REMEDIATION OF ACID MINE DRAINAGE USING METALLURGICAL SLAGS

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DECLARATION

I declare that this dissertation is my own unaided work. It is being submitted to the degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any other degree or examination in any other University.

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ABSTRACT

This research focuses on the remediation of Acid Mine Drainage (AMD) using metallurgical slags. Slag leach beds are a promising low cost and low maintenance technology for the remediation of AMD compared to potentially expensive and maintain once intensive conventional active methods that entail addition of chemicals to treat AMD. Slags are highly alkaline in nature hence they neutralise acidic water; this in turn leads to reduction of iron and sulphate concentration due to formation of iron precipitates and gypsum at higher pH values. Laboratory experiments were carried out to investigate the possibility of reducing acid, iron and sulphate concentration from synthetic AMD using two types of slag namely the basic oxygen furnace and stainless steel slag. These experiments include ratio tests, contact time tests and continuous flow studies.

Experiments were performed to determine the optimum slag to AMD ratios that would result in maximum pH increase as well as maximum iron and sulphate reduction. These experiments were carried out by varying the amount of slag in use per 1L of AMD for a given period of time. The ratio tests showed that the amount of iron and sulphate removed as well reduction of acidity increased with an increase in the slag to AMD ratio with both slags used. This was an indication that chemical reaction and precipitation was taking place. It was found that 100 g/L of slag: AMD was the optimum ratio. At that ratio a resultant pH of 12.31, 99.7% iron reduction and 75.0% sulphate reduction was achieved.

The reduction of acid, iron and sulphate concentration was rapid in the first hour of mixing slag and AMD in processes carried out to investigate the effect of contact time. It was discovered that reduction gradually decreased with time for all experiments under investigation. The continuous flow studies showed that slags were also capable of reducing acid, iron and sulphate concentration from synthetic AMD in a continuously flowing process. The data collected showed that iron was removed from 1000 mg/L to undetectable concentration while sulphate was reduced from 5000 mg/L to 743 mg/L, which translated to 85.1% decrease for a residence time of 2.0 hours. For a residence of 2.53 hours, sulphate was reduced from 5000 mg/L to 693 mg/L which translated to 86.1% decrease. The pH was also increased from 2.25 to 13.21. The Department of Water Affairs and Forestry (DWAF) standards stipulate that wastewater must have iron concentration less than 0.30 mg/L and sulphate concentration less than 400 mg/L. The results show that iron was reduced below the

DWAF general limit for wastewater while sulphate was still above that limit. A graph was also created to predict the amount of slag required to treat different AMD flowrates for different residence times and target concentrations of iron and sulphate.

The results obtained, it was shown that slags are a viable option to treating AMD. The results also revealed that basic oxygen furnace slag was better than stainless steel slag for reducing acidity, iron and sulphate concentration. Slags were able to bring about high pH values necessary for formation of iron precipitates as depicted by the Pourbaix diagram for the iron-sulphate- water system. This therefore ensured that soluble iron was removed from water in the form of various insoluble compounds. The results therefore indicate that metallurgical slags are well suited for increasing pH values of AMD and reducing iron.

DEDICATION

My late parents, Ester Shumba and Zvenyika Mack Name, my greatest pleasure would be to share this moment with them.

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CHAPTER ONE

INTRODUCTION

“All truths are easy to understand once they are discovered; the point is to discover them”.

~ Galileo Galilei

1.1 Introduction

South Africa owes most of its wealth to its mineral rich areas such as the Johannesburg metropolitan area with coal and gold being two of its most important natural resources. These resources are taken from the ground through cost effective mining methods. However, the legacy of mining in the metropolitan areas has posed challenges such as the threat of groundwater and surface water contamination arising from Acid Mine Drainage (AMD). Considering the environmental and ecological threats this poses there is a need for innovative techniques to address the situation.

AMD is acidic water laden with iron, sulphate and other metals that forms under natural conditions when geologic strata containing pyrite or other sulphide bearing minerals are exposed to the atmosphere or oxidizing environments (Fripp et al., 2000; Taylor et al., 2005; Jennings et al., 2008; Gaikwad & Gupta, 2008). These waters typically pose a risk to the environment because they often contain elevated concentrations of metals such as iron, aluminium and manganese, and possibly other heavy metals such as uranium. AMD is said to be characterised by low pH, high metal concentration (iron being the most common) and elevated sulphate levels. AMD has detrimental effects to aquatic life and threatens domestic drinking water supplies due to the low pH.

AMD caused by mine operations is a global problem, and has been a topical issue worldwide for many years. AMD has therefore attracted a great deal of attention globally while in South Africa, much has been said in media and debates carried out in parliament. According to the Inter-ministerial committee on acid mine drainage (I-MCAMD, 2010) the main focus of attention is to address the Witwatersrand gold fields around Johannesburg as it has been listed as a problematic area with respect to AMD. AMD is also associated with coal mining which follows that the Witwatersrand basin is not the only area in South Africa that is at risk AMD contamination.

AMD has a significant potential to have an impact on the environment and the health of the people that are dependent on the water around the AMD polluted region. Radioactive substances like uranium in areas affected by AMD and the obvious damaging effect that it would have on human beings living nearby is also a cause for concern (Coetzee, 2006). AMD is not only an ecological concern, but also has detrimental consequences on the economy.

This is because regions impacted by AMD experience contamination of groundwater drinking supplies, a decline in fish of economic value, recreation and tourism and cost of treatment. Clean and fresh water are vital to the agricultural and industrial sectors. Buildings and infrastructure are subject to degradation with time due to the corrosive effects of AMD (Taylor et al., 2005). It is therefore advised to minimise or avoid AMD in any way possible.

Cobbing (2008) highlighted that heavily contaminated water has been flowing into streams on the West Rand (located below the Krugersdorp-Randfontein area) since 2002. Incidents of other areas being contaminated have surfaced around South Africa. Acid mine water from the Central Basin has also been predicted to flood the tourist level of the Gold Reef City shaft and water in the Eastern Basin is expected to reach the Environmental Critical Level by June 2013 (Chapman, 2011). In the Randfontein area, acidic water is flowing towards the Krugersdorp game reserve and the cradle of humankind world heritage site. It has also been reported also that toxic water has already destroyed life in the Tweelopiespruit and Robinson Lake near Randfontein on the West Rand (Chapman, 2011).

Focus on AMD remediation in the Witwatersrand gold basin is thus of paramount importance as suggested by the alarming statistics coming through in that region not least because this is the centre of population mass in South Africa. AMD pollution in that region is threatening access to clean water and such is bound to be accompanied by several socio-economic consequences; of which human and animal health risk is of the greatest concern (Hobbs & Cobbings, 2007).

Various treatment methods have been applied on AMD both locally and globally. These methods are categorised as active and passive. Slags are solid materials that result from the smelting and refining of metals. The use of Slag Leach Beds (SLBs) as a form of passive technology has not been fully investigated, but shows a lot of potential in being one of the most efficient technologies to treat AMD.

Clean water is universally an essential resource and South Africa faces a threat to water security in the near future if the issue of AMD is not fully addressed (Cobbing, 2008; Chapman, 2011). Recent research by the Department of Water Affairs and Forestry has predicted that the demand for potable water would exceed supply by 2020 if the issue of AMD is not dealt with urgently. The effectiveness of SLBs to remediate AMD for human health, environmental protection, potential reuse and recovery of mine water should be investigated since traditional and current methods in use have proved either costly or ineffective. SLBs have the potential to treat large volumes of AMD cost effectively because of the high availability of slag in areas with a large minerals refining industry. By assessing the ability of SLBs to neutralise acid, remove sulphates and iron from AMD in this study, the potential use of slags as a long term solution to AMD treatment will be established.

1.2 Problem Statement

AMD produced in the Witwatersrand gold fields has the potential to cause environmental degradation to ecosystems, human health and threatens the water security of the area. Numerous treatment technologies have been developed in recent years to tackle problems associated with AMD including active and passive treatment technologies, but no cost-effective scheme or long term solution has yet been found. Active technologies are widely used, but have been found to be expensive (Johnson & Hallberg, 2005; Sheoran & Sheoran, 2006). Passive treatment could have long term success in remediating AMD.

SLBs involve the use of a bed of slag wastes from metal refineries and smelters to treat AMD. Research involving the use of SLBs has mainly been focused on AMD from coal mines and less has been done on gold mines. The removal capacity of slag and the risk to the environment has not been fully investigated. Concerns have been raised about slags containing harmful or heavy metals which are released into the environment, since the available slag stock and maximum amount required to adequately treat AMD has not been fully investigated. As such it is not known how much AMD can be treated before slags are fully loaded and would therefore need replacement.

1.3 Research Objectives

The central focus of this research will be the remediation of AMD using SLBs. The leach beds will be constructed and then the ability of beds to remediate AMD, with particular focus on the reduction of acidity, sulphate and iron content of a typical Witwatersrand gold basin AMD investigated. The SLBs will be filled with Basic Oxygen Furnace (BOF) and Stainless Steel (SS) slag. An artificial AMD will be simulated and leaching of minerals from the slag will be conducted and remediation of AMD evaluated.

The specific objectives are:-

(i) To investigate the ability of the different slags to reduce the acid, sulphate and iron content of a typical Witwatersrand gold basin AMD.

(ii) To investigate kinetic studies so as to determine the pH changes and the amount of iron and sulphate removed by the slag from the AMD.

(iii) To maximise the reduction of iron and sulphate concentration and acidity of AMD.

(iv) To determine the capacity of slags to maintain alkalinity and reduce acidity, iron and sulphate concentration.

1.3.1 Hypothesis

The alkaline properties of SLBs can neutralise the acid and reduce iron and sulphate levels of AMD.

1.4 Scope of Research

The following principal tasks form the scope of this study: literature review, experimental design, laboratory test data analysis, conclusions and recommendations

1.5 Dissertation layout

This dissertation is made up of five chapters, each explaining the investigations performed on this research in detail. The summary of the chapters is given below:-

Chapter One: Introduction

A brief background of AMD formation is given together with the detrimental effects that follow as a result. The different traditional and current solutions to the problem that have been employed are outlined in brief. The problem statement, dissertation aims and objectives and hypothesis of this research follow thereafter.

Chapter Two: Literature Review

An insight into the occurrence and source of AMD, effects of heavy metals and low pH on ecology and the different remediation strategies available to alleviate the effects is provided in this chapter. The various treatment methods available are touched on, explored and fully explained. Slags are described in greater detail and their general characteristics are considered as a long term solution to AMD problem.

Chapter Three: Experimental Material and Methods

This chapter presents the experimental setup and procedure used in the study. The different approaches and set of experiments performed to answer the research questions as well as the aims and objectives are given.

Chapter Four: Results and Discussion

This chapter focuses on the results obtained from the experiments performed to reduce acid, iron and sulphate concentration. From these studies it can be determined if slag offer a viable option to AMD treatment and the slag that works better is distinguished.

Chapter Five: Conclusions and Recommendations

The conclusion and recommendation for future work to be carried out of this research are summarised in this chapter.

CHAPTER TWO

LITERATURE REVIEW

“Nothing has such power to broaden the mind as the ability to investigate systematically and truly all that comes under thy observation in life”.

~ Marcus Aurelius

2.1 Background

Acid mine drainage (AMD) is a growing problem on coal and gold mines around the world (Taylor et al., 2005; Chapman, 2011). AMD is not only affecting the economies of both developed and developing countries, but is also a major environmental concern (Ochieng et al., 2010). AMD in the Witwatersrand Basin is characterised by low pH values, elevated levels of heavy metals and radioactive substances such as uranium. South Africa is no exception to this predicament. The focus of this study is the decant AMD in the Witwatersrand Basins from operating and disused mines. AMD is of concern because it leads to the depletion of aquatic life, damage of the ecosystem, and contamination of potable water and the food chain (Johnson & Hallberg, 2005; Taylor et al., 2005; Ochieng et al., 2010; Chapman, 2011). There is thus a need to develop remediation strategies to neutralise the acid levels and reduce high metal and sulphate concentrations emanating from the Witwatersrand basin. Basin on their properties, slags, the by-products of the smelting process for metals such as steel could be a long term solution to remediation of AMD.

This literature review gives an overview into AMD generation, the factors contributing to AMD, and detrimental effects that arise as a result of AMD in our environment. This study focuses mainly on the Witwatersrand basin area. The subsequent sections of this chapter explore and discuss in greater detail ways of mitigating and treating AMD. AMD remediation technologies are introduced, and discussed with examples for each of them highlighted and looked into. The current methods used in South Africa to treat acidic water are also outlined and evaluated based on their mechanisms and performances. The use of slags as a long term solution to remediating AMD is underlined and the mechanism used by slags in the remediation of AMD is finally given and concludes the section.

2.2 Overview of Acid Mine Drainage

AMD is acidic water laden with iron, sulphate and other metals that forms under natural conditions when geologic strata containing pyrite or other sulphide bearing rocks are exposed to the atmosphere or oxidizing environment (Fripp et al., 2000; Jennings et al., 2008; Gaikwad & Gupta, 2008). AMD is formed by oxidation of sulphide containing minerals exposed to both oxygen and water. The sulphide is mainly in the form of iron pyrite (FeS_2), chalcopyrite ($CuFeS_2$) and chalcocite (Cu_2S). Pyrite is associated with coal and gold deposits in the Witwatersrand, thus AMD is highly associated with coal and gold mining. Exposure of sulphide can either be spontaneously initiated or come about as a result of mining and processing of metal ores and coals from old and current mines (Durkin & Hermann, 1994; Johnson & Hallberg, 2005; Akcil & Koldas, 2006; Potgieter-Vermaak et al., 2006; Jennings et al., 2008; Sheoran et al., 2012). Sulphide is exposed the most during mining hence mining activities are the biggest contributor of AMD formation (Akcil & Koldas, 2006).

AMD is formed through a number of chemical reaction pathways, namely pyrite oxidation, ferrous oxidation and iron hydrolysis (Singer & Stumm, 1970; Stumm & Morgan, 1996). The pathways are shown and explained below:

During pyrite oxidation, pyrite is oxidized to form ferric iron, sulphate and hydrogen ions (Equation 2.1). This reaction happens undisturbed at a slow rate.

$$2FeS_2(s) + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4H^+ + 4SO_4^{2-} \qquad (2.1)$$

Pyrite + oxygen + water → ferrous iron + acidity + sulphate ion

Under conditions of low pH, soluble ferrous iron is capable of reacting further to ferric iron at a slow rate (Equation 2.2). This reaction is catalysed by a variety of bacteria depending on the pH values. This reaction also occurs when sufficient oxygen is dissolved in the water or when the water is exposed to sufficient atmospheric oxygen.

$$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O \qquad (2.2)$$

Ferrous iron + oxygen + acidity → ferric iron + water

If pyrite is in contact with ferric ion, the pyrite can be dissolved. Pyrite is thus oxidised by the reduction of ferric iron (Equation 2.3). The majority of the acid is produced during this reaction.

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (2.3)$$

Pyrite + ferric iron + water → ferrous iron + sulphate ion + acidity

Ferric ion is precipitated into hydrated iron hydroxide, $Fe(OH)_3$ (Equation 2.4). $Fe(OH)_3$ appears as a yellow, orange, or red deposit on stream bottoms commonly referred to as "yellow boy" (Singer & Stumm, 1970; Stumm & Morgan, 1996; Johnson & Hallberg, 2005).

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3(s) + 3H^+ \qquad (2.4)$$

Ferric iron + water → ferric hydroxide + acidity

The complete process of pyrite oxidation is summarised thus (Eq. 5).

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \quad (2.5)$$

Pyrite + oxygen + water → ferric hydroxide + sulphate ion + acidity

The equations above show that water from mines and drains in the form of AMD carries hydrogen ion, sulphate, ferrous and ferric ions, resulting in decreased pH values and increased levels of sulphate. The yellow boy precipitates out of the water when AMD reacts with a stream of a higher pH. This is best explained by the fact that, at a pH of 3 or higher, hydrogen ion and hydrated iron hydroxide are formed when the ferric ion reacts with water. At pH less than 3, ferric hydroxide dissolves into ferric ions. Ultimately, pH determines the precipitation of ferric hydroxide and formation of ferric ions (Tutu, 2008). This is depicted by the following equation:

$$pH \geq 3 = Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \qquad (2.6)$$

$$pH \leq 3 = Fe(OH)_3 \rightarrow Fe^{3+} + H_2O \qquad (2.7)$$

The stability regions for different iron compounds can best be described by a Pourbaix diagram for iron-sulphur-water system at 25°C shown in Figure 2.1. The dotted represent the oxygen reduction and hydrogen evolution equilibrium. The water stability region falls between those two lines. The area marked blue shows fields of stability for dissolved species while that marked in tan is for solid species.

The E-pH diagram shows that oxidation of Fe^{2+} and Fe^{3+} will result in the formation of insoluble compound or precipitates at pH values higher than 3. These compounds include ferric hydroxide ($Fe(OH)_3$), ferrous hydroxide ($Fe(OH)_2$) and $HFeO_2^-$, a complex ion. Below the pH value of 3, soluble Fe^{2+} and Fe^{3+} exist as the stable compounds of iron.

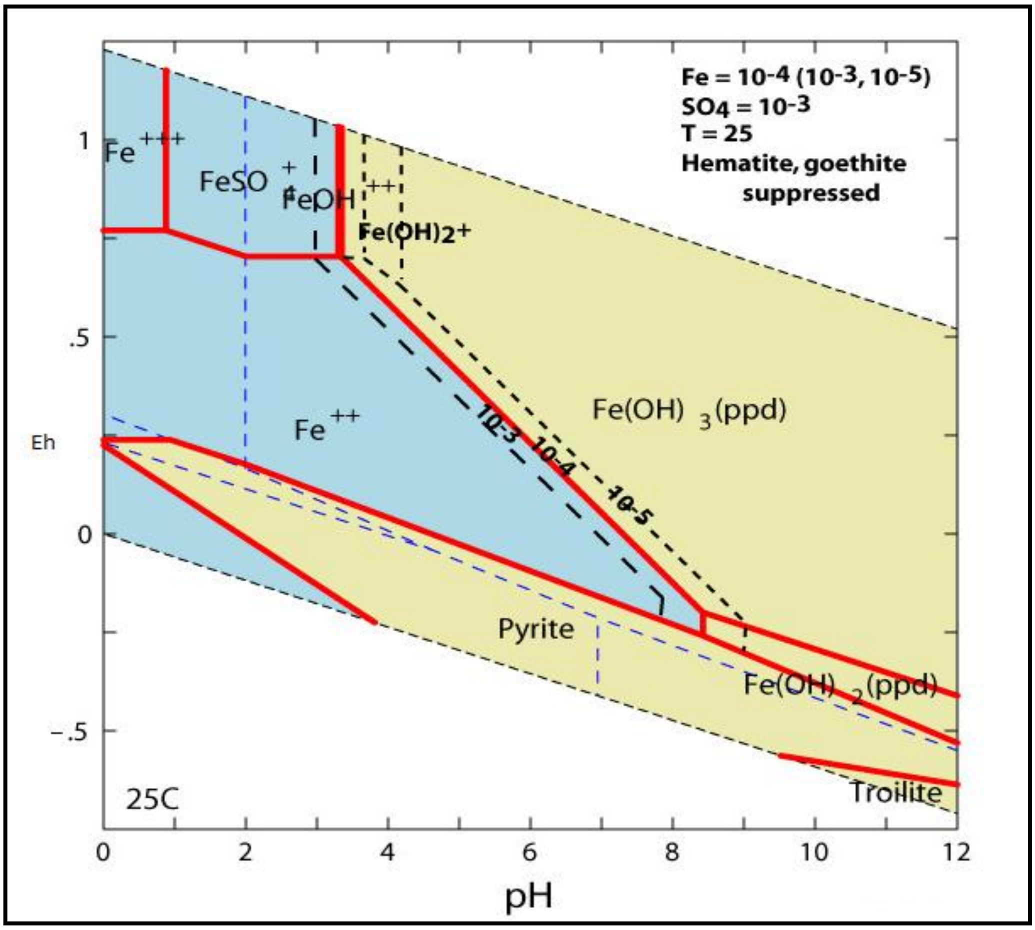

Figure 2.1: Pourbaix Diagram for the Fe-S-H_2O System at 298K (Rose 2010)

The other metal sulphides responsible for the release of metals may and may not generate acidity (Younger et al., 2002). Oxidation of these sulphide minerals is shown in the following equations:

Sphalerite $ZnS(s) + 2O_2(aq) \rightarrow Zn^{2+} + SO_4^{2-}$ (2.8)

Galena $PbS(s) + 2O_2(aq) \rightarrow Pb^{2+} + SO_4^{2-}$ (2.9)

Millerite $NiS(s) + 2O_2(aq) \rightarrow Ni^{2+} + SO_4^{2-}$ (2.10)

Greenockite $CdS(s) + 2O_2(aq) \rightarrow Cd^{2+} + SO_4^{2-}$ (2.11)

Covellite $CuS(s) + 2O_2(aq) \rightarrow Cu^{2+} + SO_4^{2-}$ (2.12)

Chalcopyrite $CuFeS_2(s) + 4O_2(aq) \rightarrow Cu^{2+} + Fe^{2+} + SO_4^{2-}$ (2.13)

2.2.1 Factors Contributing to Acid Mine Drainage

There are numerous factors that determine the ability of a mine to generate acid and release various contaminants into the environment (USEPA, 1994; Akcil & Koldas, 2006). Some of the important contributors to AMD generation are (Akcil & Koldas, 2006):

- Oxygen content
- Oxygen concentration in the water phase
- Chemical activity of Fe^{3+}
- pH
- Temperature
- Surface area of exposed metal sulphide
- Bacterial activity

Mine dumps with high permeability have higher oxygen content and thus experience higher chemical reactions. This is because atmospheric oxygen acts as a driver for oxidation reactions. If the concentration of air occupies a void fraction less than one percent, the oxidation of sulphides is substantially reduced (USEPA, 1994)

Higher chemical reaction rates have been found to be accompanied by higher temperatures due to the exothermic nature of oxidation reactions (Akcil & Koldas, 2006). According to Akcil and Koldas (2006), some sulphides generate more acid than others, while some are easily oxidised compared to others. Some of the sulphides that are easily oxidised include framboidal, pyrite, marcasite and pyrrhotite (USEPA, 1994). In essence, the physical structure of sulphide mineral will determine the reaction rates. This is because crystalline sulphides have smaller exposed surface areas than sulphides spread over a large area (Akcil & Koldas, 2006).

