloads/.pdf

Exxaro, 2007, "Annual report", <http://financialresults.co.za/exxaroar2007/opgrowth.htm>.

Foner, A.H., Robl, L.T., Hower, C. & Graham, M.U. 1999, "Characterization of fly ash from Israel with reference to its possible utilization", *Fuel*, **78**, pp. 215-223.

Furr, A.K., Parkinson, T.F., Gutenmann, W.H., Pakkala, I.S. & Lisk, D.J. 1978, "Elemental content of vegetables, grains and forages field grown on fly ash-amended soil", *J. Agric. Food Chem.*, **26**, pp. 847-851.

Gazea, B., Adam, K., Gazea, B. & Adam, K. & Kontopoulos, A. 1996, "A review of passive systems for the treatment of acid mine drainage", *Journal of Minerals Engineering*, **9**(1), pp. 23-42.

Geldenhuys, A.J., Maree, J.P., de Berr, M. & Hlabela, P. 2001, "An Integrated limestone/lime process for partial sulphate removal", CSIR, South Africa.

Gitari, M.W., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E. & Okujeni, C. 2006, "Treatment of acid mine drainage with fly ash: removal of major contaminants and trace elements", *J. Environ. Sci. Health A: Tox. Hazard. Subst.*, **41**, pp. 1729-1747.

Gitari, W.M., Petrik, L.F., Etchebers, O., Key, D.L., Iwuoha, E. & Okujeni, C. 2008, "Utilization of Fly Ash for Treatment of coal mines waste water: Solubility controls on major inorganic contaminants." *Fuel*, **87**, pp. 2450-2462.

Hammack, R.W., Dvorak, D.H. & Edenborn, H.M. 1993, "The Use of Biogenic Hydrogen Sulfide to Selectively Recover Metals from a Severely Contaminated Mine Drainage", Proceedings of the International Biohydrometallurgy Symposium, Jackson Hole, WY.

Hammack. R.W, de Vegt.A.L and Schoeneman.A.L., 2006, "The removal of sulfates and metals from mine waters using bacterial sulfate reduction: Pilot plant results," *Mine water and the Environment*.

Hedin, R.S., Nairn, R.W. and Kleinmann, R.L.P. 1994, "Passive Treatment of Coal Mine Drainage", US Bureau of Mines.

Hlabela, P., Maree, J. & Bruinsma, D. 2007, "Barium Carbonate Process for Sulphate and Metal Removal from Mine Water", *Mine Water and the Environment*, **26**, pp. 14-22.

Jenke, R.D. & Gordon, K.P. 1983, "Chemical changes in concentrated, Acidic, Metal-bearing waste when treated with Lime", *Environmental Science and Technology*, **17**(4).

Johnson, B.D. & Hallberg, K.B. 2005, "Acid mine drainage remediation options: a review", *Science of the Total Environment*, **338**, pp. 3-14.

Johnson, D. B. 2000, "Biological removal of sulfurous compounds from inorganic wastewaters", In: Lens PNL, Hulshoff Pol LW (eds) *Environmental Technologies*. International Association on Water Quality, London, pp 175–206.

Johnson, D.B. & Hallberg, K.B. 2003, "The microbiology of acidic mine waters", *Res Microbiol*, **154**, pp. 466-473.

Johnson, D.B. & Hallberg, K.B. 2004, "Biogeochemistry of the compost bioreactor components of a composite acid mine drainage passive remediation system", *Science of the Total Environment*, **338**, pp. 81-93. .

Kalin, M., Fyson, A. & Wheeler, W.N. 2006, "The chemistry of conventional and alternative treatment systems for the neutralization of acid mine drainage", *Science of the Total Environment*, **366**(2-3), pp. 395-408.

Kentish, S.E. & Stevens, G.W. 2001, "Innovations in separations technology for the recycling and re-use of liquid waste streams", *Chemical Engineering Journal*, **84**(2), pp. 149-159.

Keplar, D.A., and McCleary, E.C. 1994, "Successive Alkalinity Producing Systems (SAPS) for the treatment of acidic mine drainage", International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage Pittsburgh, P.A, pp. 195.

Kitchener, J.A. 1957, "Ion-exchange Resins", Butler and Tanner Ltd, Great Brittan.

Klink, M.J. 2003, The potential use of South African coal fly ash as a neutralization treatment option for acid mine drainage, MSc thesis, University of the Western Cape, Cape Town.

Kumpiene, J., Lagerkvist, A., Christian, M. 2006, "Stabilization of Pb and Cu contaminated soil using coal fly ash and peat", *Fuel*, **85**, pp. 2537-2544.

