# UTILISATION OF WASTE GAS SLUDGE FOR WASTE WATER TREATMENT

BY

**AMIR JAFARIPOUR**

A thesis submitted to

The University of Birmingham for the degree of

**DOCTOR OF PHILOSOPHY**

Chemical Engineering

School of Chemical Engineering

The University of Birmingham

United Kingdom

August 2013

University of Birmingham

# Abstract

This hypothesis driven research investigated the removal of Cu, Fe, Zn and Mn from synthetic metal solutions and real Acid Mine Drainage (AMD) from Wheal Jane mine in West Cornwall UK, employing waste gas sludge (BOS sludge) which is an end waste reside generated from steel production at TATA steel plant in Port Talbot in South Wales. Laboratory experiments were conducted to study the capacity and effectiveness of BOS sludge as a novel low cost material for the removal of these heavy metals from AMD solutions.

Batch experiments showed the efficiency and adsorption rates increased with reduction in BOS sludge particle size, lower in initial metal concentration, increase in BOS sludge dosage, an increase in initial pH and increase in agitation speed. Fitting of the Langmuir isotherm model to experimental data gave a good fit with correlation coefficients $R^2 \geq 0.99$ and the selectivity series of BOS sludge was: $Cu^{2+} > Fe^{3+} > Zn^{2+} > Mn^{2+}$.

Adsorption was spontaneous and high pH promoted adsorption possibly by precipitation and/or ion exchange processes which had taken place between the exchangeable cations present in BOS and solutions. For single and multiadsorbate systems, a Pseudo second order model was the most appropriate theory to satisfactorily describe experimental data and the rate limiting step for this process was chemisorption. The treatment of actual Wheal Jane mine AMD demonstrated that about 100% of Cu and Fe, 97% of Zn and 94% of Mn were removed from solution. Results from the treatment of real and synthetic AMD solutions revealed that BOS sludge worked well and hence BOS sludge could be used as a sustainable sorbent in AMD treatment technologies.

Reactor studies showed that BOS sludge was capable of removing heavy metals from continuously flowing solutions. Higher metal uptakes were achieved by the presence of mixing. The Results obtained from this study were comparable to those achieved from other passive treatment technologies. The results proved that BOS sludge as a functional adsorbent was suited for treating relatively concentrated synthetic metal solutions.

# Dedication

*I would like to dedicate this thesis to my beloved parents for their unceasing encouragement, support and guidance.*

# Acknowledgements

First and foremost I would like to express my profound gratitude to my lead supervisor Prof. Neil Rowson for his inspirational instruction, assistance and valuable guidance. I would also like to acknowledge the support and assistance given me by Dr. Gurmel Ghataora.

I wish to show my appreciation to EPSRC and Harsco Metals & Minerals Ltd, UK for providing funding and supplying the samples used in this research project. I would also like to take this opportunity to acknowledge the support provided by my industrial mentor, Mr. Richard Reasbeck throughout this project.

It would not have been possible to write this doctoral thesis without the help and support of the kind people around me, to only some of whom it is possible to give particular mention here. I am particularly indebted to my mother; I am blessed to have her for her unconditional love, patience and guidance. To my dear family, a special thank you for your constant encouragement and support throughout my years of study.

In addition I also place on record my sense of gratitude to Nastaran Edarehchi for encouraging me to embark on my studies and being stalwart at all times. Last but not least, I would like to wholeheartedly thank God who gave me the privilege and grace to pursue this study in spite of many challenges faced. The learning outcome of these past several years, both academically and personally, has been significantly positive and beneficial. The journey has been exceptionally remarkable and it has set a unique platform to tackle challenges ahead.