Water plays a crucial role in AMD generation and its transportation. Water also acts both as a reactant and medium for bacteria in the oxidation processes (USEPA, 1994). Bacteria are important in catalysing ferrous ion to ferric ion during AMD formation. Two of the bacteria active for this reaction are *Metallogenium* and *Thiobacillus ferrooxidans*, an iron bacterium (Akcil & Koldas, 2006). Bacteria thrive under suitable chemical and physical conditions of the soil and surrounding environment. One example is that of *Acidithiobacillus ferrooxidans* which performs well in water with pH less than 3.2 (Akcil & Koldas, 2006). Table 2.1

presents some of the bacteria involved in catalysing oxidation reactions and the conditions conducive for their activity.

Table 2.1: Sulfide Ore Bacteria and Their Growth Conditions (USEPA, 1994)

Microorganism	**pH**	**Temp., ºC**	**Aerobic**	**Nutrition**
Thiobacillus thioparus	4.5-10	10-37	+	autotrophic
T. ferrooxidans	0.5-6.0	15-25	+	autotrophic
T. thiooxidans	0.5-6.0	10-37	+	autotrophic
T. neapolitanus	3.0-8.5	8-37	+	autotrophic
T. denitrificans	4.0-9.5	10-37	+/-	autotrophic
T. novellus	5.0-9.2	25-35	+	autotrophic
T. intermedius	1.9-7.0	25-35	+	autotrophic
T. perometabolis	2.8-6.8	25-35	+	autotrophic
Sulfolobus acidocalderius	2.0-5.0	55-85	+	autotrophic
Desulfovibrio desulfuricans	5.0-9.0	10-45	-	heterotrophic

2.3 Acid Mine Drainage in the Witwatersrand Basins

AMD in the Witwatersrand basin occurs partly because of unpremeditated geological circumstances, but predominantly as a result of mining activities that date back over 120 years (Chapman, 2011). Gold mining in the Witwatersrand basin involved extracting the gold bearing rock, which was then transported to the surface where it was crushed and the gold was extracted. After the gold had been extracted, the crushed rock was deposited on waste heaps known as slimes or tailings dumps (Ochieng et al., 2010). Three percent of rock was in the form of pyrites and ends up on the dumps (McCarthy, 2011). Rainwater and other forms of water fall on these dumps resulting in the oxidation of the pyrite, forming sulphuric acid which percolates through the dump, dissolving heavy metals such as uranium in the process.

The acidic water laden with heavy metals emerges from the base of the dump and ends up in the local groundwater and streams as a pollution plume (McCarthy, 2011).

Water also finds its way into mining operations in a number of ways. This water originates as oxygen-containing rain and finds its way into mine workings through shafts and fractures exposed material in mine workings. The water slowly finds its way through these abandoned mines, becomes acidic, saline and enriched or laden with heavy metals. The Witwatersrand mining region or basin is of utmost concern due to the large-scale closure of mining operations since the 1970s which has led to flooding (Cobbing, 2008; I-MCAMD, 2010; Chapman, 2011).

In mines, water is continually permeating into the mine operations from various surrounding water sources. Therefore, to prevent flooding of the mines, water has to be continually pumped out. Some of the water is pumped from the mines to allow access to gold reserves while the remainder is discharged into streams after basic treatment (McCarthy, 2011). Flooding or rising levels began when individual mines shut down their operations. This led to water from the flooded mines seeping through to neighbouring mines, due to the high degree of inter-mine connectivity, and thereby increasing the pumping requirement of the neighbouring mine (Chapman, 2011). When mining operations stopped, the void created by mining slowly filled with water. Because there are high costs incurred when pumping out water from mines (Johnson & Hallberg, 2005), few mining companies were willing to incur the associated costs hence the flooding experienced now after closure of mines (I-MCAMD, 2010, Ochieng et al., 2010; Chapman, 2011). Instead, the failed clean-up costs of a legacy of mines will heavily be felt by the future generations rather than accounted for by the operating companies responsible for closed mines and the ones that are current operational (I-MCAMD, 2010).

The Witwatersrand mines are grouped into four major compartments namely, the Western basin (West Rand), Eastern basin (East Rand), Central Basin (Johannesburg) and Far Western Basin (Carletonville). It is said that water started decanting from the West Rand in 2002 while in Randfontein 15.71 megaliters are produced per day (Chapman, 2011). The water decanting from the West Rand and Randfontein is the cause of pollution being witnessed in the Krugersdorp Game Reserve and Cradle of Humankind national heritage site (Cobbing, 2008; Ochieng et al., 2010; Chapman, 2011). This is as a result of the Witwatersrand basin goldfields not being properly managed for many years (Cobbing, 2008).

2.4. Impact of Acid Mine Drainage

The Witwatersrand gold basin has elevated concentrations of iron and sulphate and very low pH. The Witwatersrand and Goldfields Mines have the potential to generate huge volumes of AMD per day and as such pose enormous challenges for South Africa (Dlamini, 2010). The region thus needs to manage its effluent to standards that are acceptable before release to the environment. Table 2.2 shows typical water qualities for the Western, Central and Eastern Basin.

AMD and its associated products result in detrimental effects on physical, chemical and biological distortion of surface water (Johnson & Hallberg, 2005; Akcil & Koldas, 2006; Ochieng et al., 2010; Chapman, 2011; McCarthy, 2011). Water is a precious resource and clean water is universally accepted to be vital for economic and social development (Cobbing, 2008). South Africa faces a threat to its water security in the near future if the issues surrounding AMD are not fully addressed (Cobbing, 2008; Chapman, 2011).

Peppas et al. (2000) and Akcil and Koldas (2006) both agree that AMD severely contaminates surface and groundwater and soil, since it is characterised by low pH and high concentration of heavy elements as well as other toxic elements. Water pollution as a result of AMD is depicted in Figure 2.2. Thus AMD threatens the clean water security and its accessibility. The low pH values reported make the water unsuitable for domestic, agricultural or industrial use (Fripp et al., 2000; Wade et al., 2002; Coetzee et al., 2006; DWAF, 2006). AMD has resulted in serious environmental consequences, notably in respect of poor environmental and water management worldwide (Johnson & Hallberg, 2005).

The impact of AMD on the economy should not be underestimated. This is because AMD has the potential to damage infrastructure and equipment due to its corrosive nature (Taylor et al., 2005; Johnson & Hallberg, 2005). High concentrations of sulphates have been said to bring about biogenic hydrogen sulphide production, which is highly reactive, corrosive and toxic under aerobic conditions (Mambo, 2011).

Table 2.2: The composition of AMD from the three major basins (NSTF & SAASTA, 2011)

Parameter	Dimension (Unit)	Western basin	Eastern basin	Central basin
Flow	(Ml/d)	20	108	60
pH		3.5	6.65	2.8
Free acidity	(mg/l as $CaCO_3$)	700	0	300
Iron(III)	(mg/l as Fe)	100		
Aluminium	(mg/l as Al)	6.4	0	3
Total acidity	(mg/l as $CaCO_3$)	2 437	1 83	1 749
Iron(II)	(mg/l as Fe)	800	102	800
Total/Free acidity		0.29	0.00	0.17
Alkalinity	(mg/l as $CaCO_3$)	0	350	
Sulphate	(mg/l as SO_4^{2-})	4800	1075	4096
Calcium	(mg/l as Ca)	528	2 16	582
Magnesium	(mg/l as Mg)	147	128	250
Manganese	(mg/l as Mn)	228	2	15
Zinc	(mg/l as Zn)	11.9		4
Cobalt	(mg/l as Co)	4.55		1.5
Nickel	(mg/l as Ni)	18		5
Copper	(mg/l Cu)	21		
Uranium	(mg/l U)	0.465		
Silicon	(mg/l Si)	11		
Barium	(mg/l Ba)	0.2		
Chloride	(mg/l as Cl)	37.03	157	180
Sodium	(mg/l as Na)	50	202	104
Potassium	(mg/l as K)			14
TDS	(mg/l)	6 777.1	2 092.0	6 060.6

DWAF (1996) stated that concentrations of sulphate that are greater 600ppm causes the water to taste bitter and results in diarrhoea in most cases. Elevated sulphate concentrations result in gypsum formation which degrades concrete structures and causes scaling in pipes and filters (Madzivire, 2009; Swanepoel, 2011). Scaling of pipes and filters reduces the heat transfer capacity while the elevated sulphate concentrations have laxative effects in humans (DWAF, 1996; Madzivire, 2009).

AMD has long term environmental impacts that include revegetation and rehabilitation difficulties (Taylor et al., 2005). This is because soils contaminated with AMD have an imbalance of necessary elements vital for plant growth. AMD is also detrimental to human health and can alter the life supporting balances of the water chemistry (Taylor, 2006). For example, mercury consumption results in damage to the nervous central system. Intake of lead is poisonous and impairs the central nervous system while uranium and arsenic bring about cancer related diseases.

Apart from acid and heavy metals being produced during AMD formation, iron (III) hydroxide (‘yellow boy’), is also a matter of concern and precipitates out of the aqueous solution at pH above 3.5 (Singer & Stumm, 1970; Stumm & Morgan, 1996). Jennings et al. (2008) are of the view that iron (III) hydroxide has the capability to physically coat the surface of stream sediments and streambeds thus destroying the habitat, fish food items and reducing light penetration. This could be fatal for aquatic species because as organisms attempt to obtain nutrients from the surroundings, they ingest iron instead. Detrimental effects posed by excess iron include interference with the uptake of manganese which is important for plant growth; clogging of fish gills; and build-up of iron and acid in animals' internal organs which eventually kills them.

The research conducted around the Witwatersrand Basin area has found high levels of radioactive material which may pose cancer risks (Coetzee & Winde, 2006). The impact of radioactive material on aquatic animals is depicted in Figure 2.3. Some studies have also shown that the development of the foetus could negatively be affected when pregnant women are exposed to low metal concentrations and lead to mental retardation (Cobbing, 2008).

Fripp et al. (2000) stated that high iron and sulphate content should be given attention because when dissolved in water and absorbed by organisms or animals can result in fatal consequences. It is therefore of paramount importance that individual mining companies accept that there are AMD hazards at individual sites and research carried out to identify ways in which AMD can be prevented and mitigated. The government should also play an active role in ensuring that laws are put in place that deal with mine closures and treatment of effluent by mining companies. Tables 2.3 and 2.4, presents the effects of iron on the aesthetics, human and household distribution systems.

Table 2.3: Effects of Iron on Aesthetics, Human Health and Household Distribution Systems (DWAF, 1996)

Iron Range (mg/L)	**Effects**
Water Quality Target Range 0 - 0.1	***No taste, other aesthetic or health effects associated with consumption and use***
0.1 - 0.3	Very slight effects on taste and marginal other aesthetic effects Deposits in plumbing with associated problems may begin to occur. No health effects; the water is generally well tolerated
0.3 - 1.0	Adverse aesthetic effects (taste) gradually increase as do possible problems with plumbing. No health effects
1 - 10	Pronounced aesthetic effects (taste) along with problems with plumbing. Slight health effects expected in young children, and sensitive individuals
10 - 30	Severe aesthetic effects (taste) and effects on the plumbing (slimy coatings). Slight iron overload possible in some individuals. Chronic health effects in young children and sensitive individuals in the range 10 - 20 mg/L, and occasional acute effects toward the upper end of this range
30 - 100	As above Long-term health effects gradually increase
100 - 300	As above Chronic health effects. Acute toxicity may begin to appear
300 - 3 000	As above Chronic and acute health effects. Accidental iron poisoning from water is rare
3 000 - 30 000	As above Lethal toxicity occurs

Table 2.4: Effects of Sulphate on Aesthetics and Human Health (DWAF, 1996)

Sulphate Range (mg/L as SO_4^{2-})	**Effects**
Target Water Quality Range ***0 - 200***	***No health or aesthetic effects are experienced***
200 - 400	Tendency to develop diarrhoea in sensitive and some non-adapted individuals. Slight taste noticeable
400 - 600	Diarrhoea in most non-adapted individuals. Definite salty or bitter taste
600 - 1 000	Diarrhoea in most individuals. User-adaptation does not occur. Pronounced salty or bitter taste
> 1 000	Diarrhoea in all individuals. User-adaptation does not occur. Very strong salty and bitter taste

Figure 2.2: Water pollution as a result of acid mine drainage (Liefferink, 2009.)

Figure 2.3: Hippopotami within one of the Receptor Dams of Acid Mine Drainage containing a sludge of radioactive and toxic heavy metals, Krugersdorp Game Reserve (Liefferink, 2009)

2.5 Acid Mine Drainage Control

Appropriate treatment methods need to be implemented to tackle threats posed by AMD. Historically, focus has mainly been on minimisation and control as the best practices (Taylor et al., 2005). Oxygen and water are the two main agents responsible for the perpetual formation of AMD. Johnson and Hallberg (2005) thus argued that it is generally preferable, although not always practical to prevent the formation of AMD by sealing of underground mines, storage of mine tailings under-water or land-based storage in sealed waste heaps. These processes will ensure that contact between minerals and oxygen and water is minimised leading to reduction of AMD formation. Efforts aimed at AMD should be centred on curbing water flow because water acts a transport medium of contaminants as well as a parameter for AMD generation (Akcil & Koldas, 2006)

Three main stages to minimise AMD have been proposed (Akcil & Koldas, 2006):

- Primary control – control of acid generation
- Secondary control –control of acid migration.
- Tertiary control - the collection and treatment of effluent.

Primary control looks at predicting the potential of processes to create AMD. This is however challenging and costly because each site has its own AMD characteristic (USEPA, 1994). Secondary control too has been found unfeasible because of absence of a standardised method for ranking, measuring and reducing AMD (Akcil & Koldas, 2006). The generation of AMD is in essence unavoidable and it is practically difficult to inhibit the formation of AMD at source. It is therefore important that more research be carried out and methods improved to prevent/ treat AMD at point source. Various methods have been proposed to tackle problems posed by AMD with mixed results to ensure treated effluents meet threshold values set by the government by removing heavy and toxic metals and maintaining acidity at acceptable levels.

2.6 Review of Acid Mine Drainage Remediation Options

Researchers have applied and used treatment methods aforementioned, yet AMD has not been completely eliminated. A number of treatment systems have also been developed to cater for various mine settings (Skousen et al., 1998; Younger et al., 2002; Johnson & Hallberg, 2005; Taylor et al., 2005; Sheoran et al., 2012).

Johnson and Hallberg (2008) and Taylor et al. (2005) identified current feasible methods to be divided into active and passive processes, with both potentially merging biological, chemical and physical approaches. Active treatment involves addition of alkaline chemicals like limestone, lime, caustic soda and ammonia while passive treatment involves developing natural chemical and biological systems that are self-operating (Gaikwad & Gupta, 2008; Ochieng et al., 2010).

Both processes aim at lowering metal and sulphate concentrations or salinity and increasing pH or lowering acidity. Methods used for active treatment include lime neutralisation, carbonate neutralisation and ion exchange while the common methods for passive treatment make use of artificial or constructed wetlands and roughing filters. The mechanisms that incorporate or merge biological, chemical and physical processes are presented in Table 2.5 below.

Table 2.5: Biological, chemical and physical mechanisms for the treatment of AMD (Taylor et al., 2005)

AMD Treatment	
pH control	Oxidation
Adsorption	Electrochemical
Absorption	Sedimentation
Complexation	Flocculation-filtration-settling
Chelation	Ion Exchange
Biological Mediation	Crystallisation
Reduction	

2.7 Active Treatment

Active treatment methods involve addition of alkaline chemicals to raise pH and precipitate metals and require regular maintenance (Jennings et al., 2008). The most used method includes addition of chemical neutralising agents (Coulton et al., 2003). Traditional neutralising agents used for AMD treatment are as follows (Johnson & Hallberg, 2005):

- Lime
- Ammonia
- Limestone
- sodium carbonate
- sodium hydroxide
- magnesium oxide
- hydroxide

The addition of alkaline chemicals increases the rate at which ferrous iron is oxidised, resulting in the precipitation of metals as hydroxides and carbonates (Akcil & Koldas, 2006). Precipitation of these metals ensures that they do not report as soluble compounds in effluent (Johnson & Hallberg, 2005; Taylor & Murphy, 2005). AMD can be treated by directly applying alkaline products into the mine discharge (Skousen & Ziemkiewicz, 1996; Zurbuch, 1996). Whitehead et al. (2005) claimed that these alkaline products could simply be incorporated into the soil.

The following chemical and physical processes are used by active systems to carry out their operations (Taylor et al., 2005):

- pH control or precipitation.
- Electrochemical concentration.
- Biological mediation / redox control (sulphate reduction).
- Ion exchange / absorption or adsorption / flocculation and filtration.
- Crystallisation.

Lime neutralisation, carbonate neutralisation and ion exchange are the most widely conventional active methods used to treat AMD (Taylor et al., 2005; Johnson & Hallberg, 2005). Reverse osmosis is another that is currently being used by Anglo American PLC in South Africa. Various advantages and disadvantages have been identified regarding the application of active treatment systems (Skousen et al., 1998; Younger et al., 2002; Johnson & Hallberg, 2005; Taylor et al., 2005; Ochieng et al., 2010). These are discussed further.

2.7.1 Advantages of Active Treatment

- Smaller surface area required for an active treatments plant compared to a passive system.
- They can cope with higher water discharges.
- More flexible and it can accommodate any acidity or acid load.

2.7.2 Disadvantages of Active Treatment

- Active systems are accompanied by high operating costs associated with alkaline chemicals.
- They require constant monitoring and maintenance.
- Skilled manpower is required for active treatment of plants. Chemical use is quite demanding and the need for constant man-power makes it unfavourable.
- The production of a solid waste/sludge/brine on addition of alkaline chemicals to AMD is a problem (Hedin et al., 1994; Cravotta, 2003; Johnson & Hallberg, 2005). The disposal and managements of this sludge is costly (Ochieng et al., 2010). Active systems thus do not provide a long term solution to AMD treatment.

2.8 Passive Treatment

Passive remediation of AMD is an alternative approach and has gained more attention in current research (Taylor et al., 2005; Johnson & Hallberg, 2005). Passive treatment systems have been used for a number of years to treat mine effluent of varying compositions and pH levels (Hedin et al., 1992; Younger, 1997). They have been argued to be the long term strategy to solving AMD problems and with further research they may become more widely used in future (Jennings et al., 2008). Passive treatment treats the effluent by developing themselves into a self-operating system that does not require constant monitoring (Ochieng et al., 2010) Passive treatment systems are mainly carbonate based and can be used with or without the addition of organic (Taylor et al., 2005). The advantages and disadvantages of passive treatment systems are listed below (Skousen et al., 1998; Younger et al., 2002; Johnson & Hallberg, 2005; Taylor et al., 2005; Ochieng et al., 2010).

2.8.1 Advantages of Passive Treatment

- They are self-operating, hence they do not require constant human monitoring

- They can treat effluent for many years.
- They are cost effective.

2.8.2 Disadvantages of Passive Treatment

- They require large surface area compared to active treatment systems.
- They cannot cope with higher effluent flow rates

Passive treatment methods used include wetlands, limestone-based beds or drains (Kleinmann et al., 1998; Taylor & Murphy, 2005), Roughing filters and Rhodes bioSURE process have been used in South Africa, but the availability of sewage sludge and other organic wastes as well as loss of interest in those technologies has made them less favoured AMD treatment (Ochieng et al., 2010; I-MCAMD, 2010). Hedin and Nairn (1993), as cited by Johnson and Hallberg (2005) and Ochieng et al. (2010) explored the feasibility of aerobic and anaerobic wetlands which are also in use in South Africa. Little research has been conducted in South Africa regarding the use of slags in treatment of AMD (Sheridan et al., 2012).

2.8.3 Wetlands

Wetlands are attached-growth bio-filters that utilise naturally occurring energy sources such as vegetation and microbial metabolic energy. The energy sources are specially adapted to naturally improve water quality through a range of physical, chemical, microbial and plant-mediated processes (Taylor et al., 2005; Johnson & Hallberg, 2005; Wallace & Knight, 2006; Sheoran & Sheoran, 2006).

Wetlands have been used for centuries as treatment methods for environmental contaminants and AMD emanating from coal mines (Weider, 1989; Gray et al., 2000; Groudev et al., 2001; Younger, 2004; Matthies et al., 2010). According to Matagi et al. (1998) and Wallace and Knight (2006) wetlands can be used for removal of iron or manganese in wastewaters from mines. Constructed wetlands can either be aerobic or anaerobic.

2.8.3.1 Aerobic Wetland

Aerobic wetlands contain vegetation planted in relatively impermeable sediments such as clay with wetland vegetation characterised by horizontal flow of water (Taylor et al., 2005).

Aerobic wetlands do not neutralise AMD or treat mine waters that are net alkaline (Taylor et al., 2005; Johnson & Hallberg, 2005), but remediate wastewater through oxidation of ferrous iron and hydrolysis of ferric iron produced as shown by Equation 2.2 & 2.4 (Johnson & Hallberg, 2005)

According to Johnson and Hallberg (2005) aerobic wetlands are shallow systems that operate by surface flow to maintain oxidising conditions and incorporate vegetation to regulate water flow and to filter and stabilise the accumulating ferric precipitates. An example of a wetland is illustrated in Figure 2.4.

Though aerobic wetlands are unable to remove various metals from effluents, their main disadvantage lies in the fact that they cannot handle typical AMD effluents and they require vast surface areas for their operation. A further disadvantage is their inability to reach pH levels greater than 8 (Taylor et al., 2005). To deal with the aforementioned disadvantages, aerobic wetlands are amended by incorporation of various carbon sources or limestone.

2.8.3.2 Anaerobic or Amended Wetlands

Anaerobic wetlands consist of organic matter such as cow or horse dung, saw dust, compost as well as limestone aggregate for their operation (Johnson & Hallberg, 2005, Lindsay et al., 2010). The carbon sources induce anaerobic conditions thereby allowing the AMD to pass through the amendment anaerobically (Johnson & Hallberg, 2005). Anaerobic wetlands have been touted as the most viable long term solution to treatment of contaminants because they offer low investment costs, minimum inputs, low operating costs and do not require machinery for their use (Dunbabin & Bowmer, 1992; Kleinmann & Hedin, 1994; Kalin, 2004; Woulds & Ngwenya, 2004; Groudev et al., 2001; Ye et al., 2001; Sheoran, 2004).