Lapakko, K.A. 1994, "Determinations for Metal Mine Waste and a Proposed Alternative", International Land Reclamation and Mine Drainage Conference and 3rd International Conference on the Abatement of Acidic Drainage, Pittsburgh, **1**, pp. 129-137.

Lawrence, R.W. and Wang, Y. 1997, "Determination of Neutralization Potential in the Prediction of Acid Rock Drainage," 4th International Conference on Acid Rock Drainage, Vancouver, BC, pp. 449.

Lottermoser, B.G. 2007, "Mine Wastes: Characterization, Treatment and Environmental Impacts". 2nd edn, Springer.

Madzivire, G., Petrik, L.F., Vadapalli, V.R.K. & Gitari, W.M. 2008, "Optimization of sulfate removal from circumneutral mine water using fly ash", 39th SACI National Convention, Stellenbosch University, Stellenbosch, South Africa, pp. 162.

Maree, J.P. 1988, "Sulphate removal from industrial effluents", PhD thesis, University of the Orange Free State, Bloemfontein.

Maree, J.P., Bosman, D.J. & Jenkins, G.R. 1989, "Chemical removal of sulphate and calcium and heavy metals from mining and power station effluents", *Water Sewage and Effluents*, **9**, pp. 10-25.

Martinez-Tarazona, M.R. & Spears, D.A. 1996, "The fate of trace elements and bulk minerals in pulverized coal combustion in a power station", *Fuel Processing Technology*, **47**(1), pp. 79-92.

Matsuura, T. 2001, "Progress in membrane science and technology for seawater desalination — a review", *Desalination*, **134**(1-3), pp. 47-54.

Mattigod, S.V., Dhanpat Rai., Eary, L.E. & Ainsworth, C.C. 1990, "Geochemical factors controlling the mobilization of inorganic constituents from fossil fuel combustion reisdues: Review of the major elements.", *Journal of Environmental Quality*, **19**, pp. 188-201.

Mattson, M.E. & Lew, M. 1982, "Recent Advances in reverse osmosis and electro dialysis membrane desalting technology ", *Desalination*, **41**(1), pp. 1-24.

McCarthy, G.J. 1988, "X-ray powder diffraction for studying the mineralogy of fly ash, in Fly Ash and Coal Conversion By-Products: Characterization, Utilization and Disposal IV.", *Mater. Res. Soc. Symp. Proc.*, pp. 75.

Moreno, N., Querol, X., Ayora, C., Pereira, C.F. & Janssen-Jurkovičová, M. 2001, "Utilization of zeolites synthesized from coal fly ash for the purification of acid mine waters", *Environment Science Technology*, **35**, pp. 3526-3534.

Morin, K.A. & Hutt, N.M. 1997, "Environmental Geochemistry of Minesite Drainage: Practical, Theory and Case Studies", MDAG, Vancouver, Canada.

Mukhopadhyay, B., Bastias, L. & Mukhopadhyay, A. 2007, "Limestone drain design parametrs for acid rock drainage mitigation", *Mine Water and the Environment*, **26**, pp. 29-45.

Myneni, S.C.B., Samuel J. Traina, S.J. & Logan, T.J. 1998, "Ettringite solubility and geochemistry of the $\text{Ca}(\text{OH})_2\text{-Al}_2(\text{SO}_4)_3\text{-H}_2\text{O}$ system at 1 atm pressure and 298 K", *Chemical Geology*, **148**, pp. 1-19.

Naido, B. 2007, "Mine water to alleviate predicted water supply stresses", Creamer Media, South Africa.

Nairn, R.W., Hedin, R.S. & Watzlaf, G.R. 1991, "A Preliminary Review of the Use of Anoxic Limestone Drains in the Passive Treatment of Acid Mine Drainage", Proceedings of the 12th Annual West Virginia Surface Mine Drainage Task Force Symposium, Morgantown, WV.

Nairn, R.W. & Mercer, M.N. 2000, "Alkaline generation and metals retention in a successive alkalinity producing system", *Mine Water and the Environment*, **19**, pp. 124-133.

Neculita, C.M., Zagury, G.J. & Brussie, B. 2007, "Passive treatment of acid mine drainage in bioreactors using sulfate-reducing bacteria: critical review and research needs", *Journal of Environmental Quality*, **36**, pp. 1-36.

Nyavor, K., Egiebor, N.O. & Fedorak, P.M. 1996, "Suppression of microbial pyrite oxidation by fatty acid amine treatment", *Science of The Total Environment*, vol. **182**(1-3), pp. 75-83.