# Table of Contents

## Chapter 4: Characterisation of BOS Sludge

## Chapter 5: Treatment of synthetic AMD with BOS sludge and other adsorbents

## Chapter 6: Treatment of Wheal Jane AMD with BOS Sludge and other adsorbents

## Chapter 7: Reactor studies for synthetic AMD treatment

## Chapter 8: Conclusions and Recommendations

**REFERENCES**
**APPENDICES**

# List of Figures

# List of Tables

# Nomenclature

$b_L$: Langmuir adsorption constant

$b_e$: desorption coefficient

C: intercept

$C_{ref}$: reference fluid phase concentration of adsorbate

$C_i$: initial metal concentration of heavy metal ions

$C_f$: final metal concentration of heavy metal ions

$C_e$: residual liquid phase concentration at equilibrium

$C_o$: initial concentration of heavy metal ions

$C_t$: metal ion concentration at time, t

dp: average particle diameter

D`: diffusion coefficient of ion

h: initial adsorption rate

$k_i$: intra-particle diffusion rate constant

$k_1$: pseudo first order rate constant

$k_2$: pseudo second order rate constant

$k_d$: distribution coefficient ratio

$k_F$: Freundlich constant

m: mass of adsorbent

$m_s$: mass of adsorbent particle per unit volume of particle free slurry

$n_F$: Freundlich constant

$q_e$: amount of solute adsorbed per unit mass of adsorbent at equilibrium

$q_{e\ max}$: maximum experimental adsorption capacity at equilibrium coverage of available adsorption sites

$q_m$: maximum adsorption capacity

$q_t$: amount of solute adsorbed per unit mass of adsorbent at time, t

Q: volumetric flow rate

$R_L$: adsorption indicator

$R^2$: correlation coefficient

RT: residence time

$r_o$: BOS particle radius

U(t): fractional attainment of equilibrium in the ion exchanger

V: volume of solution from which adsorption occurs

**Symbols:**

$\alpha$: initial adsorption rate

$\varepsilon_p$: porosity of the particles.

$\rho_t$: density of particles

# Abbreviations

| | |
|---|---|
| AAS | Atomic Adsorption Spectrometry |
| ALD | Anoxic Limestone Drain |
| AMD | Acid Mine Drainage |
| BF | Blast Furnace |
| BOF | Basic Oxygen Furnace |
| BOS | Basic Oxygen Steelmaking |
| EDS | Energy Dispersive Spectroscopy |
| EQS | Environmental Quality Standard |
| GGBS | Ground Granulated Blast Furnace Slag |
| GS | Granulated Slag |
| LD | Linz-Donawitz |
| OLC | Open Limestone Channel |
| sAMD | Synthetic Acid Mine Drainage |
| SEM | Scanning Electron Microscope |
| XRF | X-Ray Fluorescence |

# CHAPTER 1

# INTRODUCTION

## 1.1 Steel production & waste issues

Over the years, the recovery and the usage of natural resources has been problematic due to a shortage of high quality natural raw materials being experienced all over the world. On the other hand, the disposal of industrial waste or by-products has become more complicated and expensive as a result of the increasing environmental standards and shortages of suitable disposal locations. In recent years Landfill tax legislation has been introduced in many countries. In the consideration of conserving and extending the resources of quality natural raw materials and increase in environmental awareness, attention is now being focused on the recycling of industrial waste streams or by-products (Kalyoncu et al., 1999).

Integrated steel plants generate large amounts of solid wastes which are mainly blast furnace and steel furnace slags, dusts, sludges, mill scales, used refractories, etc. Studies and research on metal and waste recycling have shown that as a result of slag processing and usage in different applications, massive stoke piles of such wastes are disappearing and the land occupied by these by-products and waste streams can be reclaimed for other purposes (Zunkel and Schmitt, 1996). The normal practice is the recycling and reuse, but still there are huge amounts of wastes that are disposed of as landfills, hence there have been potential areas for innovation and study in this field to utilise steel wastes in waste water treatment.