Organic carbon amendment in treating AMD is necessary for the effectiveness of long-term treatment while metal adsorption onto organic matter occurs much faster than metal-sulphide precipitation (Lindsay et al., 2011). Amended wetlands have been applied to AMD (Wallace & Knight, 2006) while the metal removal efficiencies in amended wetlands were higher than in natural wetlands (Mays & Edwards, 2001; Lindsay et al., 2011). In a study by Sheridan et al. (2012), charcoal was used as an amendment because it was considered stable, not prone to normal biodegradation processes and had an ion adsorption capacity. In that study a mixture of plants was added to charcoal and it was shown that constructed wetlands amended with charcoal were capable of effecting some remediation on an AMD stream. Most of the applications have been centred on AMD emanating from abandoned coal mines (Batty &Younger, 2004; Simmons et al., 1997; Matthies et al., 2010), and removal of iron and/or manganese from mine effluent streams (Wallace & Knight, 2006). Stoltz (2003) explored the possibility of constructing wetlands directly on mine tailings impoundments to prevent AMD formation. He concluded that these wetlands can successfully remediate mine tailings with high element and sulphide levels, and low buffering capacity.

As suggested by Garcia et al. (2001), acid reduction is by action of sulphate-reducing bacteria (SRB). According to Lindsay et al. (2011), SRB catalyse dissimilatory (organisms that reduce elemental sulfur to sulfide, but cannot reduce sulfate to sulfide) reduction of sulphate (DSR) to sulfide coupled with organic matter (CH_2O under strictly anaerobic conditions as depicted by the following reaction (Widdel, 1988; Johnson & Hallberg, 2005).

$$SO_4^{2-} + 2CH_2O + 2H^+ \rightarrow H_2S + 2HCO_3 \qquad (2.14)$$

The reaction above shows that sulphate is converted to hydrogen sulphide while producing bicarbonate which improves water quality and decreases acidity (Stumm & Morgan, 1981; Benedetto et al., 2005). This process therefore turns a strong acid (sulphuric) into a weak acid (hydrogen sulfide) Johnson and Hallberg (2005). Ueki et al. (1998), as cited by Paulo et al. (2005) and Kalin et al. (2006) state that the substrates for SRB are formic acid, organic residues, hydrogen, methanol, ethanol and lactate which positively influence sulphate reduction in AMD (Groudev et al., 1999; Gibert et al., 2004). The disadvantage with anaerobic wetlands is the requirement for large area of land for effective treatment. Batty and Younger (2004) are of the opinion that vegetation is difficult to establish in AMD treatment applications in both aerobic and anaerobic wetlands.

Figure 2.4: Wetland for the passive treatment of mine water (Taylor et al. 2005)

2.8.4 Limestone Gravel Beds or Drains

Limestone-based beds or drains are in the form of Open/Oxic limestone drains (OLD), Anoxic limestone drains (ALD), Pyrolusite® limestone beds and Limestone diversion wells (LDW) (Taylor et al., 2005). They can be used together with organic matter and their mechanism of operation involves adding alkali to AMD at the same time trying to keep the iron in its reduced state. They have been found to be relatively inexpensive and require low-maintenance and work best for low flow AMD discharges (Skousen et al., 1998; Cravotta 2003). Figure 2.5 shows an example of a leach bed or drain.

Figure 2.5: Limestone leach bed (Ziewekeiwz & Skousen, 1998)

Taylor et al. (2005) noted the main disadvantage with limestone beds as being the regular maintenance required to ensure maximum life and effectiveness. They further pointed out that the porosity of the beds and that of organic matter is reduced as the systems get blocked with treatment precipitates. Armouring of limestone which is the coating of neutralising material with metal precipitates occurs when ferrous iron is oxidised and ferric hydroxide precipitates on the limestone. This has been identified as the key problem inhibiting the effectiveness of limestone based drains or beds. Armouring does not only hamper the substrate pathway, but reduces the effectiveness of the neutralising agent (Hedin et al., 1994; Cravotta, 2003; Potgieter-Vermaak et al., 2006; Johnson & Hallberg, 2003, 2005). A further disadvantage is that limestone ($Ca(OH)_2$) also often absorbs atmospheric carbon dioxide and forms relatively insoluble calcite ($CaCO_3$) according to the following reaction (Ziemkiewicz et al., 1998):

$$Ca(OH)_2(aq) + CO_2(s) \rightarrow CaCO_3(s) + H_2O(l) \qquad (2.15)$$

Limestone beds are effective in treating AMD from coal mines but are unsuitable for treating Witwatersrand AMD which is from gold mines (Taylor et al., 2005; Johnson & Hallberg, 2005). Taylor et al. (2005) and Ochieng et al. (2010) are in agreement that passive treatments are economically attractive and can be used for sustained periods; however they have mainly been used for coal wastewaters and are thought to be inefficient where high flow rates are involved.

2.9 Overview of Slags

Slags are a highly alkaline by-product of the smelting process for metals such as steel, copper to mention a few. Slags are highly alkaline because they are composed primarily of hydrated amorphous silica, calcium oxide and magnesium oxide (Ziemkiewicz & Simmons, 1998). Slag is formed when limestone, dolomite or lime is combined with iron in steel making. Small amounts of nickel, manganese, carbon and other elements are added to convert iron into a wide range of alloys, ranging from basic carbon steel to high grade stainless steel. These alloys have distinctive properties (Ziemkiewicz & Skousen, 1998; Skousen & Ziemkiewicz, 2005).

Slags have a wide range of applications including civil engineering work, fertiliser production, road construction, cement production and landfill (Ziemkiewicz & Skousen, 1998; Shen & Forssberg, 2002). Slags are categorised into three categories, namely ferrous slag, non-ferrous slag and incineration slag (Shen & Forssberg, 2002). This research will focus on BOF and SS slag that both fall under ferrous slag group. The two have been used for centuries as phosphatic fertiliser (Shen & Forssberg, 2002).

Both SS and BOF slag are mainly comprised of CaO, Fe, Al_2O_3, MgO and SiO_2. The iron in both slags is in the form of FeO. SiO_2 is higher in stainless steel slag than in BOF slag which makes it less basic while BOF slag has a higher Fe content than SS slag (Shen & Forssberg, 2003).

2.9.1 Acid Mine Drainage Treatment using Slags

Although various processes have been proposed for the treatment of AMD using traditional passive routes, however, none of these methods has given hope for a long term solution due to high operating costs and technological failures (Johnson & Hallberg, 2005). However, slag offers a low cost neutralisation agent than conventional alkaline adsorbents.

The potential use of slag in treatment of AMD has been studied and described by various authors (Ziemkiewicz & Skousen, 1998; Shen & Forssberg, 2002; Ziemkiewicz et al., 2002;

Feng et al., 2004; Mark & Gupta, 2009; Kruse et al., 2010; Beckman et al., 2010). Research by Ziemkiewicz and Skousen (1998) suggested direct addition of steel slag into streams affected by AMD as an alternative treatment method. Feng et al. (2004) further supported ideas by Ziemkiewicz and Skousen (1998) by citing that slag can increase the pH of acid mine water to almost neutral figures and remove heavy metals. Bowden et al. (2006) further discovered that rapid iron removal was possible using steel slag.

Slags have numerous advantages compared to other passive mechanisms, which makes them ideal for AMD treatment. Unlike both open and closed limestone, slags are able to achieve high levels of alkalinity (Ziemkiewicz & Skousen, 1998; Ziemkiewicz et al., 2002; Kruse et al., 2010). Slags convert CO_2 to an insoluble limestone unlike lime that absorbs CO_2 from the air as described by Equation 2.15. This implies that slag can be exposed to carbon dioxide without significantly reducing alkalinity for long periods. Other benefits of using SLBs include the relative ease of constructing leach beds, low levels of maintenance required and the high availability of slag for countries that produce a lot of steel like South Africa (Ziemkiewicz & Skousen, 1998; Ziemkiewicz et al., 2002; Skousen & Ziemkiewicz, 2005).

Kruse et al. (2010) pointed out that slag can remain active for treatment of AMD because SLBs can remain active and alkaline for long periods up to 6.2 years. In summary, SLBs are a very good alternative to solve the current AMD problems. Previous studies on SLBs have mainly focussed on stormwater pollution (Taylor et al., 2005); AMD from disused coal mines and direct treatment of water (Ziemkiewicz & Skousen, 2005; Beckman et al., 2010). This study will investigate the effectiveness of SLBs as a long term solution to curbing low pH values, high iron and sulphate concentrations of typical Witwatersrand basin AMD.

2.9.2 Mechanism of Slag in Acid Mine Drainage Remediation

SLBs can be used in cases where AMD has pH values that are very low and concentration of iron and sulphate are very high. In the process of remediating AMD slag uses the following mechanism (Beckman et al., 2010):

2.9.2.1 Reduction of Iron

The removal of iron in solution in slags is due to ion-exchange and acid neutralising ability that often lead to precipitation (Feng et al., 2004). Rose (2010) further stated that the oxidation of iron to Fe^{3+} determines the removal of iron. As such, removal of iron from AMD using slag occurs according to the following reactions

$$\left.\begin{aligned} &CaO + H_2O \rightarrow Ca(OH)_2 \\ &Ca(OH)_2 \rightarrow Ca^{2+} + OH^- \\ &Fe^{m+} + mOH^- \rightarrow Fe(OH)_m \end{aligned}\right\} \qquad (2.16)$$

The oxidation state of iron from the third equation of Equation 2.16 above is m. CaO found in slag reacts with water to form hydrated calcium hydroxide ($Ca(OH)_2$). Dissolution of ($Ca(OH)_2$) follows thereafter and accumulates alkalinity. Different states of iron finally react with hydroxide ions (OH^-) to forms different products depending on the resulting pH values obtained from addition of slag.

The two oxidation states of iron found in water are Fe^{2+} and Fe^{3+}. Iron can also be found in solids states that include oxides, hydroxysulfates and hydroxides. From the Eh-pH diagram for Fe-S-H_2O shown in Figure 2.1, it can be seen that the two states of iron are soluble at oxidising conditions and at pH values less than 3. The diagram further shows that at higher pH values, precipitates are likely to be formed. Apart from precipitates named in section 2.2, Rose (2010) further listed goethite (FeOOH), haematite (Fe_2O_3) and ferrihydrite ($Fe_5O_8H.4H_2O$) as the other precipitates likely to form at higher pH values.

2.9.2.2 Reduction of Sulphate

The removal of sulphate in AMD in slag can be attributed to formation of gypsum ($CaSO_4.2H_2O$) and other sulphate precipitates that can possibly form. The reactions involved in formation of gypsum in AMD are shown in equation 2.17.

Soluble or free calcium oxide in the slag dissolves in water, forms hydrated calcium hydroxide and increases alkalinity following the same mechanism as the one depicted by Equation 2.16. Sulphate is removed from water in the form of gypsum after calcium ions (Ca^{2+}) combine with sulphate ions (SO_4^{2-}) and water. Unlike iron which has a wide range of insoluble precipitates, all sulphate precipitates are soluble in water except that of barium (Ba) and lead (Pb). It follows that sulphate is removed from AMD mainly as gypsum.

$$\left.\begin{aligned} &CaO + H_2O \rightarrow Ca(OH)_2 \\ & \\ & \end{aligned}\right\}$$

$$Ca(OH)_2 \rightarrow Ca^{2+} + OH^- \quad (2.17)$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O(s)$$

Sulphate reduction is poor at low pH values (Madzivire, 2009). According to Madzivire (2009) and Rose (2010) some of the sulphate compounds formed between AMD and slag at low pH values include shwertmannite ($Fe_8O_8(OH)_{5.5.}(SO_4)_{1.25}).nH_2O$ and jarosite ($Fe_3(SO_4)_2(OH)_6$). This means that gypsum formation is mainly responsible for the reduction sulphate.

2.9.2.3 Reduction of Acid

The ability of slags to increase the pH is due to the presence of soluble calcium oxide that accumulates alkalinity in acidic water. Calcium oxide undergoes reactions listed in Equation 2.16 and Equation 2.17 to produce hydroxide ions that are strongly basic. The hydroxide ions formed in turn neutralises AMD to produce neutral water (Beckman et al., 2010). The other reaction brings about pH increase in as follows

$$CaO + H^+ \rightarrow Ca^{2+} + OH^- \quad (2.18)$$

Slag thus presents a viable technology designed to treat AMD in the sense that it is able to provide a stable support medium for vegetation, as well as effectively reduce acidity levels. A comparison of performance of slags for treating mine water has not been done. SLBs are different from limestone leach beds because they contribute a strong base in the form of hydroxide to the affected water unlike lime leach beds that contribute carbonate (CO_3^{2-}). The OH^- is advantageous because it neutralises the H^+ produced by AMD to form neutral water. The strong OH^- also makes the stream very alkaline such that, the metals precipitate out of the water.

CHAPTER THREE

EXPERIMENTAL MATERIAL AND METHODS

“.......in the discussion of natural problems we ought to begin not with the Scriptures, but with experiments, and demonstrations”.

~ Galileo Galilei

3.1 Introduction

This chapter focuses on the preparation of materials as well as the approach methodology taken to achieve the set of proposed aims and objectives. The methods used to test and analyse the results are given. The chapter is concluded with a summary.

The reduction of acidity, iron and sulphate concentration from AMD was studied using metallurgical slags. The BOF and SS slag were the two slags used throughout this research. This study dealt with the effect three parameters that include slag: AMD ratio, contact time and flowrate had on neutralising AMD as well as reducing iron and sulphate concentration. The study was therefore divided into three parts dealing with varying the slag: AMD ratio, contact time and flowrate of AMD. The parameters that were investigated for remediation of AMD are detailed as follows:-

(i) Effect of slag to AMD ratio on the reduction of acidity, iron and sulphate concentration from the AMD - this involved varying the ratio of slag:AMD from 20g of slag per liter of simulated AMD (20 g/L) to 140 g/L.

(ii) Effect of contact time between slag with AMD on the remediation of AMD - this involved sampling and analysing the product of leaching at 30 minutes time intervals for up to 4 hours, for the chosen slag:AMD ratio combinations. Four hours was chosen because it was sufficient for the reaction between the slag and simulated AMD to take place.

(iii) Effect of changing flowrate/ residence time on amount of iron and sulphate removed from AMD – this experiment entailed investigating reduction by varying the flowrate of the feed from low to considerable high flowrate.

To achieve the requirements of the aforementioned aims and objectives, an appropriate experimental set-up was therefore designed and used for the purposed of the study.

3.2 Experimental setup

3.2.1 Process Flow Chart

The process flow sheet for the reduction of acidity, iron and sulphate concentration from AMD in a slag leach beds is shown in Figure 3.1.

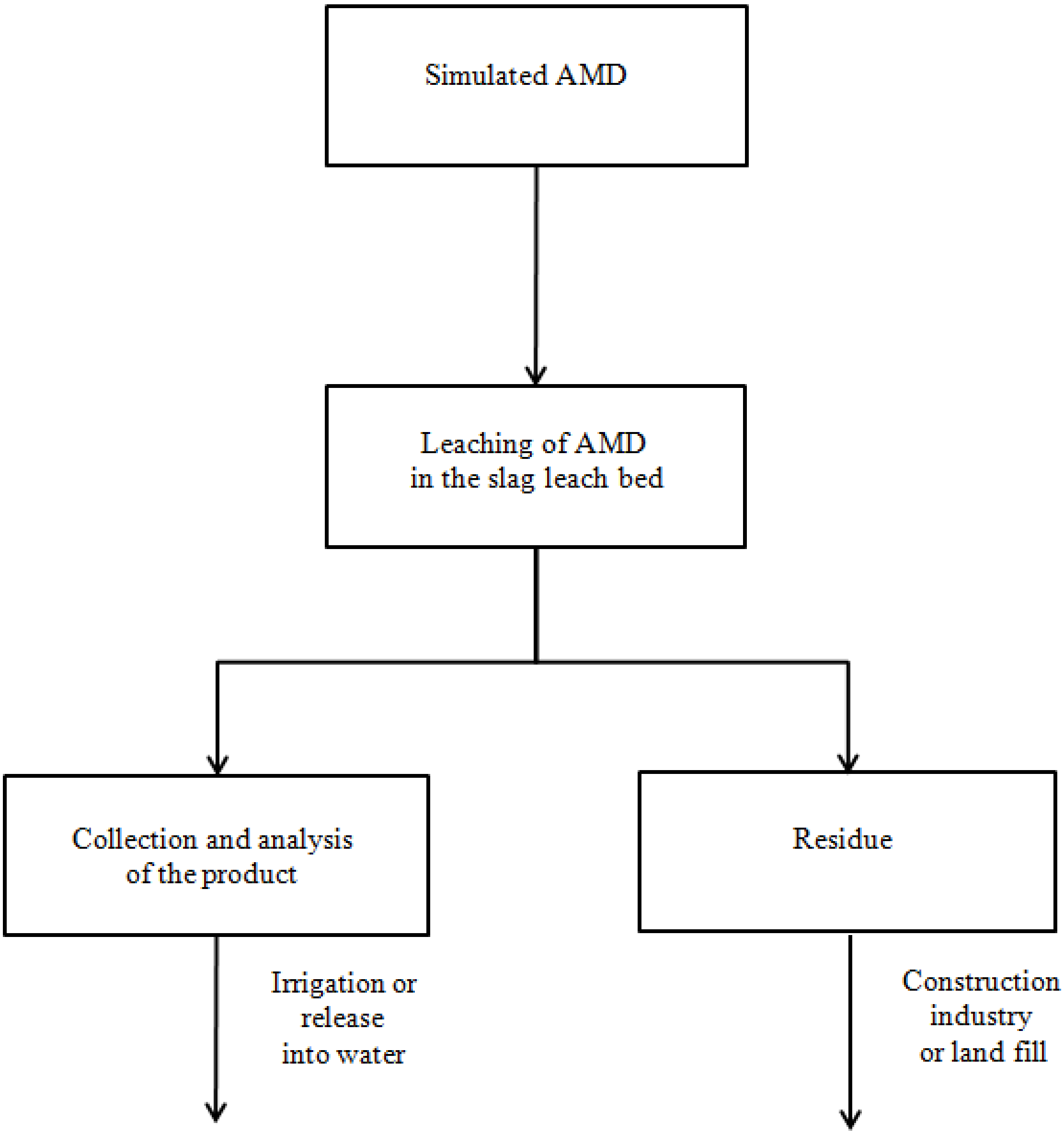

Figure 3.1: Process flow sheet for acid, iron and sulphate reduction in a slag leach bed

The resulting residue needs consultation with construction experts to evaluate if it can be used further for road construction and so forth. However, that is not the purpose of this research. The extract after removal of solids after sampling was analysed for acidity and neutralised with calcium carbonate if the pH is below acceptable values.

3.3 Materials

3.3.1 Slag

The slag used throughout the research was obtained from Harsco Metals and Minerals, South Africa. Slags were used in this study because they are highly alkaline in nature and their characteristics have the ability to create high pH values that may results in reduction of toxic heavy metals through formation of precipitates and gypsum. They have potential because they exhibit high acid neutralising potentials over time while maintaining their porosity thereby removing contaminants. The slag samples used in this research were analysed by Scrooby's Laboratory Service from the SLS-ICP analysis. The results of the composition of both slags used are presented in Table 4.1.

3.3.2 Reagents

The reagents used in this research included hydrated ferrous sulphate, sulphuric acid and calcium carbonate. The ferrous sulphate ($FeSO_4{\cdot}7H_2O$) used was obtained from Protea Chemicals, South Africa and assayed as 90% pure. The sulphuric acid used in this study was analytical grade obtained from Merck, South Africa while calcium carbonate was sourced from Associate Chemical Enterprises. The Sulphuric acid assayed 95-99% pure.

3.4 Experimental Procedure

3.4.1 Acid Mine Drainage Simulation

A typical Witwatersrand gold basin AMD with low pH and elevated concentration of metals and sulphate was simulated in the laboratory (I-MCAMD, 2010; van Wyk, 2012). Synthetic AMD was prepared by dissolving in weighed amounts of hydrated ferrous sulphate ($FeSO_4{\cdot}7H_2O$) and sulphuric acid (H_2SO_4) in distilled water for desired volume make up. The composition of the simulated AMD used in this study was based on those compositions found in previous studies and the concentrations were within the range of a typical Witwatersrand gold basin. Sodium hydroxide pellets were gradually added to adjust the pH of simulated AMD to between 2 and 3 (I-MCAMD, 2010; van Wyk, 2012). NaOH, $FeSO_{4.}7H_2O$ and H_2SO_4 were used because the focal point of this research dealt with acidity, iron and sulphate concentration. Solution loss through sampling and evaporation was compensated by addition of distilled water. The synthetic AMD was created according to recommendations by Potgieter-Vermaak et al. (2006) and Sheoran et al. (2012). The pH, iron and sulphate concentration of the AMD prepared and used during the course of the study is presented in Table 3.1 below.

Table 3.1: The pH, iron and sulphate concentration of the synthetic AMD used during the study

	pH	Fe (mg/L)	SO_4^{2-}
Solution A	2.5	600	4800
Solution B	2.25	1000	5000

3.4.2 Ratio Tests

Samples were prepared to give slag:AMD ratios of 20, 40, 60, 80, 100, 120 and 140 g/L (grams of slag per litre of AMD) by adding an appropriate amount of slag to AMD from a prepared stock solution. The masses of slag used in the experiments ranged from 20 g to 140 g and the solution volume used was 1L. The samples were placed in 2L beakers and left for four hours to allow for sufficient time for the reaction to take place. The products after extraction were filtered from the slag residue and each sample was then analysed for acidity, iron and sulphate content. The pH was measured with a digital pH metre while iron and sulphate were measured using a Spectroquant® UV/VIS Spectrophotometer Pharo 300. The pH profiles as well as graphs illustrating concentration of iron and sulphate against slag:AMD ratio were plotted thereafter and discussed in detail.

3.4.3 Contact Time Studies

Samples were prepared to give slag:AMD ratios of 20, 40, 60, 80, 100 g/L by adding appropriate amounts of slag to a stock solution of AMD. The masses of slag used in these experiments ranged from 100 g to 5000 g and the solution volume used was 5L. The samples were placed in 5L beakers and a 5ml solution was sampled after every 30 minutes and stored in 50ml sample test tubes for analysis. The sampled solutions were tested for pH, iron and sulphate levels as described above. Graphs depicting pH, iron and sulphate content against time for different slag to AMD ratios were then plotted for comparison

3.4.4 Continuous Flow Studies

The experimental apparatus consisted of a feeding tank; two SLBs made up of BOF and SS slag. The slags provided were measured to have a void fraction of approximately 0.4 and both slags provided for this study had mean particle size of < 2mm. The experimental apparatus consisted of a feeding tank; two SLBs made up of BOF and SS slag. The peristaltic pump was initially calibrated using water before the experiment could commence. The pump was first run for 10 minutes for the tube used to assume its final shape before calibration could be started. The pump was calibrated using a stopwatch and a measuring. A calibration graph was then plotted depicting the measured flowrate as a function of pump speed and is illustrated in Appendix E (Figure E1).