Nyquist, Richard. A., Putzig, Curtis. L., Leugers, M. Anne. 1997, "Infrared and Raman Spectral Atlas of Inorganic Compounds and Organic Salts Text and Explanation", 1st edn, Gulf Publishing Company, USA.

Pérez-López, R.P., Nieto, J.M. & Ruiz de Almodóvar, G. 2007, "Utilization of fly ash to improve the quality of the acid mine drainage generated by oxidation of a sulphide-rich mining waste: column experiments", *Chemosphere*, **67**, pp. 1637-1646.

Parkhurst, D.L. and Appelo, C.A.J. 1999, "User's guide to PHREEQC (version 2)-A computer program for speciation, batch-reaction, one-dimensional transport, and inverse geochemical calculations", USGS.

Perkins, R.B. & Palmer, C.D. 1999, "Solubility of ettringite ($\text{Ca}_6[\text{Al}(\text{OH})_6]_2(\text{SO}_4)_3 \cdot 26\text{H}_2\text{O}$) at 5–75°C", *Geochimica et Cosmochimica Acta*, **63**(13/14), pp. 1969-1980.

Petrik, L.F., Hendricks, N., Ellendt, A. & Burgers, C. 2006., "Toxic element removal from water using zeolite adsorbents made from solid residues", WRC, South Africa.

Petrik, L.F., White, R.A., Klink, M.J., Somerset, V.S., Burgers, C.L. & Fey, M.V. 2003, "Utilization of South African fly ash to treat acid coal mine drainage, and

production of high quality zeolites from the residual solids", Proceedings of the International Ash Utilization Symposium, University of Kentucky, Centre of Applied Energy Research, , pp. 1-26.

Pinetown, K.L., Ward, C.R. & van der Westhuizen, W.A. 2007, "Quantitative evaluation of minerals in coal deposits in the Witbank and Highveld Coalfields, and the potential impact on acid mine drainage", *International Journal of Coal Geology*, **70**(1-3), pp. 166-183.

Postgate, J.R. (ed) 1984, "The Sulphate-Reducing Bacteria", 2nd edn, Cambridge University Press., New York.

Potgieter-Vermaak, S.S., Potgieter, J.H., Monama, P. & Van Grieken, R. 2006, "Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage", *Minerals Engineering*, **19**(5), pp. 454-462.

Ríos, C.A., Williams, C.D. & Roberts, C.L. 2008, "Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites", *Journal of Hazardous Materials*, **156**(1-3), pp. 23-35.

Robb, G. A., Robinson, J. D. F. 1995, "Acid drainage from mines", *The Geographical Journal*, **161**(1), pp. 47-55.

Rowley, M., Warkentin, D.D. & Sicotte, V. 1997, "Site demonstration of the biosulfide process at the former Britannia mine", Proceedings of the Fourth International Conference on Acid Rock Drainage, Vancouver, BC, pp. 1531.

Roy. D.M., Luke. K., Diamond. S. 1985, "Characterization of fly ash and its reactions in concrete.", *Mater. Res.Soc. Symp. Proc.*, **43**, pp. 3-20.

Schoeman J.J & Steyn A 2001, "Investigation into alternative Water Treatment Technolgies for the treatment of underground mine water discharged by Grootvlei Proprietary Ltd Into the Blesbokspruit in South Africa ", *Desalination*, **133**, pp. 13-30.

Seth, R. & Ghazi, M.A. 1997, "Release of sorbed sulfate from iron oxyhydroxides precipitated from acid mine drainage associated with coal mining", *Environmental Science and Technology*, **31**, pp. 2136-2140.

Skousen, J., Renton, J., Brown, H., Evans, P., Leavitt, B., Brady, K., Cohen, L. and Ziemkiewicz, P. 1997, "Neutralization Potential of Overburden Samples Containing Siderite", *Journal of Environmental Quality*, **6**(3), pp. 673-681.

Skousen, J.G., Smith, R.M., Sencindiver, J.C. 1990, "The development of the acid base account. Green Lands", *West Virginia Mining and Reclamation Association*, **20**(1), pp. 32-37.

Smit, J., Sibilski, U.E. 2003, "Pilot Plant Study to Treat Typical Gold Mine Minewater Using the SAVMIN Process", *Water in Mining Conference*, Brisbane, Australia.

Smit, J.P. 1999, "The purification of polluted mine water", *International symposium of Mine Water & Environment for the 21st Century* Seville, Spain.