Steel production plants use raw materials, air, water, fuel and power to produce steel. The production of steel is generally carried out in of three furnace types, the basic oxygen, the electric arc furnace or the open hearth furnace. Regardless of the type of furnace used or grade of steel produced, steel making is accompanied by the emission of a large quantity of dust and subsequent sludge.

Utilisation of industrial waste materials from steel-making processes such as steel slag and blast furnace slags has been established in a number of applications in the civil engineering sector. In general the slags and the sludge are produced at different stages within different processes during steelmaking process. Although most these wastes have similar chemical constituents, the proportions and their composition can be different in a number of ways (Personal communication, 2011).

These wastes contain some valuable resources and elements such as iron, zinc, lead, calcium, etc., which can be recovered and reused within in steel-making process or can be used as raw materials elsewhere (Shen and Forssberg, 2003; Proctor et al., 2000). These wastes are now being considered as a secondary resource of certain elements, rather than an end-waste and have been used as in adsorption studies in many areas such as heavy metals removal from aqueous solutions in treating industrial wastes or cleaning water.

In addition, for some applications, these waste materials can have comparable or even better properties than functional materials such as zeolites or activated carbon in treating an environmental pollutant such as Acid Mine Drainage (AMD) in a cost effective manner (Simmons et al., 2002; Mack and Gutta, 2009).

The recycling of waste gas sludge (BOS sludge) as an end waste of steelmaking process has been problematic due to its complexity in structure and is one of the challenges that steel producers have encountered in recent years. Thus it is thought to use this material elsewhere such as for waste water treatment purposes. In this study, as well as synthetic acid mine drainage, Wheal Jane Mine acid mine drainage as a case study will be used. The acidic solutions produced at this mine will be collected, sampled and contacted with BOS sludge to determine the capacity of BOS sludge as a low cost sorbent for treating AMD.

## 1.2 Waste recovery

The Basic Oxygen Furnace dust (BOF) and waste gas sludge (BOS sludge) represent two of the three largest volume wastes typically land-disposed by iron and steel plants (Environmental Leadership, 1998). Many processes developed to treat dust and sludge have not reached pilot plant scale. Some methods have been commercialised for a period of time and then have been stopped due to high energy costs or financial reasons. It is believed that the major reason for a number of failures is that it is more economical to extract metals from ores than from waste materials (Pickles et al., 2000). This can be due to limited data provided by process developers, researchers and inadequate literature reviews available.

There are specific challenges particularly facing the utilisation of waste gas sludge that relate to technology and applications including cost, processing, energy conservation and emissions involved. The current activities in relation to treatment of this waste material are carried out in an inconsistent manner. They are generally configured by a low level of scientific understanding of the chemical and physical processes involved; hence the "best" technique is not yet established.

Nevertheless researchers still believe that there is a viability of recycling these materials into useful products such as hot metal for steel production, raw material in non-ferrous industry (zinc industry) and road construction or even in cement production (civil engineering) (Sharma et al., 1993). However detailed and scientific investigation is essential to establish the scope of the problems associated with recovering the valuable materials from different slag and sludge wastes and proposed utilisations must be carefully evaluated in order to be practical. Table 1.1 outlines the applications for some of the main steelmaking wastes generated.

**Table 1.1: Common uses for different slags generated at steel plants** *(Source: Mueller et al., 2005)*.

| Blast Furnace Slag (BFS) | | | Steel Furnace Slag (BOS) |
|---|---|---|---|
| Air-cooled | Expanded Slag | Granulated | |
| Asphalt aggregate | Road base | GGBS cement | Asphalt aggregate |
| Concrete aggregate | Concrete masonry | Roller compacted concrete | Cement raw feed |
| Cement raw feed | Lightweight concrete | Soil cement | Mine buffer |
| Agriculture | Insulation | Agriculture/Soil Amendment | AMD water treatment |
| Roof aggregate | Low density fillers | Road base | Agricultural/soil amendment and stabilisation |
| Rail road ballast | --- | --- | Railroad/railway ballast |
| Low density fillers | --- | --- | Road base |
| AMD water treatment | --- | --- | Low density fillers |
| Glass manufacture | | | |
| Insulation/ mineral wool | | | |
| Agriculture/Soil Amendment | | | |