Solution B presented in Table 3.1 was used in this experiment. The solution was pumped into both the SS and BOF fixed slag leach bed using a peristaltic pump. The column bed heights for both leach beds were prepared such that the slag occupied 1200 ml in volume. The synthetic AMD was fed in an upwards flow motion from the base of the slag leach bed Flowrates, 4 ml/min, 8 ml/min, 12 ml/min and 16 ml/min were used which translated to 2, 1, 0.5 and 0.25 hrs of residence time. The experiments were repeated two times for each flowrate used.

Sampling of the product from the SLBs was conducted every 2 hours during operating days. The product of remediation sampled for each run was analysed at ambient conditions. The collected samples were analysed for sulphate and iron and the pH. The schematic layout of the SLB is illustrated in Figure 3.2

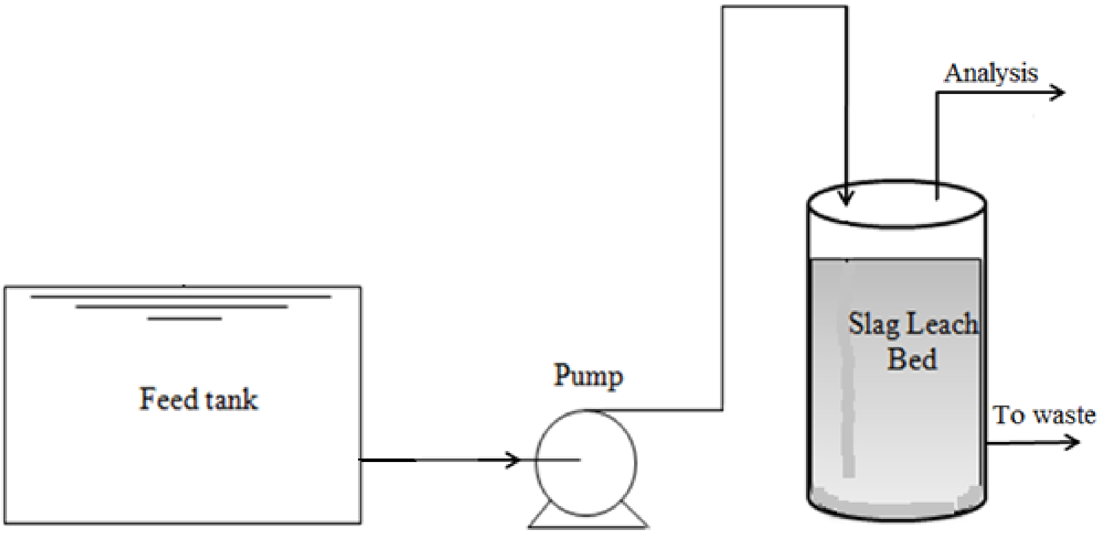

Figure 3.2: A proposed schematic layout of constructed SLB design. Artificial AMD flows from the feed tank to the SLBs through inlet valves via plastic pipes. AMD is then treated by the SLBs and collected in the beakers situated after the outlet valves for analysis

3.5 Analytical Techniques

3.5.1 pH

The pH of all sampled products of leaching was measured using a Metrohm 744 pH meter. The pH was calibrated with Metrohm buffer solutions at pH = 4, 7 and 9. After use the electrode was washed with distilled water and then dried to prevent contamination of subsequent tests. The electrode was then stored in 3M KCl solution to prevent desiccation.

3.5.2 Spectroquant® UV/VIS Spectrophotometer Pharo 300

A Spectroquant® UV/VIS Spectrophotometer Pharo 300 was used to analyse iron and sulphate ion concentration in solution. The instrument used parameters such as wavelength range, light source and warm-up time to analyse ion concentration of choice as highlighted in the Spectroquant® UV/VIS Spectrophotometer operating manual in Table 3.2 (Merck KGaA, 2010).

Figure 3.3: Spectroquant® UV/VIS Spectrophotometer

Table 3.2: Operating conditions of the photometer

Light source	Wavelength range	Light sensor	Warm-up time
Xenon flashlamp	190 – 1100nm	Photo diode	15 min

The photometer can perform measurements such as concentrations, wavelength, and profile kinetics even in the UV range. The photometer is able to detect bar codes for numerous Spectroquant tests. The iron and sulphate Merck test kits were used during the study. These test kits had reference numbers of 114791 and 114761 respectively. The concentration range for the iron test kit was 0.005 – 5.0 mg/L, while that of sulphate was 20 – 300 mg/L. The sampled products were thus pre-treated by dilution, for them to fall within correct concentration ranges before use for a chosen test kit.

3.5.3 Testing for Iron Concentration

Iron concentration was analysed as specified in instructions in the Merck Iron Test Kit manual. The effluent sample was first pre-treated to ensure that its concentration fell within the range of the iron test kit concentration range. The sample was kept within the desired range by mixing a small quantity of the sample with distilled water in a measuring cylinder. The pre-treated sample was kept at a temperature between 10 – 40 ºC and pH adjusted to be within the range 1- 10. The pH was adjusted with the use of sodium hydroxide or hydrochloric acid if necessary. Five millilitres of the pre-treated sample was then transferred into a test tube, after which, three drops of reagent Fe-1 were added and mixed. The solution was let stand for a reaction time of 3 minutes. The sample was then filled into the cells and measured in the photometer.

3.5.4 Testing for Sulphate Concentration

Sulphate concentration was analysed as specified in instructions in the Merck Sulphate Test Kit manual. The effluent sample was pre-treated with distilled water using the same procedure performed with the iron test to fall within the sulphate test kit concentration range. The pre-treated sample was kept within a temperature range 15- 40 ºC and pH was adjusted within range 2 - 10 with the use of sodium hydroxide or hydrochloric acid when necessary. A 2.5 ml sample was then pipetted into a screw capped test tube, followed by the addition of two drops of reagent SO_4-1 and mixed. One level microspoon of reagent SO_4-2 was again added to the mixture, closed and mixed. The test tube with the mixture was heated in a water bath at a temperature of 40 ºC for a reaction time of 5 minutes. The test tube was shaken occasionally during heating. 2. 5 ml of reagent SO_4-3 was added to the sample and filtered through a glass funnel using filter paper afterwards. The filtered extract was collected in screw capped test tube, and four drops of reagent SO_4-4 was added to the filtrate and mixed. The mixture was heated in a water bath at 40 ºC for a reaction time of 7 minutes, shaking occasionally. The sample was then transferred in a cell and measured in a photometer.

The dilution of samples as part of pre-treatment and subsequent calculation of the analysis sample was calculated according to Equation 2.19.

$$C_1V_1 = C_2V_2 \tag{2.19}$$

Where C_1 = the actual sample concentration

V_1 = the volume of sample pipette out

C_2 = the concentration as measured by the Spectroquant

V_2 = volume of the sample after dilution

The formula hereunder was used to calculate the % reduction or % removal of iron and sulphate from simulated AMD sample treated with slag.

$$\%\, reduction = \left[\frac{C_1 - C_2}{C_1}\right] \times 100 \tag{2.20}$$

Where C_1 = the feed concentration

C_2 = the concentration measured by the spectroquant

3.6 Data Analysis

Data was collected after carrying out the experimental test work and results analysed using MS Excel. The data collected was used to compare the relationships between acidity, iron and sulphate concentration against slag:AMD, contact time and flowrate/residence time. The amount of iron and sulphate extracted during the course of the study was subsequently calculated (see example in Appendix A).

3.7 Summary

This chapter presented and discussed the materials and the approach taken in executing the objectives and aims of this study. The following activities made up the fulcrum of the laboratory testing aspect of the study:

- The choice of slag used and the properties
- Reagents used
- AMD simulation
- Design of the SLBs
- Experimentation
- Determination of iron and sulphate concentration
- Data analysis and interpretation of results. The results obtained from the experimental or test works were recorded. Correlations between the variables under study and iron and sulphate recovery were determined and discussed graphically and analytically.

CHAPTER FOUR

RESULTS AND DISCUSSION

"There is no such thing as a failed experiment, only experiments with unexpected outcomes"

~ Richard Buckminster Fuller

4.1 Introduction

The layout of the experiments performed is schematically summarized in a flowchart in Figure 4.1.

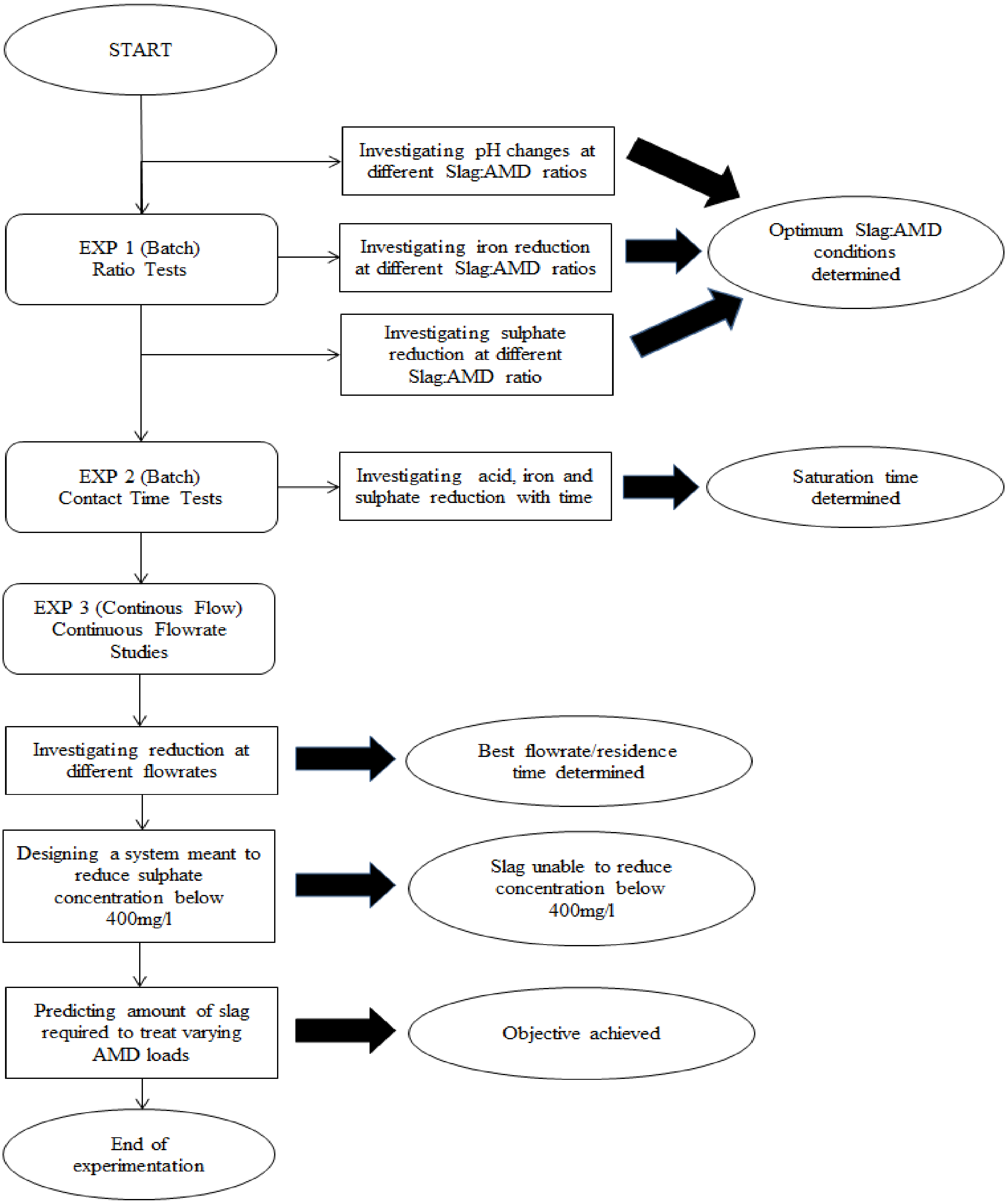

Figure 4.1: Experimentation layout

The reduction of acidity, iron and sulphate concentration was carried out with the use of stainless steel (SS) and basic oxygen furnace (BOF) slag. Both slags were chosen because they exhibit high levels of alkalinity and can readily be used to treat AMD.

This chapter will present and discuss the results obtained from experiments performed to reduce iron and sulphate levels from AMD as well as acidity. The effect of various parameters such as slag to AMD ratio, contact time and residence time on the reduction of initial acidity, iron and sulphate concentrations in the AMD were determined.

4.2 Characterisation of Slags

The chemical composition of the two slags used in this study was analysed with a SLS-ICP and is given in Table 4.1.

Table 4.1: Compositions of BOF and SS slag used

Element	Reported as	Composition of BOF slag (mass %)	Composition of SS slag (mass %)
Carbon	C	1.06	0.76
Sulphur	S	0.34	0.13
Manganese	MnO	1.42	1.27
Phosphorus	P_2O_5	0.46	0.049
Silicon	SiO_2	15.2	26.8
Chromium	Cr_2O_3	0.31	1.91
Nickel	NiO	≤0.01	0.31
Copper	CuO	0.19	0.07
Aluminium	Al_2O_3	5.52	5.87
Vanadium	V_2O_5	0.48	0.05
Titanium	TiO_2	4.02	0.68
Cobalt	CoO	≤0.01	≤0.01
Calcium	CaO	38.7	36.0
Magnesium	MgO	6.80	13.0
Iron	FeO	16.5	5.54

The two slags mainly comprised of calcium oxide or lime (CaO), silicon dioxide (SiO_2), iron (II) oxide (FeO), magnesium oxide (MgO) and aluminium oxide (Al_2O_3). The SiO_2 was 11.6% more in SS slag than in BOF slag which made it less basic. The BOF slag had a higher Fe and CaO content than SS slag as shown in Table 4.1. The BOF slag is expected to release more alkalinity to the AMD than SS slag because it has a higher content of CaO. Both slags were expected to undergo similar chemical reactions (Equation 2.16, Equation 2.17 and Equation 2.18) regardless of the difference in their compositions.

4.3 Effect of slag:AMD ratio on Remediation of AMD

Experiments were performed to evaluate the effect of ratio of slag:AMD on remediating AMD. These experiments aimed at optimising the use of slag in AMD treatment by determining the ratio that would bring about higher iron and sulphate reduction as well pH values. The performed experiments were carried out in batch processes in same laboratory conditions for a period of four hours. The AMD was simulated or synthesised and made comparable to mine water in the Witwatersrand gold basin (Appendix A). Solution A presented in Table 3.1 was used in this experiment. The experimental data in Appendix C (Tables C1 and C2) should be used as reference, for the results obtained in this section. The average of runs performed under similar laboratory conditions make up the content of results that will be discussed. The percentage reduction of iron and sulphate was calculated as shown in Appendix B.

4.3.1 The pH Changes of Acid Mine Drainage

Figure 4.2 shows that the pH of AMD increased when the slag to AMD ratios for both slags used in the study were increased. The value of pH increased from 2.5 to 6.01 for SS slag and 12.11 for BOF after four hours. A ratio of 100 g to IL of AMD was the optimum ratio observed and it was at that ratio that an increase in the amount of slag had no appreciable impact on the pH. This could be a result of saturation of the slag.

During the treatment of AMD, lime dissolved into solution and produced strongly basic hydroxide ions, which resulted in a pH increase as illustrated by Equation 2.16, Equation 2.17 and Equation 2.18. The pH increased when slag to AMD ratio was increased because this also led to more calcium oxide being added into water. This therefore led to increased production of hydroxide ions and accumulation of alkalinity. Hydroxide ions then combined with the acidic solution to form water.

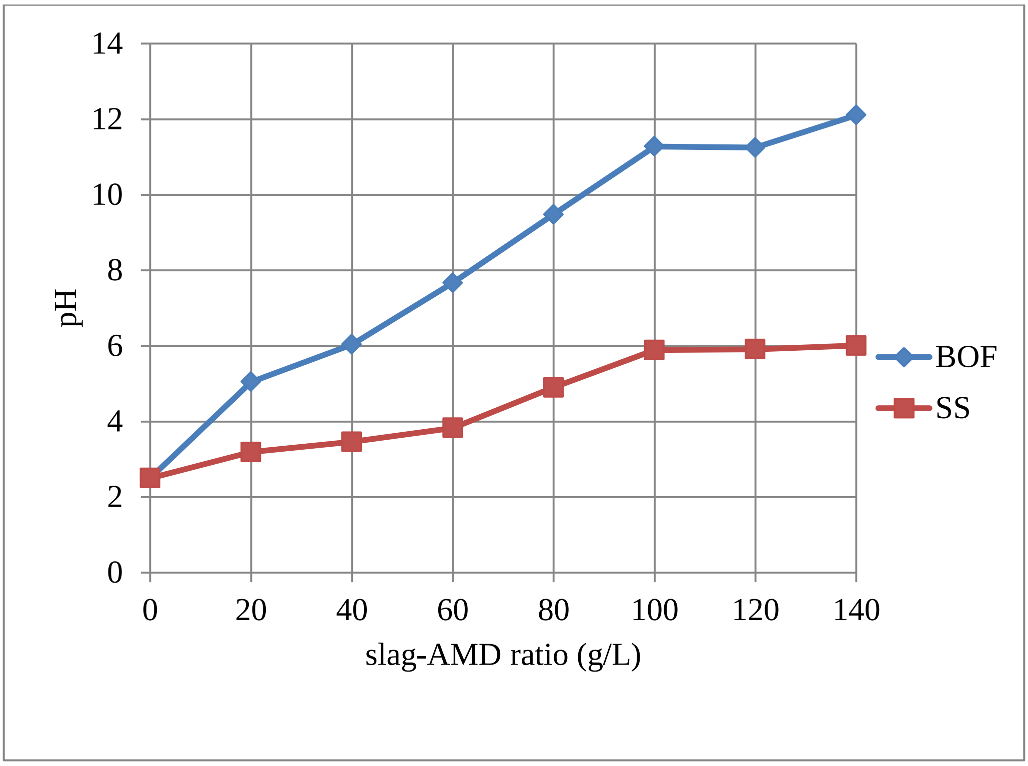

Figure 4.2: The pH changes at different slag to AMD ratios for different slags after four hours [pH^{o}=2.5]

It can clearly be seen from Figure 4.2 that BOF slag had more neutralising ability than SS slag. This is due to the fact that BOF slag had more calcium oxide content than SS slag as shown by the data in Table 4.1. This can also be attributed to SS slag having more silicon dioxide than BOF slag in its composition. Shen and Forssberg (2003) suggested that high silicon dioxide content in compounds tend to make them less alkaline. This therefore means that BOF slag provided more alkalinity to free hydrogen ions in acidic water than SS slag. From the experiments conducted, the pH appeared to remain constant after a ratio of 100 grams of slag per litre of AMD. This could mean that the slag had reached it maximum saturation of the batch. It follows that maximum pH change is achieved at that ratio.

4.3.2 Reduction of Iron Concentration in Acid Mine Drainage

The percent reduction of iron concentration in AMD at different slag:AMD ratios are shown in Figure 4.3. As seen from the figure, iron reduction increased with an increase in the slag:AMD ratio for both slags used. The highest percentage iron reduction recorded was 63.6% for SS slag while 99.7% iron reduction was recorded for BOF slag. The highest iron reduction was recorded at the pH values, which are 6.01 and 12.11 for SS and BOF respectively. From the graph above it can be seen that iron was reduced by almost 100% at slag to AMD ratios of 100, 120 and 140 g/L for BOF slag. The pH values of 11.28, 11.25 and 12.11 were recorded at those ratios.

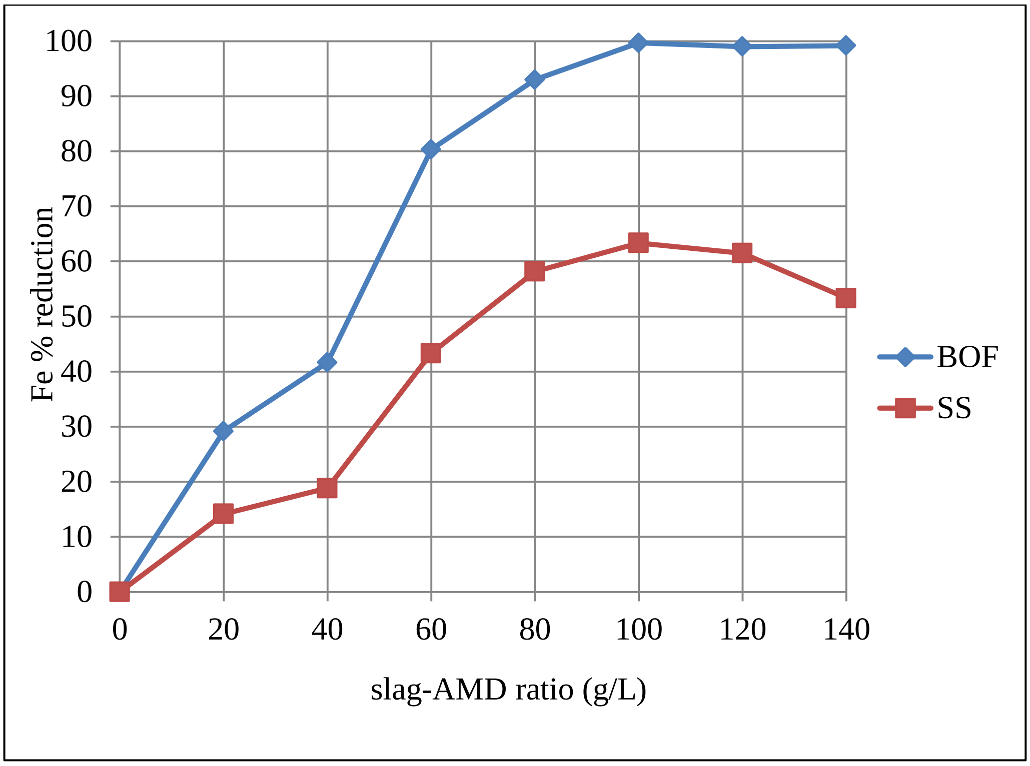

Figure 4.3: Reduction of iron at different slag to AMD ratio for different slags after four hours [Fe^{o} = 600mg/l]

Almost all the soluble iron removed using BOF slag and this was attributed to the formation of various precipitates. From the Pourbaix diagram for Fe-S-H_2O shown in Figure 2.1, it can be seen that precipitates form stable regions at pH values around 9 or more. The mechanism in which iron forms some precipitates is shown in Equation 2.16. The Pourbaix diagram shows that precipitates such as ($Fe(OH)_3$) and ($Fe(OH)_2$) are formed while Rose (2010) claimed that more iron precipitates such as (FeOOH), (Fe_2O_3) and ($Fe_5O_8H.4H_2O$) could also be formed at various pH values. It follows that in experiments performed in this study these precipitates were formed since pH values of more than 9 were recorded when BOF slag was used.