Sobek, A.A., Schuller, W.A., Freeman, J.R. and Smith, R.M. 1978, "Field and laboratory methods applicable to overburden and minesoils", EPA 600/2-78-054, pp. 203.

Somerset, V., Petrik, L. & Iwuoha, E. 2008, "Alkaline hydrothermal conversion of fly ash precipitates into zeolites 3: The removal of mercury and lead ions from wastewater", *Journal of Environmental Management*, **87**, pp. 125-131.

Somerset, V., Petrik, L. & Iwuoha, E. 2005, "Alkaline Hydrothermal Conversion of Fly Ash Filtrates Into Zeolites 2: Utilization in Wastewater Treatment", *Journal of Environmental Science & Health, Part A: Toxic/Hazardous Substances & Environmental Engineering*, **40**(8), pp. 1627-1636.

Steed, V.S., Suidan, M.T., Gupta, M., Miyahara, T., Acheson, C.M. & Sayles, G.D. 2000, "Development of a sulfate-reducing biological process to remove

heavy metals from acid mine drainage", *Water Environment Research*, **72**, pp. 530-535.

Stumm, W. & Morgan, J.J. 1996, "Aquatic Chemistry", Wiley & Sons, New York.

Stumm, W. & Morgan, J.J. 1981, "Aquatic chemistry", 2nd edn, John Wiley & Sons, New York.

Summers, R., Clarke, M., Pope, T. & O'Dea, T. 1998, "Western Australian fly ash on sandy soils for clover production", *Commun Soil Sci Plant Anal*, **29**, pp. 2757-2767.

Taylor, H.F.W. 1998, "Cement Chemistry", 2nd edn, Thomas Telford, London.

Tzoneva, D. 2008, "Mine water treatment plant under way", Creamer Media, South Africa.

Uhlmann, W., Buttcher, H., Totsche, O. & Steinberg, C.E.W. 2004, "Buffering of Acidic Mine Lakes: The relevance of Surface Exchange and Solid Bound Sulphahte", *Mine Water and Environment*, **23**, pp. 20-27.

Valerdi-Pérez, R., López-Rodríguez, M. & Ibáñez-Mengual, J.A. 2001, "Characterizing an electro dialysis reversal pilot plant", *Desalination*, **137**(1-3), pp. 199-206.

Van den Berg, J.J., Cruywagen, L., De Necker, E. & Hodgson, F.D.I. 2001, "The suitability and impact of power station fly ash for water quality control in coal opencast mine rehabilitation: Acid Mine Drainage Neutralization, Conditioning and Partial", VINNICOMBE, D.A 2000.

Wesche, K. 1991, "Characterization of fly ash in Fly Ash in Concrete: Properties and Performance", Taylor & Francis, pp. 3-22.

Wieder, R.K. & Lang, G.E. 1982, "Modification of acid mine drainage in a freshwater wetland", Proceedings of the Symposium on Wetlands of the

Unglaciated Appalachian Region, ed. B.R. McDonald, West Virginia University, Morgantown, USA, pp. 43.

Wingenfelder, U., Hansen, C., Furrer, G. & Schulin, R. 2005, "Removal of heavy metals from mine waters by natural zeolites", *Environ. Scie. Technol.*, **39**, pp. 4606-4613.

WISA, 2009, 12/03/2009-last update, "Domestic Water Quality Guidelines", Water Institute of South Africa: <http://www.ewisa.co.za/domesticguidelines>.

World Health Organization 2008, "Guidelines for drinking-water quality, third edition, incorporating first and second addenda Volume 1 – Recommendations", WHO Press, Geneva.

Younger, P.L., Banwart, S.A. & Hedin, R.S. 2002, "Mine Water: Hydrology, Pollution, Remediation", Dordrecht Kluwer Academic Publishers.

Yunusa, I.A.M., Eamus, D., DeSilva, D.L., Murray, B.R., Burchett, M.D., Skilbeck, G.C. & Heidrich, C. 2006, "Fly ash: An exploitable resource for management of Australian agricultural soils", *Fuel*, **85**, pp. 2337-2344.

Zhang, M. & Reardon, E.J. 2003, "Removal of B, Cr, Mo, and Se from Wastewater by Incorporation into Hydrocalumite and Ettringite", *Environmental Science and Technology*, **37**(13), pp. 2947-2952.

Ziemkiewicz, P.F., Skousen, J.G., Brandt, D.L., Sterner, P.L. & Lovett, R.J. 1997, "Acid mine drainage treatment with armored limestone in open limestone channels", *Journal of Environmental Quality*, **26**, pp.1017-1024.