## 1.2.1 Recycling BOS sludge into steelmaking process
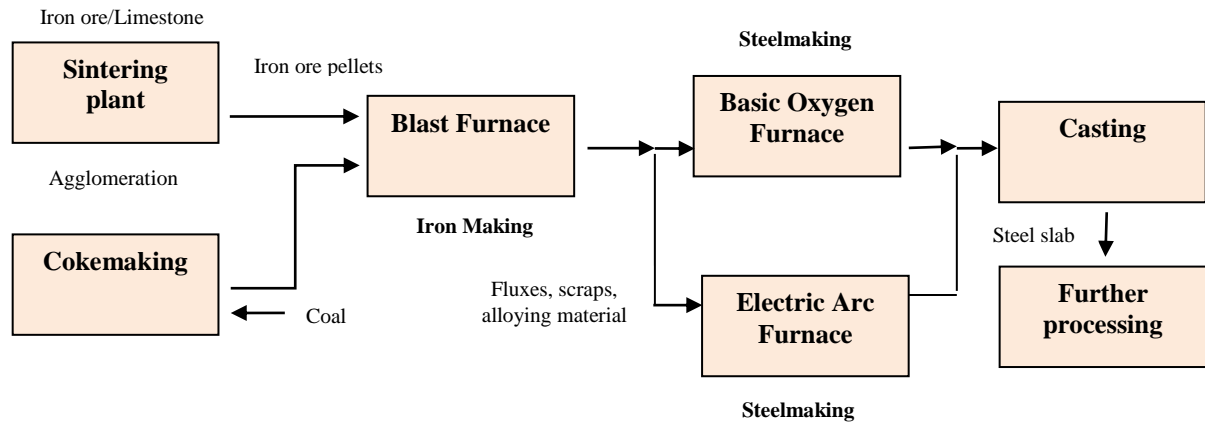


**Figure 1.1: Simplified process flow diagram for steelmaking** *(Adapted from: Branca and Colla, 2012)*.

The fine solid particles recovered after wet scrubbing of the gas generated from basic oxygen steel furnace in the sludge form are known as waste gas sludge (BOS sludge). It is crucial for steel plants to develop a process of recycling this waste material. However direct utilisation is problematic for a number of reasons.

In iron and steel making process, the presence of Pb, K, Na, S, Cd, Cu, cyanides, oils, halides and as well significant quantities of Zn cause major problems (Makkonen et al., 2002; Das et al., 2002; Ellis et al., 1999). The reuse of waste flue dust or waste gas sludge in sintering plant or blast furnace has been limited and has caused the following problems:

➢ Operational difficulties/ unacceptable hot metal composition;

➢ Alkaline elements accumulate in blast furnace due to cyclic reactions and hinder the normal operation;

➢ Loss of permeability of the burden, it is thought that the zinc accumulation inside the furnace causes the formation of hard bank materials, which causes the formation of bridges and irregular flows of the mix. The permeability of the mix is expected to affect the relative amount of Zn to be condensed either as Zn metal or ZnO (Lee and Kozak, 1993).

➢ Cracking of refractory bricks and linings;

➢ Zinc forms a circuit in the furnace, resulting in extra coke consumption; the effect of zinc circulation on coke consumption depends mainly on the operating conditions. The recirculation of zinc within the furnace causes formation of banks and bridges in the furnace burden, which results in channels of gas flowing upwards, and decreases the efficiency of use of the chemical and heat energy of the off-gas, and increases the coke consumption of the blast furnace. (Shchukin et al., 1991).