The low iron reduction values obtained for SS slag are likely due to the fact that low pH values were obtained. The Eh-pH diagram in Figure 2.1 shows that below pH values of 9, the stable forms of iron are Fe^{2+}, Fe^{3+} and $FeSO_4^+$. These were unwanted and harmful forms of iron in water reported by the Spectroquant in the analysis of treated AMD. SS slag showed low iron reduction because of its inability to bring about pH values greater than 9 that will result in the formation of iron precipitates. This was because the SS slag had more silicon dioxide content in its composition (Table 4.1). It was therefore thought that the silicon dioxide could likely have formed a glassy protective layer that prevented the free lime from releasing all the hydroxide ions in acidic water to react with Fe^{3+}.

4.3.3 Reduction of Sulphate Concentration in Acid Mine Drainage

The percent reduction of sulphate concentration in AMD at different slag:AMD ratios are also shown in Figure 4.4. As seen from the figure, sulphate reduction increased with increase in slag: AMD ratio for both slags used. The maximum iron reduction percentage recorded was 39.8% for SS slag while 75% sulphate reduction was recorded with the use of BOF slag. It was also noted that maximum sulphate reduction was achieved at the optimum slag to AMD ratio (100g/L), where pH values of 11.28 and 5.89 were recorded for BOF and SS slag respectively.

Both slags used in this study did not contain barium and lead in their composition (Table 3.1) hence $(Fe_8O_8(OH)_{5.5.}(SO_4)_{1.25}).nH_2O$ which forms at pH values between 2.8 and 4.5 and $(Fe_3(SO_4)_2(OH)_6)$ which forms at pH values below 2.8 were expected to have been formed (Rose 2010). It was therefore hypothesized sulphate reduction was due to formation of gypsum in the slag and sludge (Eq. 2.17) and other complex precipitates, though this work did not analyse either. In Figure 4.4, it can be seen that BOF slag reduced sulphate concentration more than SS slag by about 35%.

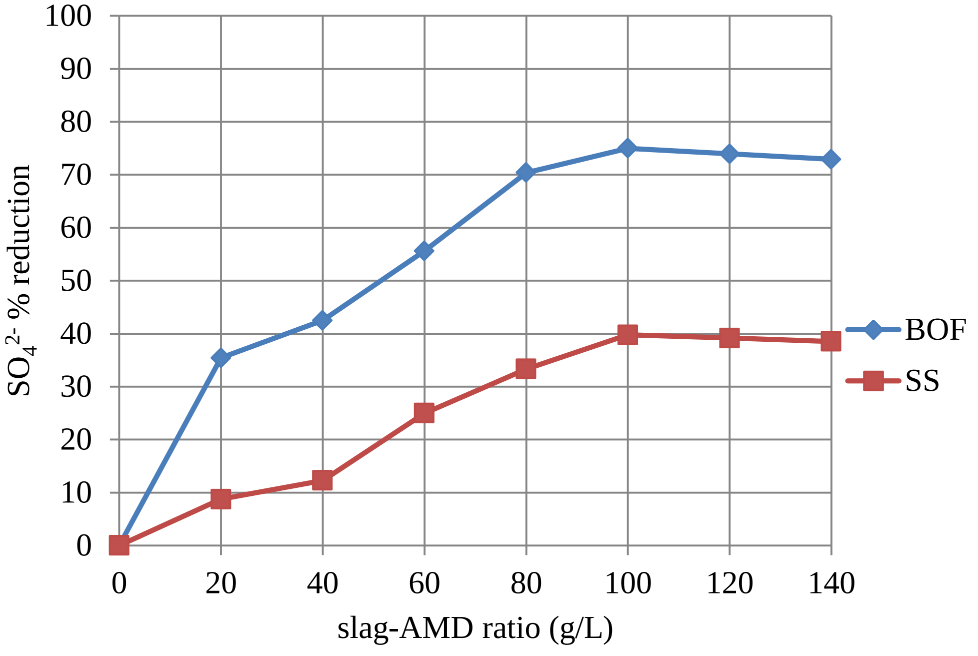

Figure 4.4: Reduction of sulphate at different slag to AMD ratio for different slags after four hours [SO_4^{2-o}= 4800mg/l]

4.4 Contact Time Tests

After establishing the optimum ratio of slag and AMD, time kinetic experiments were carried out to investigate how the reduction of acid, iron and sulphate concentration varied with time. Solution A presented in Table 3.1 was also used in this experiment. These experiments were performed by sampling from 5L beakers small amounts of solution treated from different slag-AMD ratios every 30 mins for four hours. The samples were then taken for analysis to determine the pH, iron and sulphate concentrations in the spectrophotometer at the same laboratory conditions.

The experimental data in Appendix D (Tables D1 – D10) should be used as reference, for the results obtained in this section. The results that will be discussed in this section are derived from the average of runs performed under similar laboratory conditions.

4.4.1 The pH Changes of Acid Mine Drainage using SS and BOF Slag

The pH changes for SS and BOF slag: AMD ratios of 20, 40, 60, 80 and 100 g/L over a period of four hours are shown in Figure 4.5 and Figure 4.6. The figures show that the pH of

AMD increased with an increase in contact time between AMD and both slags. Figure 4.5 and Figure 4.6 also show that the increase in pH was dependent on the slag to AMD ratio. The pH increased rapidly in the first 30 mins and reached steady state for all slag: AMD ratio combinations. The pH increase was higher for BOF slag compared to SS slag. The maximum pH reached for BOF was 11.28 while 5.89 was reached for SS.

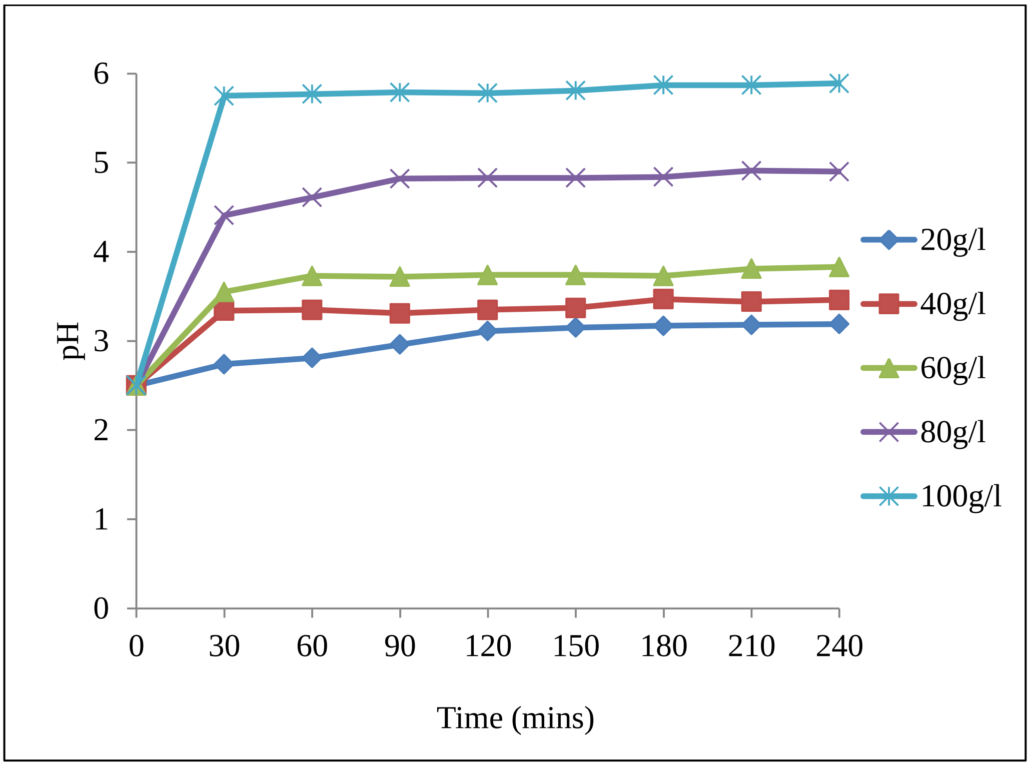

Figure 4.5: pH changes at different times for different SS slag to AMD ratios for four hours

An increased interaction between slag particles and AMD was observed upon mixing the two. This therefore could have made the reaction rapid and resulted in high pH values within the first 30 mins. The pH values abruptly remained almost constant after 30 mins which can be attributed to the system having reached its saturation. The porosity of slag was expected to decline with time which might also have resulted in less free calcium oxide being made available to increase the pH of AMD further.

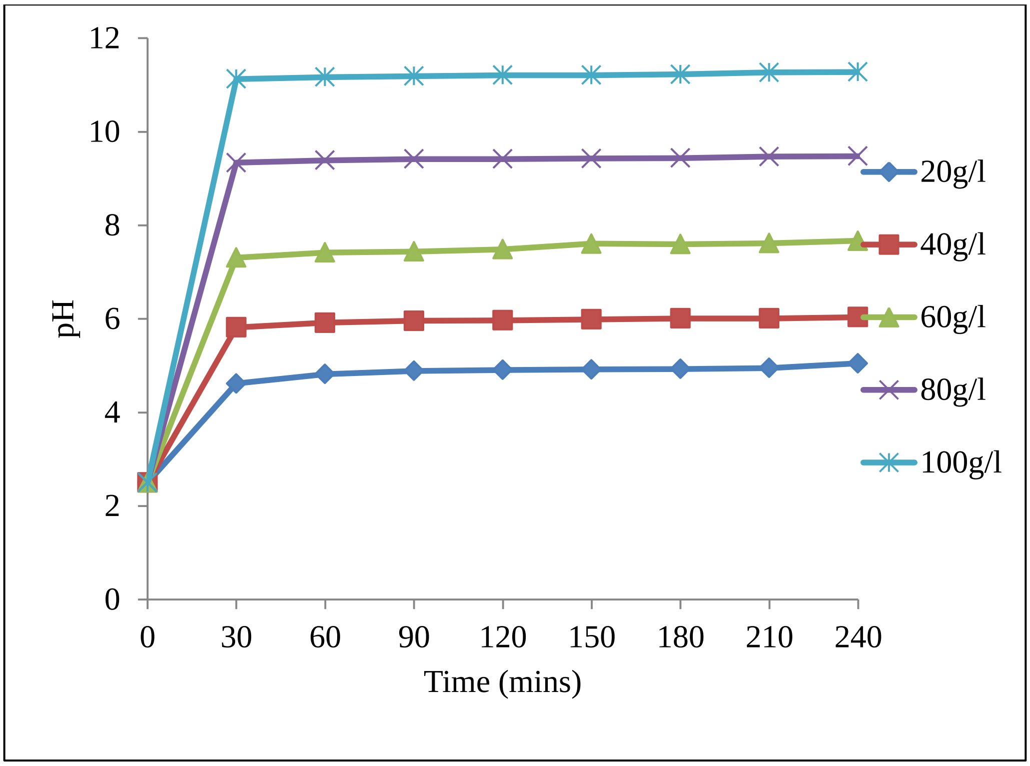

Figure 4. 6: pH changes at different times for different BOF slag to AMD ratios four hours

4.4.2 Reduction of Iron Concentration in Acid Mine Drainage using SS and BOF Slag

Figure 4.7 and Figure 4.8 show the reduction of iron concentration in the synthetic AMD for SS and BOF slag: AMD ratios of 20, 40, 60, 80 and 100 g/L over a period of four hours. Both figures show a decline in iron concentration with time and reduction increased with increase in slag: AMD ratio. Iron concentration for SS slag leach bed was reduced from 600 mg/L to minimum concentrations of 515, 487, 340, 251 and 220 mg/L for slag to AMD ratios of 20, 40, 60, 80 and 100 g/L respectively after 4 hrs. Iron concentration for BOF slag leach bed was reduced from 600 mg/L to minimum values of 425, 350, 118, 52 and 2 mg/L for slag to AMD ratios of 20, 40, 60, 80 and 100 g/L respectively after 4 hrs.

Iron was reduced much faster in BOF slag than SS slag. Iron concentration was very low after 3 with BOF slag for a slag to AMD ratio of 100 g/L. A significant amount (220 mg/L) of iron was detected when SS slag was used for the same ratio. The rate of iron reduction reached saturation after 30 mins for both slags which translated to the time for which rapid pH values were recorded.

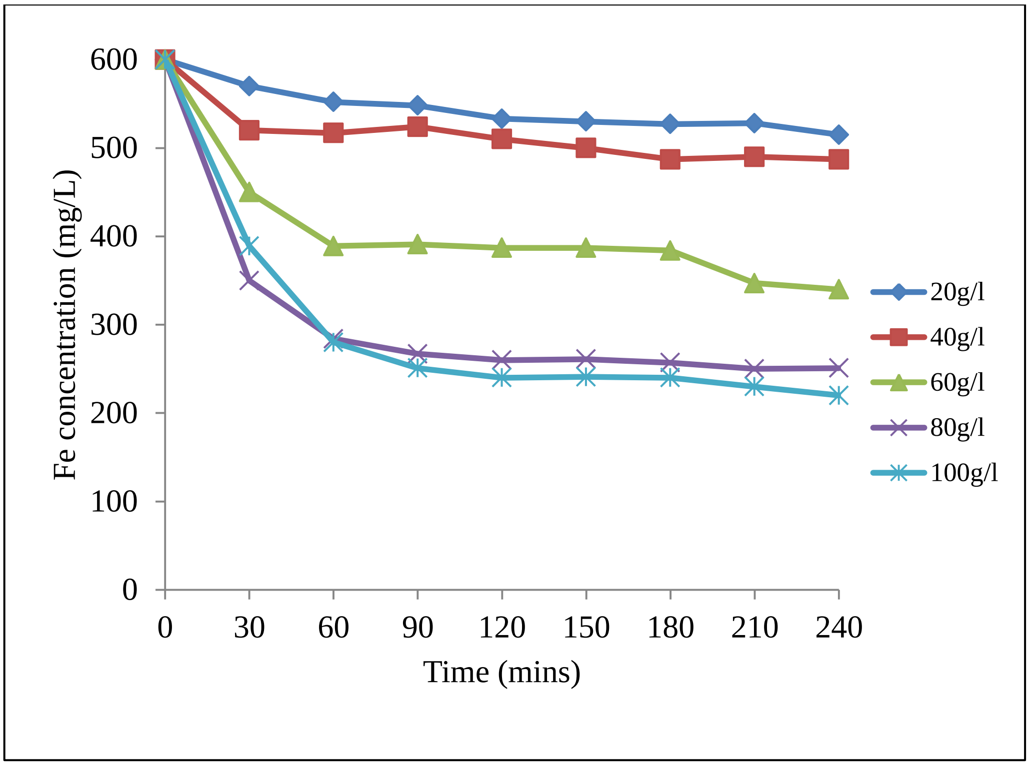

Figure 4.7: Reduction of iron at different times for different SS slag to AMD ratios for four hours

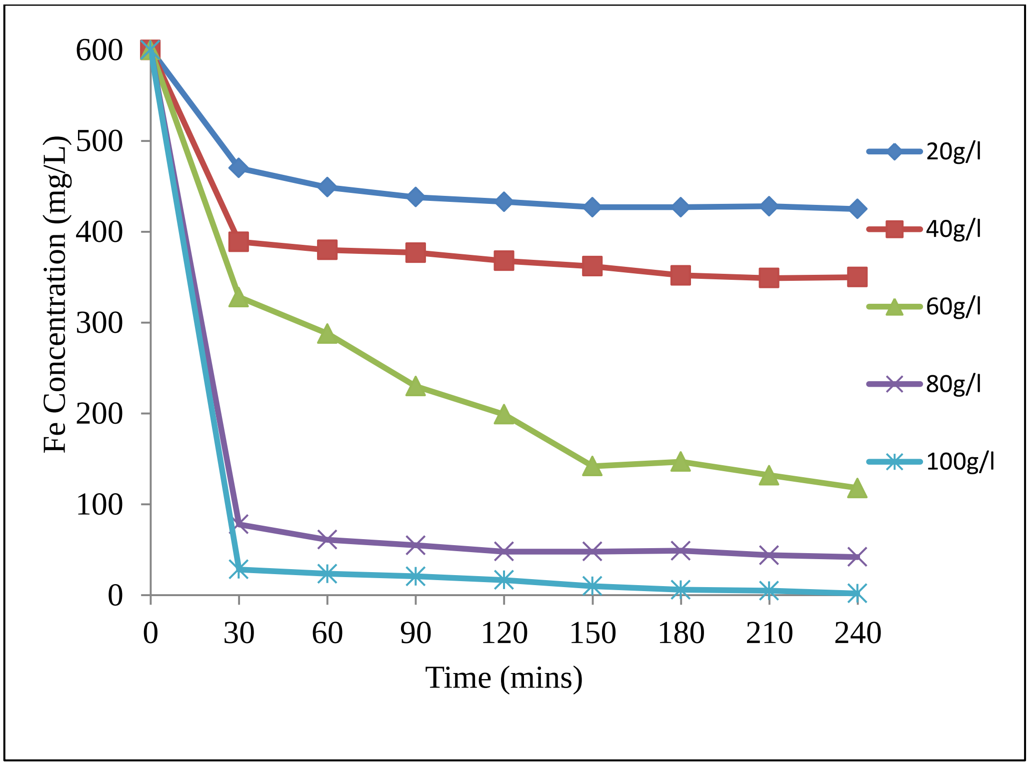

Figure 4.8: Reduction of iron at different times for different BOF slag to AMD ratios four hours

At pH values higher than 9 precipitates were formed which resulted in reduction of soluble iron into insoluble compounds. Precipitation of these metals ensured that they did not report as harmful soluble compounds in the effluent (Johnson & Hallberg, 2005, Taylor et al., 2005). Iron reduction increased as the slag to AMD ratio was increased and it gradually slowed down with time when pH increase slowed.

4.4.3 Reduction of Sulphate Concentration in Acid mine Drainage using SS and BOF Slag

Figure 4.9 and Figure 4.10 show the reduction of sulphate concentration in the synthetic AMD for SS and BOF slag: AMD ratios of 20, 40, 60, 80 and 100 g/L over a period of four hours. Both figures show that sulphate concentration declined with time and the reduction increased with increase in slag: AMD ratio. The reduction of sulphate concentration from the AMD in both the SS and BOF slag leach beds after four hours at different slag:AMD ratios are presented in Table 4.2.

Table 4. 2: Reduction of sulphate concentration from AMD in SS and BOF slag leach beds after four hours at different slag:AMD ratios

Slag:AMD Ratio (g/L)	Feed SO_4^{2-} (mg/L)	Treated SO_4^{2-} (mg/L) SS slag leach bed	Treated SO_4^{2-} (mg/L) BOF slag leach bed
20	4800	4380	3100
40	4800	4210	2760
60	4800	3600	2130
80	4800	3200	1420
100	4800	2890	1200

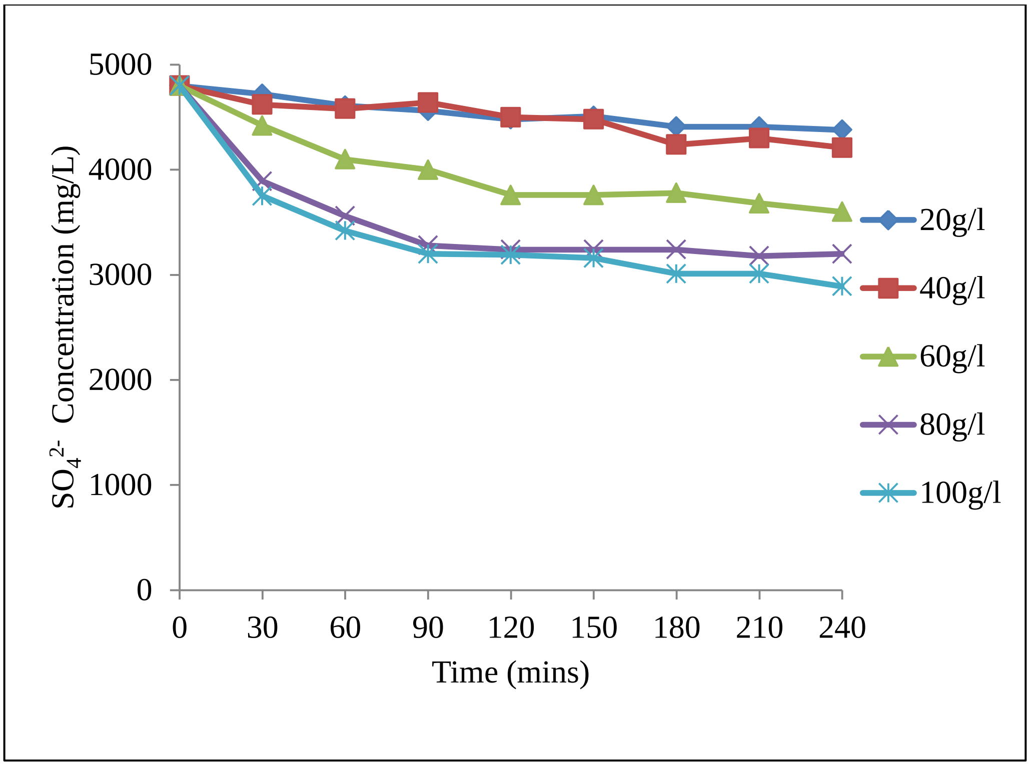

Figure 4.9: Reduction of sulphate at different times for different SS slag to AMD ratios for four hours

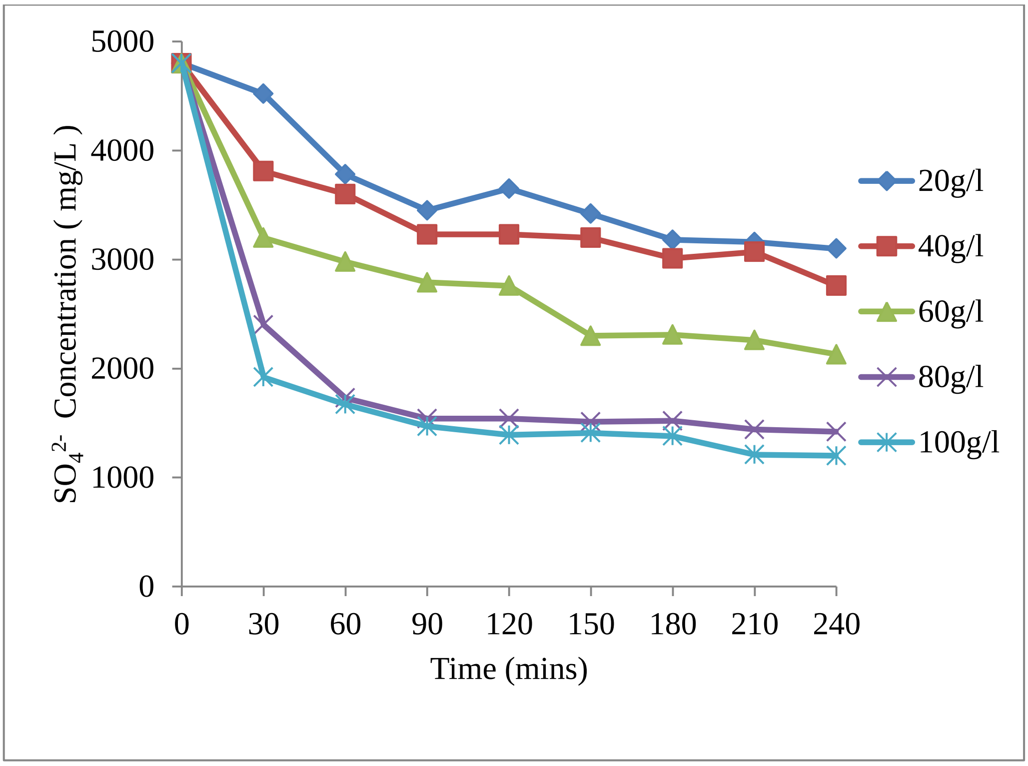

Figure 4.10: Reduction of sulphate at different times for different SS slag to AMD ratios for four hours

4.5 Continuous Flowrate Studies

The batch experiments performed showed that the slag could directly be added to the AMD for treatment provided heavy metals are not leached; however this was not tested in this study. The results obtained agreed with Skousen and Ziemkiewicz (1996) and Zurbuch (1996) who claimed that AMD can be treated by directly applying alkaline products into the mine discharge.