➢ The volatility of zinc and its condensation in cooler region of blast furnace causing problems. The condensation temperature, either as Zn metal or ZnO, increases with the increase in Zn concentration in the gas phase. These temperatures are certainly within the range prevalent in the mix burden above the reaction zone. The condensed Zn metal or ZnO will travel down with the mix and increase local Zn content. Once the condensed ZnO alters the permeability of the mix, the gas from the crucible may flow through channels. Under such circumstances, most of the Zn vapour will not have enough time to exchange energy and be oxidised by air at the top of the mix (Lee and Kozak, 1993).

A number of processes for recycling the particulates are in use or under development such as pelletising, briquetting, magnetic hydrocyclones, physical separations and many others. However there are still obstacles in recycling this waste material as they contain a high moisture content which makes them pasty and form agglomerates, therefore they must be optimally dried. Build-up of impurities with each recycle causes high amount of non-ferrous metals e.g. Zn, Pb to be increased in the system. The method of charging recycled material to the furnace (e.g. to sinter machine) also needs to be taken into consideration as particle size can influence the charging method and hence increase operating costs.

## 1.2.2 BOS sludge as an adsorbent for Acid Mine Drainage treatment

Britain has a long history of mining for coal, metal ores and other minerals. The number of mines is enormous, reports address in Wales, the South West and Northumbria over

3,700 sites exist, though not all are causing serious pollution. No metal mines are still in use; the last large tin mine in Cornwall closed in 1998. Monitoring and studies have shown that a large number of abandoned metal mines are significant contributors to heavy metal and toxic pollution into rivers and seas. The liability in relation to this matter still remains a subject of concern (Environment Agency, 2008).

A newer approach of utilising this waste material (BOS) deserves attention as a potential and alternative solution to recycling routes. As mentioned above another environmental concern in the United Kingdom is the presence of Acid Mine drainage (AMD) due to the increasing number of abandoned mines which leads to AMD discharges into the surrounding areas. This research has indicated that there may be a good potential for the usage of BOS sludge as an adsorbent for Acid Mine Drainage treatment.

Acid Mine Drainage (AMD) is an environmental pollutant resulted from a combination of weathering and mining activities. Acid mine waters have low pH-values and high concentrations of toxic metals (arsenic, beryllium, boron, cadmium, chromium, copper, lead, molybdenum, nickel, selenium, and vanadium) which are not biodegradable and thus tend to accumulate in the environment causing various threats in nature (Skousen and Ziemkiewicz, 1996; McGinness et al., 1999).

There are a number of Acid Mine Drainage (AMD) treatment technologies and these fall into two broad categories, passive and active treatment. Since conventional methods have a number of shortcomings; which are greater land utilisation, production of large secondary solid waste, high capital and operating costs particularly when treating relatively dilute solutions alternative methods need to be developed.

Using steel wastes such as BOS sludge can be an improvement on work carried out at present on slag aggregates as a filter media for waste water treatment (Harsco, 2013). BOS sludge may be used as a long lasting product for treating acidic metal bearing streams in a manner which minimises the volumetric generation of sludge on site. Typical acid mine drainage streams with pH values as low as 2 depending on water chemistry and flow rates can be pumped to the surface and treated in an integrated plant.

The metal sulphate concentrations and dissolved heavy metals combine with calcium ions in the lime present in the steel wastes, which leads to neutralisation reaction in which heavy metals precipitate out and water can then be discharged into public streams or even further treated for domestic uses. The treated AMD can also be used in agriculture, for instance in the irrigation of different plants.

The ideal technique for treating AMD should include the following factors (McGinness et al., 1999):

➤ Reduced land utilisation (small plant);

➤ Relatively more effective and efficient compared to conventional methods such as precipitation technology;

➤ Low cost (capital and operating cost);

➤ Produce small amounts or no solid wastes for disposal;

➤ Simple to operate (low labour levels);

➤ Utilise a waste material as a sorbent.


## 1.3 Motivation and Aims of Thesis

The concept of using one waste material (BOS sludge) to remove metals from another pollutant (AMD) has particular attractions. The BOS sludge is stockpiled on site at Port Talbot creating a space and contaminant issue. If these materials could be used to treat local AMD in South Wales in an efficient and cost effective manner, it would solve two environmental problems.

This thesis reviews number of technologies in use and some of those that have been proposed for recovering steel slags. The recycling of BOS sludge still remains as one of the challenges and there is not adequate literature available. In order to illuminate the problems involved with handling, processing, disposal and treatment of steelmaking wastes including waste gas sludge, the thesis begins by giving an overview of utilisation routes of a number of steel waste materials.

This study addresses the issue of millions of tonnes of Waste Gas Sludge which have accumulated over years in a waste stockyard at Tata Steel plant in Port Talbot (South Wales). This project has two aims; first to investigate different methods and techniques of recycling and utilisation of Waste Gas Sludge (BOS sludge) within the steelmaking process and also to develop a low cost alternative usage of this waste material with commercial value as a product that can be sold for treatment of Acid Mine Drainage.

Main focus has been on the treatment of Acid Mine Drainage (AMD). Waste Gas Sludge (BOS sludge) was used to study its efficiency on the removal of heavy metal ions from AMD solutions. Only four heavy metal ions were considered in this investigation; these are $Fe^{3+}$, $Cu^{2+}$, $Zn^{2+}$ and $Mn^{2+}$. These were chosen because they are some of the main heavy metal ions present in most AMD solutions (Swash and Monhemius, 2005; Coulton et al., 2003). The effectiveness of BOS sludge as an adsorbent in AMD treatment was further investigated by using the BOS sludge to treat AMD from Wheal Jane Mine (Cornwall, UK) and synthetic AMD solutions.

## 1.4 Thesis Structure

This thesis is divided into a number of chapters, each explaining different aspects of the investigation. A summary of each chapter is given below.

### Chapter 1: Introduction

A brief background to the wastes produced by steelmaking process is given together with different potential solutions to the problem. An outline of the motivation and the objectives of this thesis are also briefly discussed.

### Chapter 2: Literature Review

This chapter gives an introduction to the steelmaking process and the types of wastes that are produced as by-products. It also gives an overview into the various methods that have been utilised in order to recycle and recover wastes within steelmaking process; different waste recovery technologies available and the environmental impact aspects of BOS steelmaking.

An explanation into the formation and occurrence of Acid Mine Drainage problem (AMD) is also given; its sources; environmental impact; prevention and the different treatment methods available. A review of previous research involving the use of different inorganic adsorbents for the removal of heavy metals from AMD such as blast furnace slag, lignite, natural zeolite, coal fly ash and others are also presented.

### Chapter 3: Materials and Methods

The materials used in this research, that is, chemicals and adsorbent materials are described in this chapter. The experimental techniques used in order to remove heavy metals and separate metals from one another and also to determine the efficiency of waste gas sludge (BOS sludge) as a sorbent in treating acid mine drainage (AMD) are

described in details. The solution analysis techniques used are described such as Atomic Adsorption Spectrometry and pH measurements.

**Chapter 4: Characteristics of BOS Sludge**

The different methods used to characterise the properties of waste gas sludge (BOS sludge) are described in this chapter. The main methods were Scanning Electron Microscopy (SEM), Energy Dispersive X-ray Analysis (EDS) and X– Ray Fluorescent (XRF).

The other properties of waste gas sludge (BOS sludge) such as porosity, moisture content, density and surface area using BET were also determined as well as full wet chemical analysis of the material.

In addition this chapter reports the scoping study carried out on the BOS sludge. This section used physical separation methods (froth floatation, magnetic separation and selective screening) in an attempt to remove zinc from BOS sludge to allow internal recycling of the iron units associated with the BOS sludge.