Further experiments were carried out in a continuous process that represents a model situation experienced by mine effluent. Solution B presented in Table 3.1 was used in this experiment. The experiments were performed at flowrates of 4, 8, 12 and 16 ml/min translating to residence times of 2, 1, 0.5, 0.25 hours in same laboratory conditions. The experimental data in Appendix E (Tables E1 – E10) should be used as reference, for the results obtained in this section. The average of runs performed under similar laboratory conditions make up the content of results that will be discussed in this section. This section focuses on BOF slag because SS slag shown to be less effective in remediation of AMD. Nonetheless the data obtained for the SS slag can be found in Appendix E (Tables E1-E10 and Figure E2-E4).

4.5.1 Effect of Flowrate on increasing the pH

The pH changes for treated effluent at flowrates of 4, 8, 12 and 16 ml/min in leach bed occupying a volume of 1.2L over a period of 12hrs continuous process using BOF slag are illustrated in Figure 4.11. The feed pH of the simulated AMD was 2.25 and can also be seen in Figure 4.11. The maximum pH values recorded were 13.21, 11.02, 9.89 and 7.87 for flowrates of 4, 8, 12 and 16 ml/min respectively. Figure 4.11 show that pH increased rapidly in the first two hours of sampling before gradually declining during the course of the experiment as more AMD was fed. The pH values recorded were higher for BOF slag than SS slag (Appendix E).

As expected, we found an increase in pH with an increase in residence time (decreasing flowrate). This is because there is more contact time between slag and AMD at longer time. The pH gradually declined with time as illustrated in the Figure 4.11.

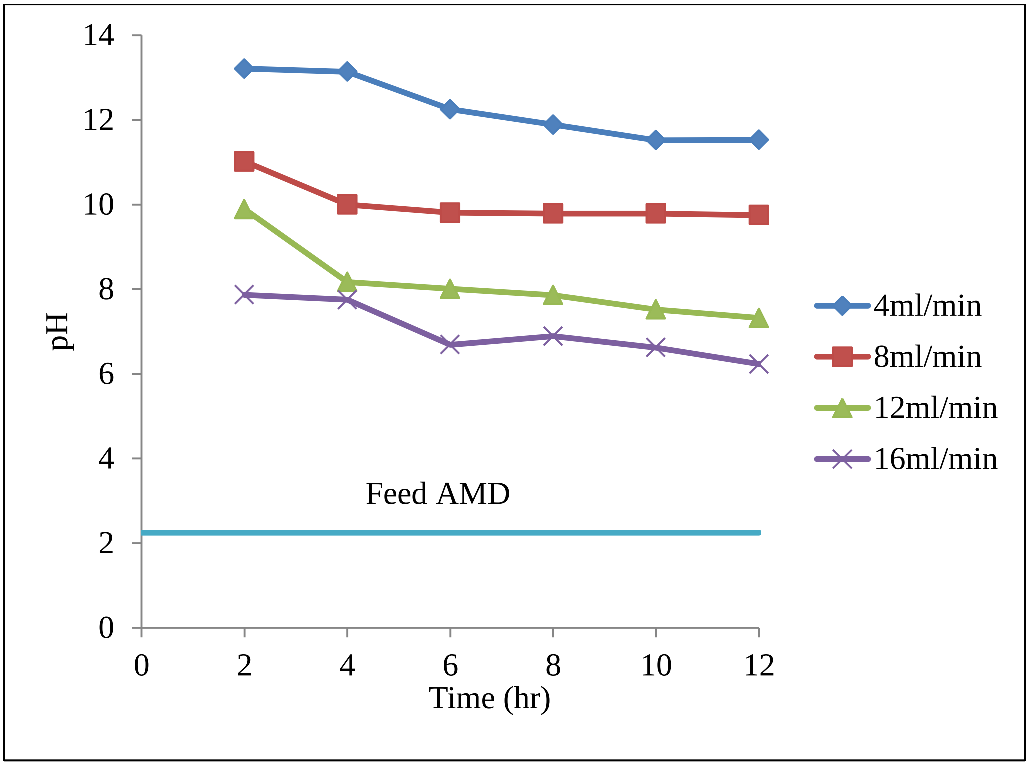

Figure 4.11: Effect of flowrate on reduction of acid for BOF slag for a period of 12 hrs

This could be attributed to reduced permeability of slag which got depleted over time which therefore reduced free lime to react with the AMD. However, the pH values recorded were still high enough to bring about precipitation of iron and formation of gypsum.

4.5.2 Effect of Flowrate on Reducing Iron Concentration in Acid Mine Drainage

The iron reduction from AMD at flowrates of 4, 8, 12 and 16 ml/min over a period of 12 hrs in continuous process using BOF slag is shown Figure 4.12. From the figure, one can see that reduction in iron concentration was higher at low flowrate and decreased as the flowrate was increased. The feed concentration of iron was 1000 mg/L. Iron was reduced to undetectable concentration as shown in the graph for feed flowrate of 4ml/min and 8ml/min. The Concentration began to increase during the course of the experiment which translates to the time pH values began to drop.

Precipitates of iron were thought to have been formed at high pH values. These precipitates of iron therefore ensured that no soluble iron ions were detected by analysis during that time. At low flowrate, these would have been filtered by the slag. At higher flowrate, less time was afforded to soluble lime to react and bring about high pH values necessary for formation of precipitates.

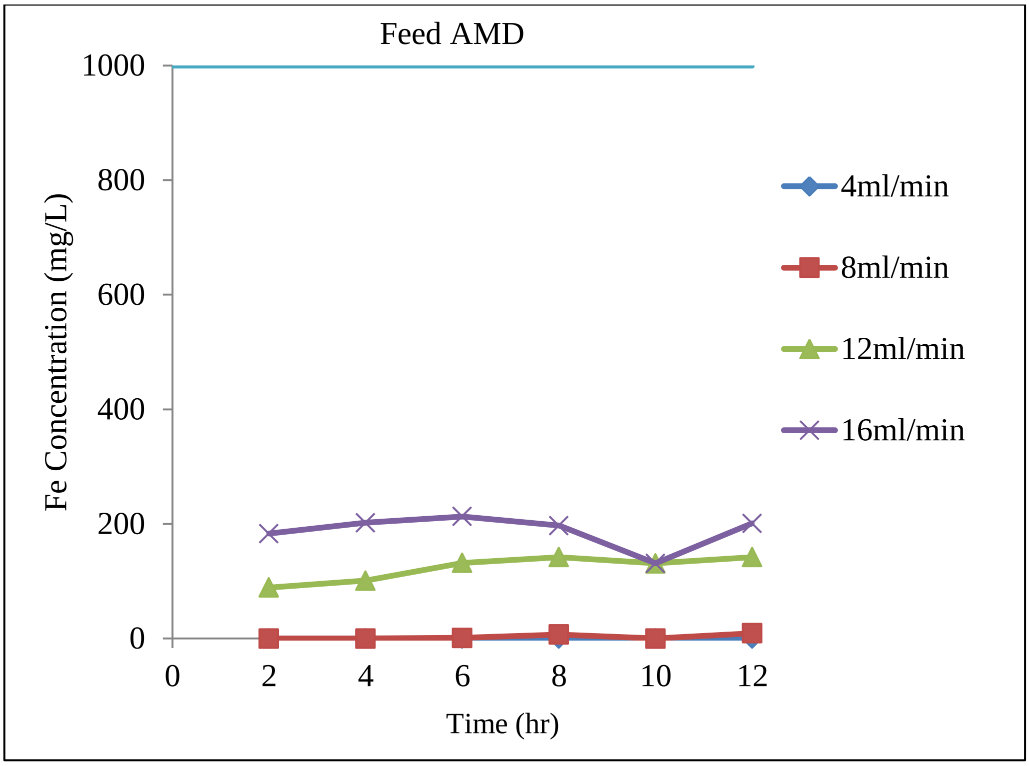

Figure 4.12: Effect of flowrate on reduction of iron after treatment with BOF slag for a period of 12 hrs

4.5.3 Effect of Flowrate on Reducing Sulphate Concentration in Acid Mine Drainage

Figure 4.13 shows sulphate reduction from AMD at flowrates of 4, 8, 12 and 16 ml/min over a period of 12 hrs in continuous process using BOF slag. As seen in the figure, the reduction of sulphate concentration from AMD was also higher at low flowrate and decreased as the flowrate was increased. The feed composition sulphate was 5000 mg/L and reduced to a minimum concentration of 743 mg/l for a flowrate of 4 ml/min. That minimum concentration achieved was still above the DWAF general limit for wastewater (DWAF, 1996). Sulphate reduction was lower for high feed flowrates. BOF slag reduced sulphate much better than SS slag. The data obtained for SS can be found in Appendix C.

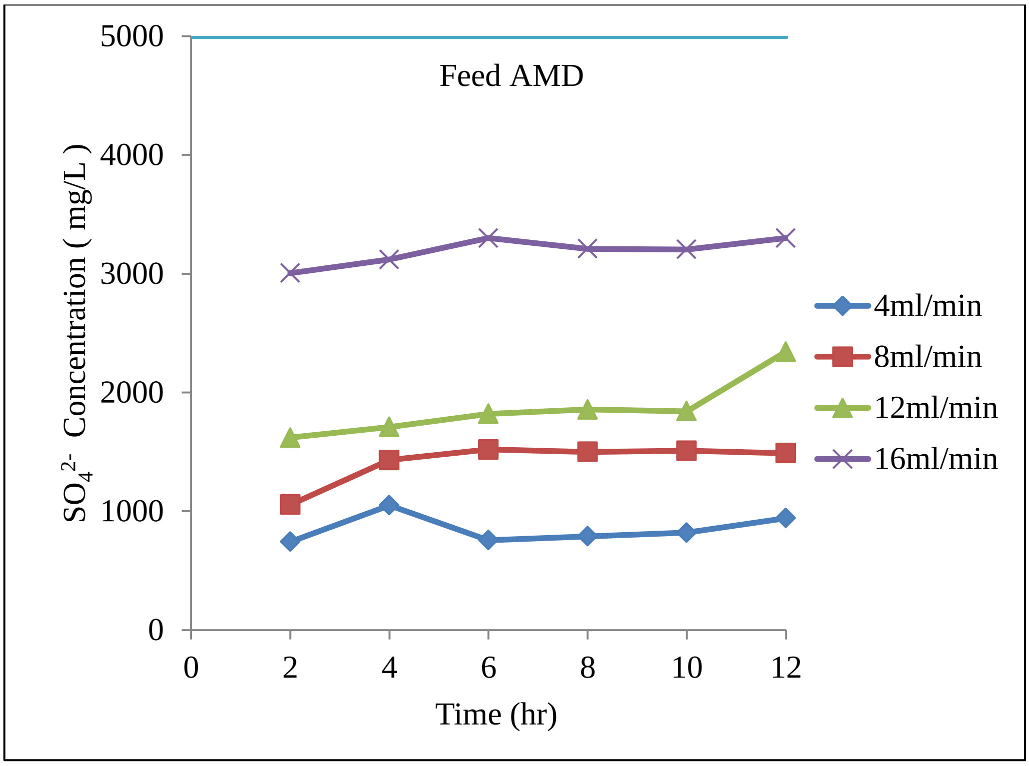

Figure 4.13: Effect of flowrate on sulphate reduction after treatment with BOF slag for a period of 12hrs

4.5.4 Effect of Residence Time on Reducing Iron and Sulphate Concentration in Acid Mine Drainage

The experiments carried out were able to reduce iron to levels below DWAF general limit for disposal of wastewater into a water resource, but sulphate levels were still above the limit (DWAF, 1996). It was decided to design the continuous process in way that would be to reduce sulphate concentration to below 400 mg/L. Concentration of sulphate and iron were thus plotted against residence time and a correlation was established. The residence time capable of reducing sulphate concentration below 400 mg/L was tabulated from the equation relating concentration to residence time.

Figure 4.13 shows how iron and sulphate concentration reduction from AMD changed at different residence times for flowrates of 4, 8, 12 and 16ml/min. From the figure, it can be seen that the reduction of iron and sulphate concentration was greatest at a residence time of 2 hours. Skousen and Ziemkiewicz (2005) and Kruse et al. (2010) claimed that slag leach beds required one to three hours of residence time for their design. The results obtained therefore agree with those obtained by the aforementioned authors.

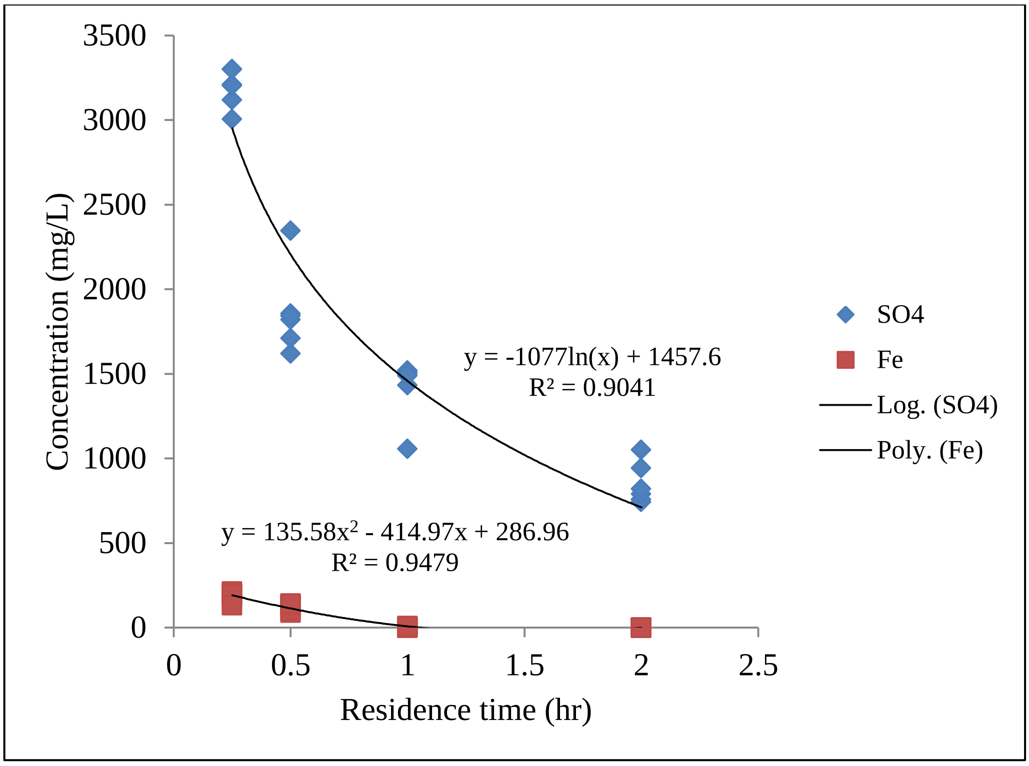

Figure 4.14: Iron and sulphate reduction at different residence times

From Figure 14.14, it can be seen that sulphate levels were above 400mg/L (DWAF general limit for wastewater). Sulphate reduction in synthetic AMD using BOF as a function of time was given as

$$y = -1077\ln(x) + 1457.6$$

Where y was the sulphate concentration and x, was the residence time. According to the equation a residence time of 2.67 hrs would be required to sulphate concentration of 400 mg/L. A flowrate of 3 ml/min needed to be fed to the slag bed to achieve that concentration according to the calibration curve found in Appendix E (Figure E1). That flowrate was fed to the slag bed for 2 days to ascertain how acid, iron and sulphate concentration changed with time. The results are presented in the next section.

4.5.5 The Effect of Design Residence Time on pH Changes of Acid Mine Drainage

The pH changes of AMD for the designed residence time of 2.67 hrs using BOF slag over a period of two days are shown in Figure 4.15 shows. Solution B presented in Table 3.1 was used for this study and had a pH 2.25, increased to a maximum value of 13.31 in the first two hours and decreased thereafter throughout the course of the experiment. The study was carried out starting at 8 am and ending at 8 pm hence the unavailability of data between 12 hrs and 24 hrs. The pH was well above 9 on the first day of the run which was high enough to highly neutralise the acidic water. It then dropped sharply overnight, was above the feed pH.

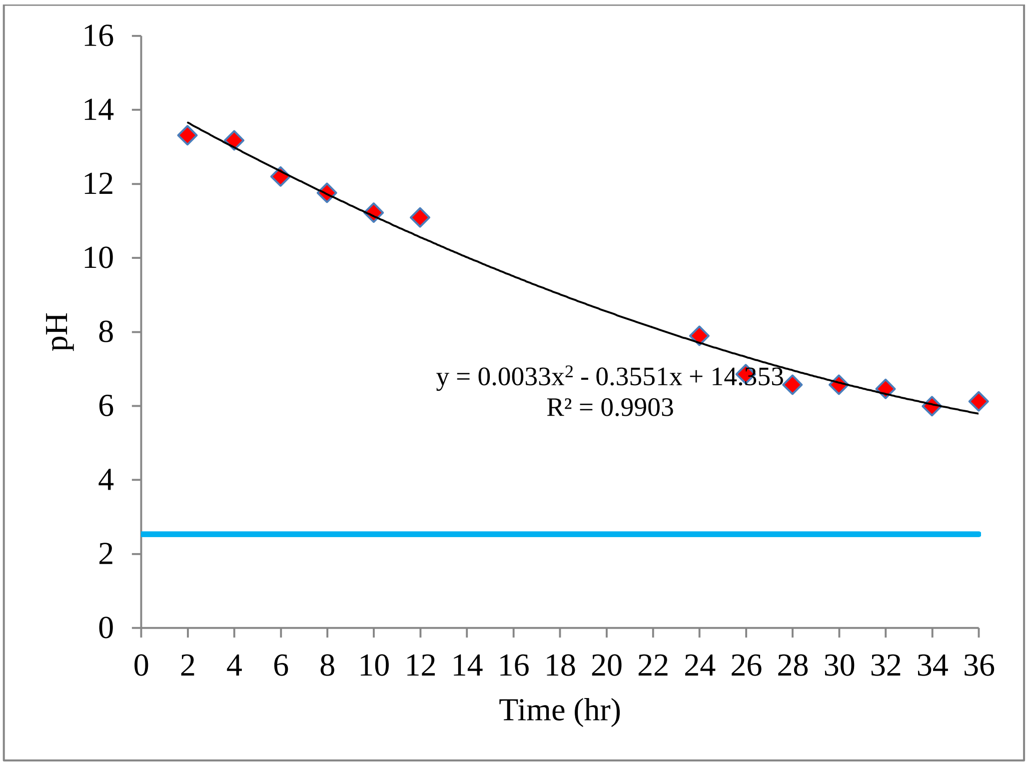

Figure 4.15: Reduction of acid for a continuous process using BOF slag for duration of 2 days

4.5.6 The Effect Design Parameters on Reducing Iron Concentration in Acid Mine Drainage

The reduction of iron in the AMD with a design residence time of 2.67 hrs using BOF slag over a period of two days in comparison to feed concentration is shown in Figure 4.16. The feed composition iron was 1000 mg/L and was reduced to below detection limit as shown in the graph in the first 10-12 hrs. After 12 hours the concentration of iron increased to significant values. The average concentration of iron between 0-12 hrs, 12-24 hrs and 24-36 hrs can also be seen in Figure 4.16. The iron concentration began to increase afterwards as the pH decreased to values where soluble iron could now exist.