**Chapter 5: Treatment of synthetic AMD with BOS sludge and other adsorbents**

In this chapter, experiments are described for the removal of iron, copper, zinc and manganese ions from single and multi-mixture component solutions of synthetic AMD (sAMD). This chapter describes the experiments performed in order to determine the efficiency of BOS Sludge as a functional adsorbent. BOS sludge was contacted with sAMD solutions containing desired heavy metals under different conditions, for example, different initial solution pH, different mass dosages, different contact times and variable initial metal concentrations. The results of various methods such as encapsulated method and other techniques are also discussed in details.

**Chapter 6: Treatment of Wheal Jane AMD with BOS sludge and other adsorbents**

The results of real AMD treatment using BOS sludge are compared with removal rates of other steelmaking wastes such as blast furnace slags and are described and discussed in details. Performance of these wastes is reviewed in terms of metal adsorption efficiency and possible mechanisms of copper, iron, zinc and manganese.

**Chapter 7: Reactor studies for synthetic AMD treatment**

A semi pilot scale reactor was designed and built to scale up for AMD treatment. This reactor was operated as a fixed bed and mixed vessel. The reactor was a basic cubic tank constructed of rigid Perspex with length of 25.5cm, height 20cm and width of 22cm with working capacity of 11L. Reactor studies are described in detail in this chapter; this includes a description of removal rate of heavy metals from synthetic acid mine drainage solutions and also the effect of particle size, residence time and variable mass dosage of BOS sludge are examined.

**Chapter 8: Conclusions and Recommendations**

This chapter presents a summary of the findings and conclusions of the work performed in this project and recommendations are given for further studies and research.

# CHAPTER 2

# LITERATURE REVIEW

## 2.1 Introduction

The steel industry produces waste materials as much as or even more than any other manufacturing business. Million tonnes of steel are produced per year and this in return, produces million tonnes of wastes in the form of slag, dust and sludge. In the United Kingdom waste recovery in steel plants is an issue caused by tonnes of waste materials accumulated as waste stocks. These waste materials represent significant resources of iron and other metals which can be recycled internally or used as other products for different sectors.

Substantial quantities of sludge and slag are generated as waste materials or by-products every day from steel industries. Most of the slag is usually used in aggregates and road construction materials particularly blast furnace slags. The remaining waste mainly comprises of iron oxide which is a prominent example of raw materials for other industries. By recycling such wastes for metal recovery, they can be reclassified as secondary material. The development of the use of these materials has come about as a result of practical experience, technological innovation and research work.

Over the last few years the industry has been required to comply with more environmental standards and regulations. Steel wastes are composed of considerable amounts of potentially valuable metals and elements. Not all materials can be recycled due to some harmful components like Zn, Pb, Cd, S and many others as a result of processing contaminated scrap metal. Therefore such dusts and sludges depending upon their harmful elements have been classified as hazardous (Fleischanderl et al., 1999).

The recycling capabilities of unit operations (blast furnace (BF), Basic oxygen furnace (BOF) and sintering plant) in the process are different due to the contents of the waste streams. It is possible to recycle small amounts of appropriate dusts, scales and sludge

to the sinter plant to the BF or even to the BOS unit; however this cannot be an overall solution to the waste problem because they only deal with some of the waste and also are very costly. Some of these processes use briquetting machines or pelletising systems. Thus, a more comprehensive solution needs to be provided as an optimal stage or separate units need to be proposed in order to treat waste streams as a feed material back into the steelmaking process.

Different approaches also need to be developed for the wastes to be used as functional and useful products for other sectors. An example of this can be a functional product in treating industrial wastes and cleaning water for example Acid Mine Drainage treatment (Bailey et al., 1999).

An important environmental issue in the United Kingdom and globally is the presence of Acid Mine Drainage (AMD) due to the increasing number of abandoned mines (coal and metal mines). This leads to AMD discharges into the surrounding areas which is a threat to the environment (Hughes et al., 1994).