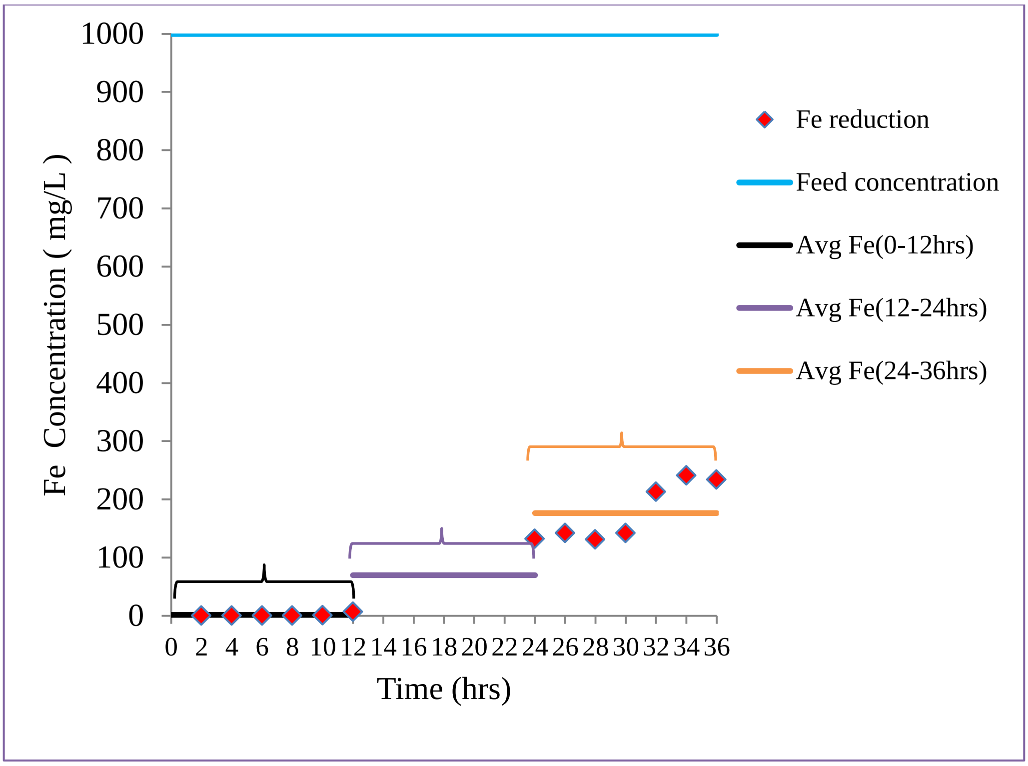

Figure 4.16: Reduction of iron for a continuous process using BOF slag for duration of 2 days

4.5.7 The Effect Design Residence Time on Reducing Sulphate Concentration in Acid Mine Drainage

The reduction of sulphate in the AMD with a design residence time of 2.67 hrs using BOF slag over a period of two days in comparison to feed concentration is shown in Figure 4.17. From the figure, it can be seen that the feed composition of sulphate was 5000mg/L and that the sulphate concentration was well below the feed composition in the first 10-12hrs of leaching. The sulphate concentration then began to increase because less calcium was available to form gypsum. The average concentration of sulphate between 0-12 hrs, 12-24 hrs and 24-36 hrs can also be seen in Figure 4.17. The design was made so as to reduce sulphate concentration to less than 400 mg/L. However than values was not achieved as expected from the calculation made from Figure 4.14.

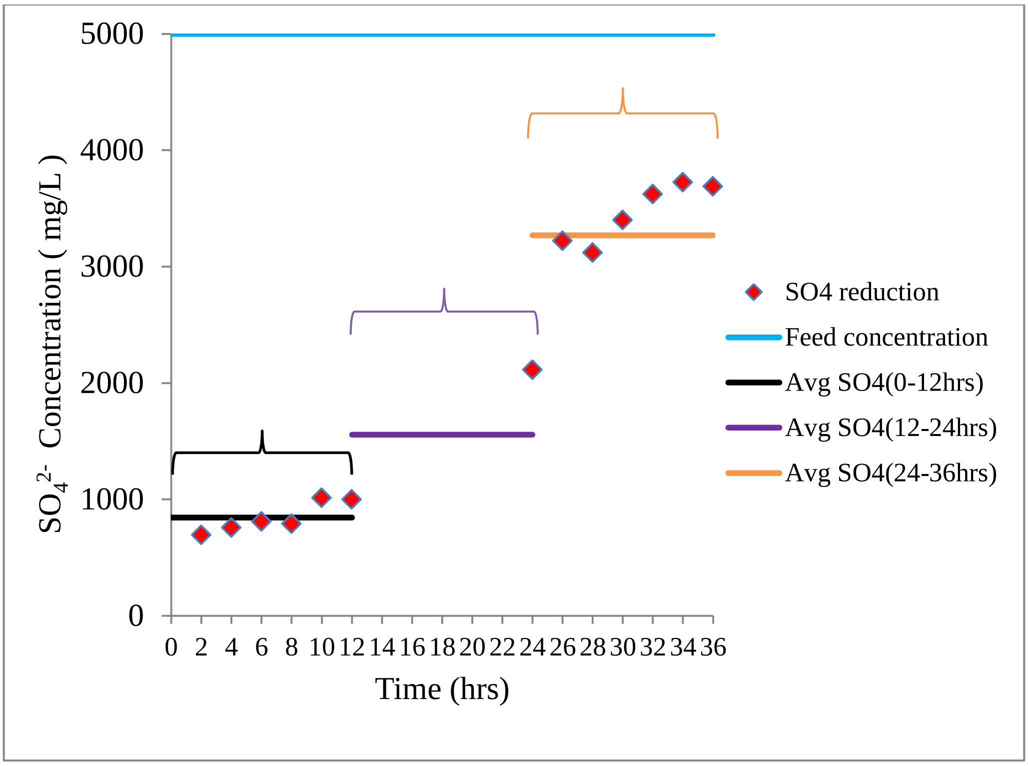

Figure 4.17: Reduction of sulphate for a continuous process using BOF slag for duration of 2 days

4.6 Design to Predict Amount of Slag Needed for Different AMD Flowrate

It is important that the mass or volume of slag is known when treating AMD of varying flowrates or loads. This section looks at predicting the amount of slag needed to treat a specific flowrate of AMD to produce an effluent to a desired average iron and sulphate concentration. Equation 4.1 and 4.2 were thus used to achieve the aforementioned objective. The residence time τ, void fraction ε, volume V, feed flowrate Q and mass of slag V_{slag} were all related according to the following equation.

$$\frac{\varepsilon V_{slag}}{Q} = \tau \qquad (4.1)$$

The volume of the slag required for a chosen flowrate is therefore given by the equation hereunder for a chosen flowrate is therefore given by the equation hereunder

$$V_{slag} = \tau \times \frac{Q}{\varepsilon} \qquad (4.2)$$

The average AMD concentration leaving the process is shown in Table 4.3. In Figure 4.1 the amount of slag required for a set of feed flowrates is illustrated to achieve a specified set of outlet concentrations. The experimental data in Appendix E (Tables E11 – E15) should be used as reference, for the results illustrated in Figure 4.18.

Table 4.3: The average AMD concentration leaving the process after 12 hrs of treating AMD

Residence time (hrs)	Average Fe concentration (mg/l)	Average SO_4^{2-} concentration (mg/l)
0.25	187.8	3190.2
0.5	122.8	1865.7
1	2.83	1417.8
2	0	853
2.67	1.33	843.5

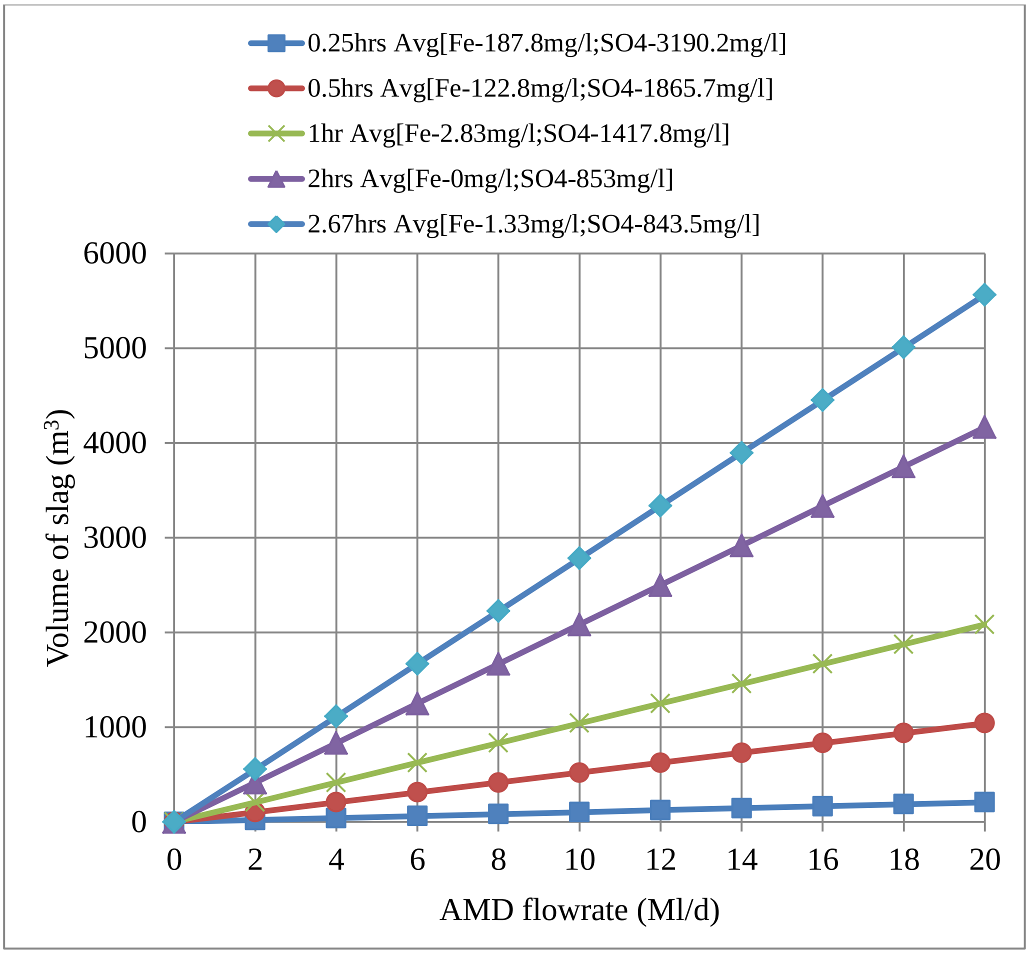

Figure 4. 18: A prediction of the amount of slag required to treat different feed flowrates of AMD can be established from this figure. The amount of slag required for a fixed AMD flowrate increases with an increase in residence time. Each line has target average iron and concentrations. For example, if it was

required to treat 12Ml/d of AMD and the target concentrations of iron and sulphate were 1.33 and 843.5 mg/l respectively, approximately 3300m^3 of slag would be needed with a residence time of 2.67hrs.

According to I-CAMD (2010) the volume of decant in the Witwatersrand Basin has been found to range between 12 and 20Ml/d. The target iron and sulphate concentration need to be considered before predicting the amount of slag required to treat the AMD. Under this condition, that is treating these flowrates, the slag would have to be replaced after the residence time specified. The figure shows that the amount of slag required increased with an increase in the feed flowrate. It also shows that more slag is required with an increase in residence time for a fixed AMD flowrate.

This implies that if one were to treat 20ML per day, after 2.67 hours about 5500 m^3 of slag would need replacing, and the final concentration would be approximately 1.33ppm Fe and 843.5 ppm sulphate. If one were to treat 20ML per day after 0.5 hours, about 200 m^3 of slag would need replacing, and the final concentration would be approximately 187.8ppm Fe and 3190.2 ppm sulphate. The average concentration of iron and sulphate for the 12 hour duration of running the experiment at different residence times given, hence the slag would need to be replaced twice a day.

CHAPTER FIVE

CONCLUSION AND RECOMMENDATIONS

“Any new fact or insight that I may have found has not seemed to me as a ‘discovery’ of mine, but something that has been there and that I had chanced to pick up”.

~ Subrahmanyan Chandrasekhar

This research aimed at understanding the effectiveness of metallurgical slags in remediation a typical Witwatersrand gold basin AMD characterised by low pH values and elevated concentrations of iron and sulphate, by investigating the following: the effect of varying the slag to AMD ratio, the effect of contact time between slag and synthetic AMD and effect of flowrate of AMD in a continuous process. The results showed that slags were effective in neutralising highly acidic water, reducing iron and sulphate concentration. The BOF slag outperformed the SS slag substantially.

From the results obtained in this study, it was shown that acid, iron and sulphate reduction depended on the amount of slag added per 1L of synthetic AMD, the contact time between slag and AMD and flowrate of synthetic AMD fed to the SLBs. The ratio tests showed that acid, iron and sulphate reduction increased with increase in slag to AMD ratio. This is due to the fact that more slag means more calcium oxide was added to leach and react with synthetic AMD to bring about high pH values that led to formation of iron precipitates and gypsum. A ratio of 100g slag to 1L of AMD was found to be the optimum at which maximum reduction was achieved for both BOF and SS slag in the batch experiments. At that ratio 63.6% iron reduction with SS slag compared to 99.7% iron reduction was achieved with BOF slag while 39.8% sulphate reduction with SS slag compared to 75% sulphate reduction was achieved with BOF slag at the same ratio. SS slag managed to increase the pH of synthetic AMD from 2.5 to 6.01 compared to 12.11 for BOF slag.

Acid, iron and sulphate reduction was found to be very rapid in the first hour of contact between slags with AMD in the batch processes. Remediation of AMD was also successful in a continuous flow process. Acid, iron and sulphate concentration reduction was higher at low flowrates translating to a residence time of 2 hours; pH was increased from 2.25 to 13.21, iron was reduced to undetectable and sulphate was reduced from 5000 mg/L to 743 mg/L with BOF slag. The flow process designed to reduce sulphate concentration to below DWAF general limit for wastewater made from a residence time of 2.67 hrs: reduced iron completely and reduced sulphate from 5000 mg/L to 693 mg/L which was still above the threshold. Overall, the BOF slag outperformed SS slag in reducing acid, iron and sulphate concentration. The results obtained showed that slags were better suited to increasing pH and iron removal and they provide a viable alternative to lime/limestone.

The design to predict the amount of slag required to treating different feed flowrates of AMD for target iron and sulphate concentration, showed that the slag needed increased with an increase in the feed flowrate. It also shows that more slag is required with an increase in residence time for a fixed AMD flowrate. To achieve the set targets, the slag needed replacement twice a day.

From the knowledge gathered during the course of this work, future work should focus on establishing the toxicity of any trace metals or elements that may leach into water during the removal of acid, iron and sulphate. A brown precipitate, presumably iron precipitate was formed during experimentation hence future work has to focus on ways of either getting it out or possibly treating it, as it potentially has detrimental effects on the environment. Further research should be carried out to ascertain the treatment lifespan of the slag and the composition of the slag residue after neutralisation and iron and sulphate removal. This will enable us to know if it can be used further for useful purposes like road construction and land filling. This means embarking on long term kinetic studies and understanding the mechanism of treatment. The slag could also be used in conjunction with constructed wetlands, because they are effective at reducing sulphate through biological processes.

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“The physician himself, if sick, actually calls in another physician, knowing that he cannot reason correctly if required to judge his own condition while suffering”.

~ Aristotle

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APPENDICES

"It is the weight, not numbers of experiments that is to be regarded".

~ Isaac Newton

APPENDIX A

SAMPLE PREPARATION AND COMPOSITION

“Measure what can be measured and make measureable what cannot be measured”.

~ Galileo Galilei

A.1 Sample Preparation

Synthetic AMD A

Iron concentration: 600 mg/L Sulphate concentration: 4800 mg/L pH: 2.5

3.0g hydrated ferrous sulphate

0.027ml sulphuric acid

The reagents above were dissolved in 1L of distilled water to make the compositions of iron, sulphate and acid also listed above. The pH of the solution was adjusted to pH 2.5 with calcium carbonate assayed 99.0% which mixed was thoroughly with the solution. To make up a 20L stock solution, the weighed amounts of reagents were equally increased by a ratio of 20.

Synthetic AMD B

Iron concentration: 1000 mg/L Sulphate concentration: 5000 mg/L pH: 2.25

5.0g hydrated ferrous sulphate

0.03ml sulphuric acid

The above reagents were dissolved in 1L of distilled water to make the compositions of iron, sulphate and acid listed above. The pH of the solution was adjusted to pH 2.5 with calcium carbonate which was mixed thoroughly with the solution.

A.2 Slag Composition

The slag samples used in this research were analysed by Scrooby's Laboratory Service from the SLS-ICP analysis. The compounds found by the SLS-ICP analysis included SiO_2, P_2O_5, CaO, MgO, MnO, FeO, S, Cr_2O_3, NiO, CuO, Al_2O_3, V_2O_5, TiO_2 and CoO. The compositions of these compounds were recorded as mass percentage and are listed in Table 2.1.

APPENDIX B

SAMPLE CALCULATIONS

"But there is another reason for the high repute of mathematics: it is mathematics that offers the exact natural sciences a certain measure of security which, without mathematics, they could not attain".

~ Albert Einstein

Iron and Sulphate Concentration (mg/L)

The treated samples were first pre-treated to ensure that their concentrations fell within the concentration range (0.005 – 5.0 mg/L) for the iron test kit and (20 – 300mg/L) for sulphate test kit, to obtain the exact concentrations. The pre-treated samples were then filled into the cells and measured in the Spectroquant® UV/VIS Spectrophotometer Pharo 300 in mg/L. Pre-treatment techniques are shown in Section 3.2.

Example

The formula hereunder was used to calculate the concentration of the simulated AMD sample treated with slag.

$$C_1V_1 = C_2V_2$$

Where C_1 = the actual concentration

V_1 = the volume of sample pipette out

C_2 = measured concentration in the photometer

V_2 = volume of the sample after dilution

After treatment,

Volume of sample pipette out = 2.5 ml

Volume of the sample after dilution = 1000 ml

Concentration as measured by the Spectroquant = 1.50 mg/L

Actual concentration = $\frac{1.5\times1000}{2.5}$ = 600 mg/L

Example

The formula hereunder was used to calculate the % reduction of iron and sulphate from simulated AMD sample treated with slag.

$$\%\, reduction = \left[\frac{C_1 - C_2}{C_1}\right] \times 100$$

After treatment

The actual concentration = 515 mg/L

Feed concentration = 600 mg/L

% reduction = $\left[\frac{600-515}{600}\right] \times 100$ = 14.4%

APPENDIX C

EFFECT OF SS SLAG: AMD RATIO ON ACIDITY, IRON AND SULPHATE CONCENTRATION

"I find that the harder I work, the more luck I seem to have".

~ Thomas Jefferson

Table C.1: Experimental data for reduction of acid, Fe and SO_4^{2-} with different SS slag to AMD ratios after four hours

Slag – AMD Ratio (g/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	pH	% Fe Reduction	% SO_4^{2-} Reduction
0	0	0	2.5	0	0
20	515	4380	3.19	14.16667	8.75
40	487	4210	3.46	18.83333	12.29167
60	340	3600	3.83	43.33333	25
80	251	3200	4.9	58.16667	33.33333
100	220	2890	5.89	63.33333	39.79167
120	231	2920	5.91	61.5	39.16667
140	280	2950	6.01	53.33333	38.54167

Table C.2: Experimental data for reduction of acid, Fe and SO_4^{2-} with different BOF slag to AMD ratios after four hours

Slag – AMD Ratio (g/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	pH	% Fe Reduction	% SO_4^{2-} Reduction
0	0	0	2.5	0	0
20	425	3100	5.05	29.16667	35.41667
40	350	2760	6.04	41.66667	42.5
60	118	2130	7.67	80.33333	55.625
80	42	1420	9.48	93	70.41667
100	2	1200	11.28	99.66667	75
120	6	1250	11.25	99	73.95833
140	5	1300	12.11	99.16667	72.91667

APPENDIX D

EFFECCT OF CONTACT TIME ON ACIDITY, IROM AND SULPHATE CONCENTRATION

"All men by nature desire to know".

~ Aristotle

Table D.1: Experimental data for reduction of acid, Fe and SO_4^{2-} using 20g of SS slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	571	4710	569	4720	570	4720	2.74
60	552	4660	552	4560	552	4610	2.81
90	548	4560	548	4560	548	4560	2.96
120	533	4485	533	4475	533	4480	3.11
150	530	4511	530	4509	530	4510	3.15
180	527	4425	527	4395	527	4410	3.17
210	528	4410	528	4410	528	4410	3.18
240	515	4380	515	4380	515	4380	3.19

Table D.2: Experimental data for reduction of acid, Fe and SO_4^{2-} using 40g of SS slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	522	4620	518	4620	520	4620	3.34
60	517	4580	518	4580	517.5	4580	3.35
90	524	4641	524	4639	524	4640	3.31
120	511	4400	510	4600	510.5	4500	3.35
150	490	4483	510	4477	500	4480	3.37
180	487	4240	488	4240	487.5	4240	3.47
210	490	4301	491	4299	490.5	4300	3.44
240	487	4210	487	4210	487	4210	3.46

Table D.3: Experimental data for reduction of acid, Fe and SO_4^{2-} using 60g of SS slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	450	4422	450	4418	450	4420	3.55
60	389	4100	389	4100	389	4100	3.73
90	391	4000	391	4000	391	4000	3.72
120	387	3760	387	3760	387	3760	3.74
150	387	3760	387	3760	387	3760	3.74
180	384	3780	384	3780	384	3780	3.73
210	347	3680	347	3680	347	3680	3.81
240	340	3600	340	3600	340	3600	3.83

Table D. 4: Experimental data for reduction of acid, Fe and SO_4^{2-} using 80g of SS slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	348	3890	352	3890	350	3890	4.41
60	284	3560	285	3560	284.5	3560	4.61
90	269	3280	265	3280	267	3280	4.82
120	259	3240	261	3240	260	3240	4.83
150	267	3240	255	3240	261	3240	4.83
180	257	3240	258	3240	257.5	3240	4.84
210	246	3180	254	3180	250	3180	4.91
240	251	3200	251	3200	251	3200	4.9

Table D.5: Experimental data for reduction of acid, Fe and SO_4^{2-} using 100g of SS slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	390	3750	389	3750	389.5	3750	5.75
60	278	3420	282	3420	280	3420	5.77
90	250	3200	252	3200	251	3200	5.79
120	241	3190	239	3190	240	3190	5.78
150	241	3160	241	3160	241	3160	5.81
180	233	3010	247	3010	240	3010	5.87
210	226	3010	234	3010	230	3010	5.87
240	221	2890	219	2890	220	2890	5.89

Table D.6: Experimental data for reduction of acid, Fe and SO_4^{2-} using 20g of BOF slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	469	4520	471	4520	470	4520	4.62
60	449	3780	449	3780	449	3780	4.82
90	431	3450	445	3450	438	3450	4.89
120	433	3650	433	3650	433	3650	4.91
150	428	3420	427	3420	426	3420	4.92
180	427	3180	427	3180	427	3180	4.93
210	428	3160	428	3160	428	3160	4.95
240	425	3100	425	3100	425	3100	5.05

Table D.7: Experimental data for reduction of acid, Fe and SO_4^{2-} using 40g of BOF slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	389	3810	390	3810	389.5	3810	5.82
60	381	3600	379	3600	380	3600	5.92
90	372	3230	382	3230	377	3230	5.96
120	368	3230	368	3230	368	3230	5.97
150	362	3200	362	3200	362	3200	5.99
180	351	3010	353	3010	352	3010	6.01
210	349	3070	349	3070	349	3070	6.01
240	351	2760	350	2760	350.5	2760	6.04

Table D.8: Experimental data for reduction of acid, Fe and SO_4^{2-} using 60g of BOF slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	325	3215	331	3185	328	3200	7.31
60	288	2982	288	2978	288	2980	7.42
90	231	2793	229	2787	230	2790	7.44
120	200	2760	198	2760	199	2760	7.49
150	143	2300	142	2300	142.5	2300	7.61
180	143	2311	151	2309	147	2310	7.6
210	132	2260	132	2260	132	2260	7.62
240	120	2130	116	2130	118	2130	7.67

Table D.9: Experimental data for reduction of acid, Fe and SO_4^{2-} using 80g of BOF slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	77	2423	79	2367	78	2400	9.34
60	61	1733	61	1727	61	1730	9.39
90	55	1540	55	1540	55	1540	9.42
120	43	1536	83	1546	48	1540	9.42
150	48	1507	48	1513	48	1510	9.43
180	49	1520	49	1520	49	1520	9.44
210	43	1440	45	1440	44	1440	9.47
240	42	1420	42	1420	42	1420	9.48

Table D.10: Experimental data for reduction of acid, Fe and SO_4^{2-} using 100g of BOF slag to 1L of AMD at different times

Time (mins)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	600	4800	600	4800	600	4800	2.5
30	28.22	1917	28.66	1923	28.44	1920	11.13
60	23.58	1670	23.66	1670	23.62	1670	11.17
90	20.72	1470	20.7	1470	20.71	1470	11.19
120	16.7	1392	16.7	1388	16.7	1390	11.21
150	10.1	1410	10.1	1410	10.1	1410	11.21
180	5	1381	7	1379	6	1380	11.23
210	5	1210	6	1210	5	1210	11.27
240	2	1993	2	1207	2	1200	11.28

APPENDIX E

CONTINUOUS FLOW STUDIES

"You cannot teach a man anything; you can only help him discover it in himself".

~ Galileo Galilei

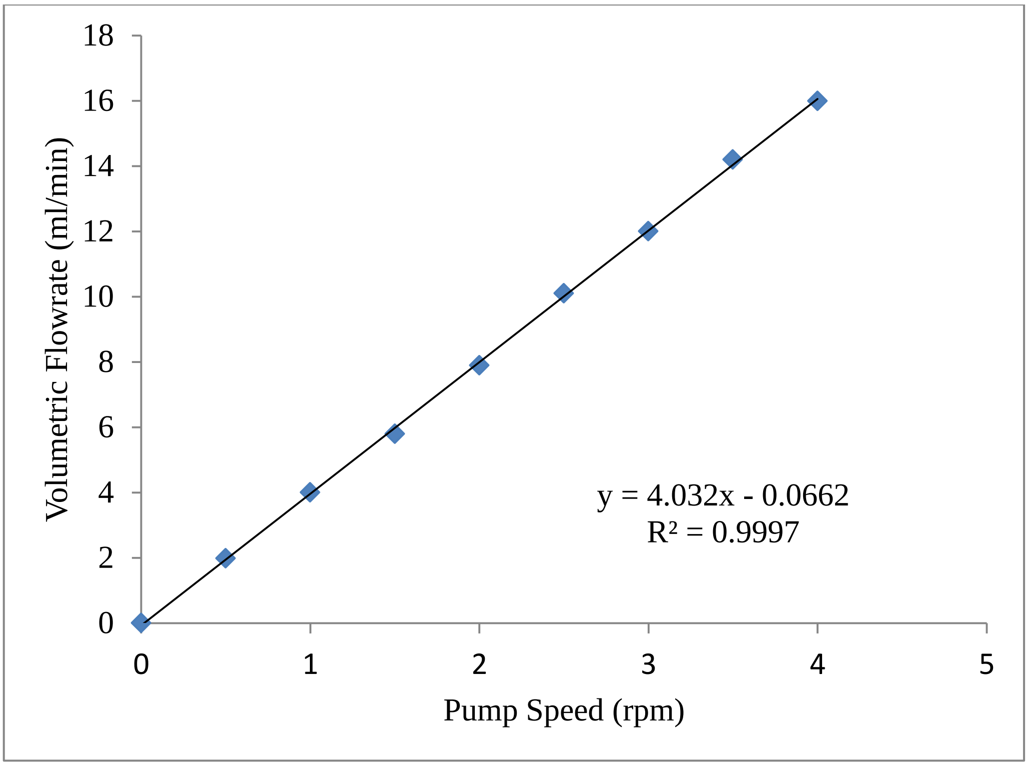

Figure E. 1: Peristaltic pump calibration curve

Table E.1: Experimental data for reduction of acid, Fe and SO_4^{2-} using SS slag with feed flowrate of 4ml/min at different times

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	0	0	0		0	0	0
2	311	2397	313	2403	312	2400	7.31
4	330	2566	360	2568	345	2567	6.99
6	342	2589	346	2591	344	2590	6.91
8	352	2610	352	2610	352	2610	6.89
10	387	2692	387	2688	387	2690	6.75
12	371	2721	374	2719	373	2720	6.75

Table E.2: Experimental data for reduction of acid, Fe and SO_4^{2-} using SS slag with feed flowrate of 8ml/min at different times

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	0	0	0	0	0	0	0
2	390	3117	390	3123	390	3120	5.38
4	410	3414	412	3432	411	3423	4.89
6	434	3489	428	3491	431	3490	4.5
8	431	3341	411	3341	421	3341	4.52
10	443	3595	443	3595	443	3595	4.51
12	446	3510	440	3490	443	3500	4.5

Table E.3: Experimental data for reduction of acid, Fe and SO_4^{2-} using SS slag with feed flowrate of 12ml/min at different times

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	0	0	0	0	0	0	0
2	740	4422	715	4424	720	4423	3.35
4	686	4450	688	4450	687	4450	3.13
6	530	4230	530	4230	530	4230	2.91
8	667	4310	667	4310	667	4310	2.92
10	670	4200	670	4200	670	4200	2.9
12	680	4610	682	4610	681	4610	2.9

Table E.4: Experimental data for reduction of acid, Fe and SO_4^{2-} using SS slag with feed flowrate of 16ml/min at different times

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	0	0	0	0	0	0	0
2	820	4721	820	4719	820	4720	3.18
4	825	4823	835	4823	830	4823	3.07
6	825	4758	829	4762	827	4760	2.98
8	830	4611	832	4609	831	4610	2.9
10	827	4745	827	4745	827	4745	2.86
12	857	4780	863	4778	860	4779	2.72

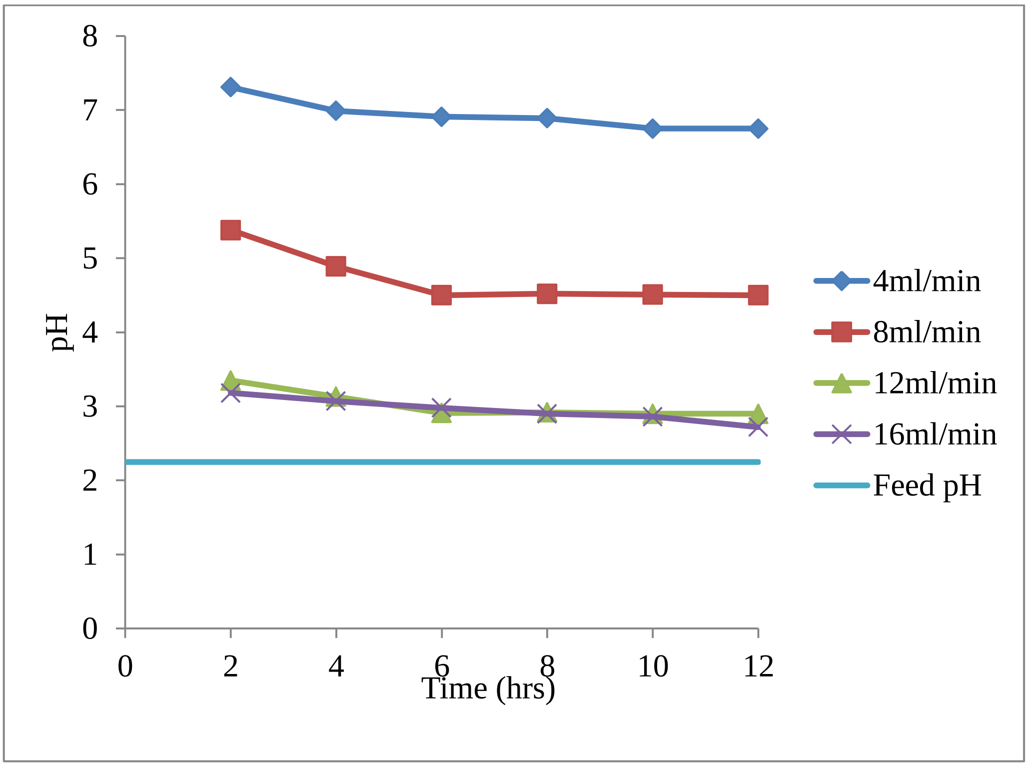

Figure E.2: Effect of flowrate on reduction of acidity from AMD using SS slag for a period of 12 hrs

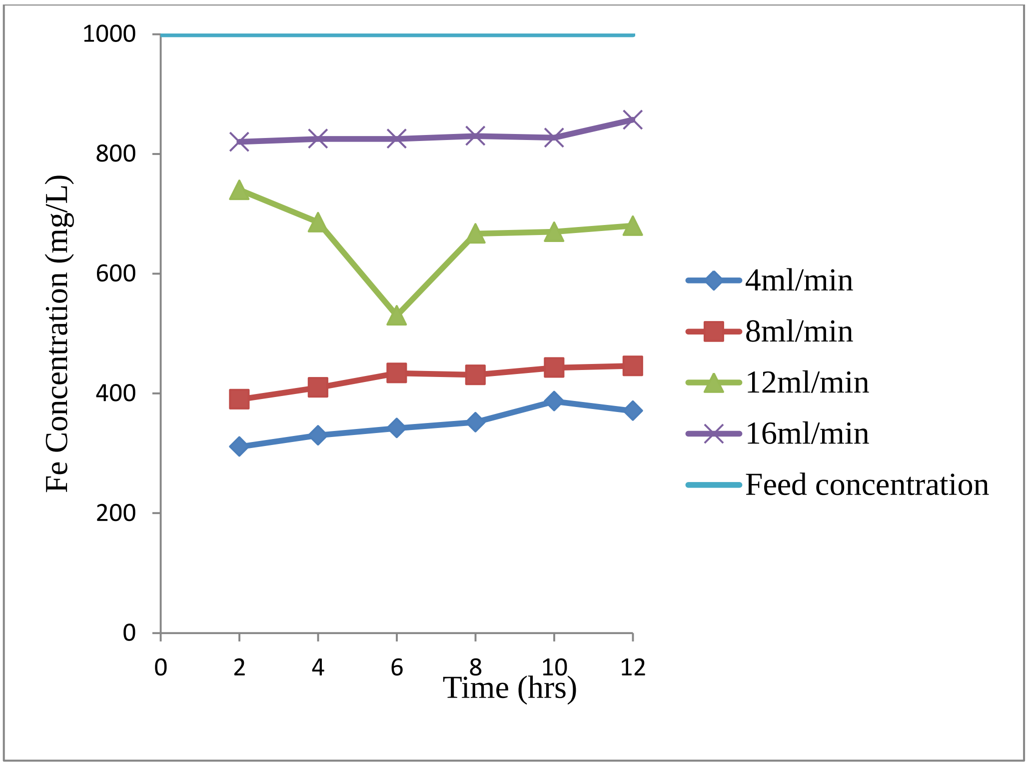

Figure E.3: Effect of flowrate on reduction of iron concentration from AMD using SS slag for a period of 12 hrs

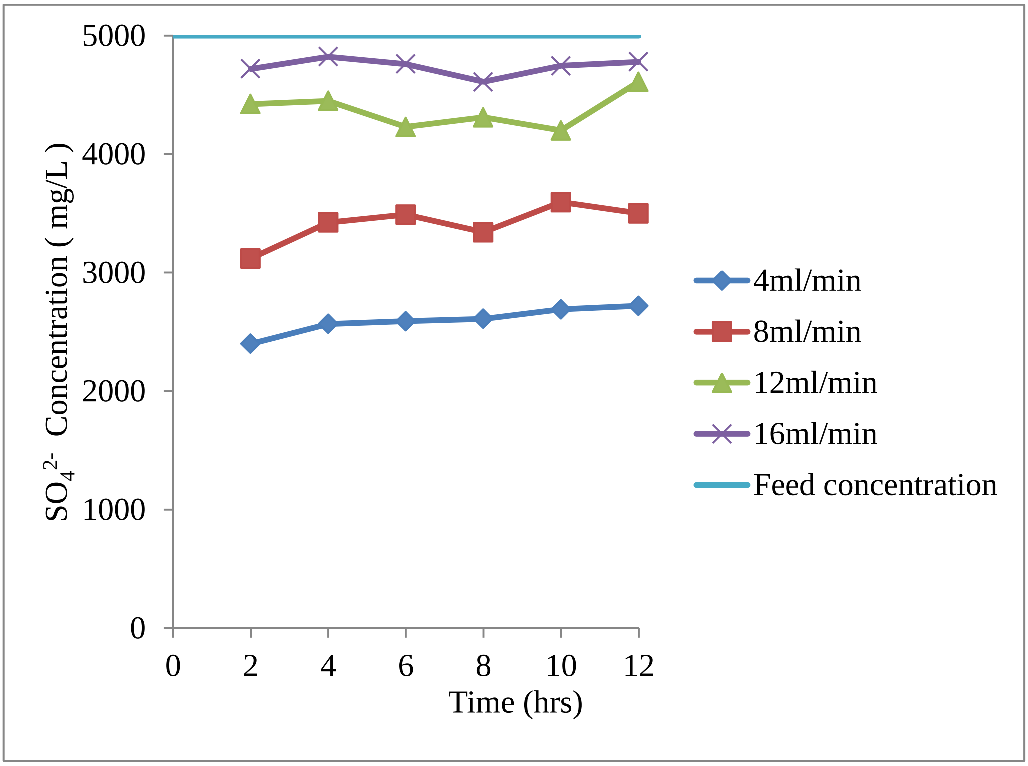

Figure E.4: Effect of flowrate on reduction of sulphate concentration from AMD using SS slag for a period of 12 hrs

Table E.5: Experimental data for reduction of acid, Fe and SO_4^{2-} using SS slag with feed flowrate of 4ml/min at different times

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	0	0	0	0	0	0	0
2	0	740	0	746	0	743	13.21
4	0	1050	0	1050	0	1050	13.14
6	0	755	0	759	0	757	12.25
8	0	789	0	789	0	789	11.89
10	0	819	0	821	0	820	11.52
12	0	935	0	951	0	943	11.53

Table E.6: Experimental data for reduction of acid, Fe and SO_4^{2-} using BOF slag with feed flowrate of 8ml/min at different times

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	0	0	0	0	0	0	0
2	0	1056	0	1056	0	1056	11.02
4	0	1432	0	1432	0	1432	10
6	1	1520	1	1520	1	1520	9.81
8	5	1500	9	1500	7	1500	9.79
10	0	1510	0	1510	0	1510	9.79
12	7	1489	11	1489	9	1489	9.75

Table E.7: Experimental data for reduction of acid, Fe and SO_4^{2-} using BOF slag with feed flowrate of 12ml/min at different times

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	0	0	0	0	0	0	0
2	88	1620	90	1620	89	1620	9.89
4	101	1710	101	1710	101	1710	8.17
6	132	1820	132	1820	132	1820	8.01
8	141	1857	143	1857	142	1857	7.86
10	129	1842	132	1842	131	1842	7.52
12	142	2345	142	2345	142	2345	7.32

Table E.8: Experimental data for reduction of acid, Fe and SO_4^{2-} using BOF slag with feed flowrate of 16ml/min at different times

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	Fe (mg/L)	SO_4^{2-} (mg/L)	
0	0	0	0	0	0	0	0
2	179	3005	187	3005	183	3005	7.87
4	201	3120	203	3120	202	3120	7.75
6	213	3300	213	3300	213	3300	6.69
8	210	3210	184	3210	197	3210	6.89
10	125	3205	137	3205	131	3205	6.62
12	201	3301	201	3301	201	3301	6.23

Table E.9: Experimental data for reduction of Fe and SO_4^{2-} using BOF slag at different residence times and running time

τ (hours)	Running Time (hours)	Fe (mg/L)	SO_4^{2-}(mg/l)
0.25	2	183	3005
0.25	2	202	3120
0.25	2	213	3300
0.25	2	197	3210
0.25	2	131	3205
0.25	2	201	3301
0.5	4	89	1620
0.5	4	101	1710
0.5	4	132	1820
0.5	4	142	1857
0.5	4	131	1842
0.5	4	142	2345
1	8	0	1056
1	8	0	1432
1	8	1	1520
1	8	7	1500
1	8	0	1510
1	8	9	1489
2	12	0	743
2	12	0	1050
2	12	0	757
2	12	0	789
2	12	0	820
2	12	0	943

Table E.10: Experimental data for reduction of acid, Fe and SO_4^{2-} using BOF slag with design residence time of 2.67 hours

Time (hours)	Run 1		Run 2		Average		pH
	Fe (mg/L)	SO_4^{2-} (mg/l)	Fe (mg/L)	SO_4^{2-} (mg/l)	Fe (mg/L)	SO_4^{2-} (mg/l)	
0	0	0	0	0	0	0	0
2	0	693	0	693	0	693	13.31
4	0	759	0	755	0	757	13.17
6	0	811	0	809	0	810	12.19
8	0	789	0	789	0	789	11.75
10	0	1013	2	1011	1	1012	11.22
12	9	989	5	1011	7	1000	11.09
24	130	2112	134	2114	132	2113	7.89
26	141	3221	143	3223	142	3222	6.85
28	129	3110	133	3130	131	3120	6.57
30	142	3401	142	3401	142	3401	6.57
32	216	3623	210	3623	213	3623	6.45
34	240	3725	242	3723	241	3724	5.99
36	234	3690	234	3690	234	3690	6.12

Table E.11: Experimental data for obtaining volume of slag required for different AMD flowrates with residence time of 0.25 hrs

τ (days)	ε	Q (Ml/d)	V(L)	V (m^3)
0	0	0	0	0
0.010417	0.4	2	0.020833	20.83333
0.010417	0.4	4	0.041667	41.66667
0.010417	0.4	6	0.0625	62.5
0.010417	0.4	8	0.083333	83.33333
0.010417	0.4	10	0.104167	104.1667
0.010417	0.4	12	0.125	125
0.010417	0.4	14	0.145833	145.8333
0.010417	0.4	16	0.166667	166.6667
0.010417	0.4	18	0.1875	187.5
0.010417	0.4	20	0.208333	208.3333

Table E.12: Experimental data for obtaining volume of slag required for different AMD flowrates with residence time of 0.5 hrs

τ (days)	ε	Q (Ml/d)	V(L)	V (m^3)
0	0	0	0	0
0.020833	0.4	2	0.104167	104.1667
0.020833	0.4	4	0.208333	208.3333
0.020833	0.4	6	0.3125	312.5
0.020833	0.4	8	0.416667	416.6667
0.020833	0.4	10	0.520833	520.8333
0.020833	0.4	12	0.625	625
0.020833	0.4	14	0.729167	729.1667
0.020833	0.4	16	0.833333	833.3333
0.020833	0.4	18	0.9375	937.5
0.020833	0.4	20	1.041667	1041.667

Table E.13: Experimental data for obtaining volume of slag required for different AMD flowrates with residence time of 1 hr

τ (days)	ε	Q (Ml/d)	V(L)	V (m^3)
	0	0	0	0
0.041667	0.4	2	0.208333	208.3333
0.041667	0.4	4	0.416667	416.6667
0.041667	0.4	6	0.625	625
0.041667	0.4	8	0.833333	833.3333
0.041667	0.4	10	1.041667	1041.667
0.041667	0.4	12	1.25	1250
0.041667	0.4	14	1.458333	1458.333
0.041667	0.4	16	1.666667	1666.667
0.041667	0.4	18	1.875	1875
0.041667	0.4	20	2.083333	2083.333

Table E.14: Experimental data for obtaining volume of slag required for different AMD flowrates with residence time of 2 hrs

τ (days)	ε	Q (Ml/d)	V(L)	V (m^3)
0	0	0	0	0
0.083333	0.4	2	0.416667	416.6667
0.083333	0.4	4	0.833333	833.3333
0.083333	0.4	6	1.25	1250
0.083333	0.4	8	1.666667	1666.667
0.083333	0.4	10	2.083333	2083.333
0.083333	0.4	12	2.5	2500
0.083333	0.4	14	2.916667	2916.667
0.083333	0.4	16	3.333333	3333.333
0.083333	0.4	18	3.75	3750
0.083333	0.4	20	4.166667	4166.667

Table E.15: Experimental data for obtaining volume of slag required for different AMD flowrates with residence time of 2.67 hrs

τ (days)	ε	Q (Ml/d)	V(L)	V (m^3)
0	0	0	0	0
0.11125	0.4	2	0.55625	556.25
0.11125	0.4	4	1.1125	1112.5
0.11125	0.4	6	1.66875	1668.75
0.11125	0.4	8	2.225	2225
0.11125	0.4	10	2.78125	2781.25
0.11125	0.4	12	3.3375	3337.5
0.11125	0.4	14	3.89375	3893.75
0.11125	0.4	16	4.45	4450
0.11125	0.4	18	5.00625	5006.25
0.11125	0.4	20	5.5625	5562.5