A number of methods have been used by researchers and companies for acid mine drainage treatment including precipitation (Matlock et al., 2002; Hammarstrom et al., 2003; Lung et al., 1986), electrochemical remediation (Chartrand et al., 2003), oxidation and hydrolysis (Diz and Novak, 1998; Michalakos et al., 1997; Hustwit et al., 1992), neutralisation (Doya and Duchesne, 2003; Polat et al., 2002), ion exchange and solvent extraction (Zabban et al., 1972), ion exchange and precipitation (Wang et al., 2003; Feng et al., 2000), titration (Jenke and Diebold, 1983), biosorption (Tarleton et al., 1984; Gerber et al., 1985), adsorption (Mohan and Chander, 2001; Webster et al., 1998; Xu et al., 1997; Deorkar and Tavlarides, 1998; Zamzow and Murphy, 1992; Gibert et al., 2005; Nassar et al., 2004; Jusoh et al., 2005).

At present in the UK, a number of technologies have been practically applied to the AMD problem e.g. at Wheal Jane Mine these include (Environment Agency 2008; Johnson and Hallberg, 2005):

- Anaerobic cells - designed to promote bacterial sulphate reduction and increase alkalinity, hence precipitation of copper, iron, zinc and cadmium achieved;

- Rock filters - designed to promote the growth of algae and hence high pH to remove manganese as an oxide;

- Reed beds technology (aerobic cells) - designed to cause precipitation of iron as ferric hydroxide/oxyhydroxide.

Adsorption has evolved under different methods for metal ion removal. Due to the high cost of activated carbon and other adsorbents for water treatment, a search for substitutes is underway. Such adsorbents should be readily available, economically feasible, and should be regenerated with ease. Several researchers have studied less expensive materials for the removal of heavy metal ions from solutions such as zeolites (Motsi et al., 2010; Wingenfelder et al., 2005; Moreno et al., 2001), activated sludge (Utgikar et al., 2000;), collophane (Fuerstenau et al., 1997), hydrous manganese dioxide (White and Siddique, 1997), and zero valent iron (Wilkin and McNeil, 2003).

The objective of this chapter is to discuss the waste recovery methods and limitations in relation to BOS sludge and other by-products generated from steel plants, main focus will be on utilisation routes, recovery issues, and more importantly the treatment of Acid Mine Drainage by inorganic solid wastes as sorbents of heavy metal cations in AMD.

## 2.2 Steelmaking process

### 2.2.1 Steel production

Steel is a heterogeneous material which mostly consists of iron. The steel making process involves removing carbon and other impurities such as silicon, manganese, phosphorus and sulphur from pig iron and scrap. During the nineteenth century, Henry Bessemer stated that this could be achieved by blowing air through molten metal. In mid- twentieth century metallurgists started using oxygen instead of air. The introduction of this technology created concern about the effects of oxygen on finished steel products. Various studies have been reported on how oxide inclusions can modify the physical properties of metal. However basic oxygen steel making incorporates procedures for removing most of the dissolved oxygen and the most steel in the world is produced in the Basic Oxygen Furnaces (American Iron and Steel Institute, 2013; Kalyoncu et al., 1999).

Steel production utilises raw materials (iron ore, coke, and limestone), air, water, fuel and power to produce steel. The production of steel is generally carried out in three furnace types, the basic oxygen, the electric arc furnace or the open hearth furnace. Basic oxygen steel making (BOS, BOF, Linz-Donawitz-Verfahren, LD-converter) process is the second step in producing steel in which molten pig iron from the blast furnace with recycled steel scrap added are converted into steel with different grades. The basic oxygen process is the most popular and effective steel making method in which the Basic Oxygen Furnace has a capacity up to 400t and the production cycle of about 40-50min (American Iron and Steel Institute, 2013), Figure 2.1 presents process flow diagram of steelmaking process.
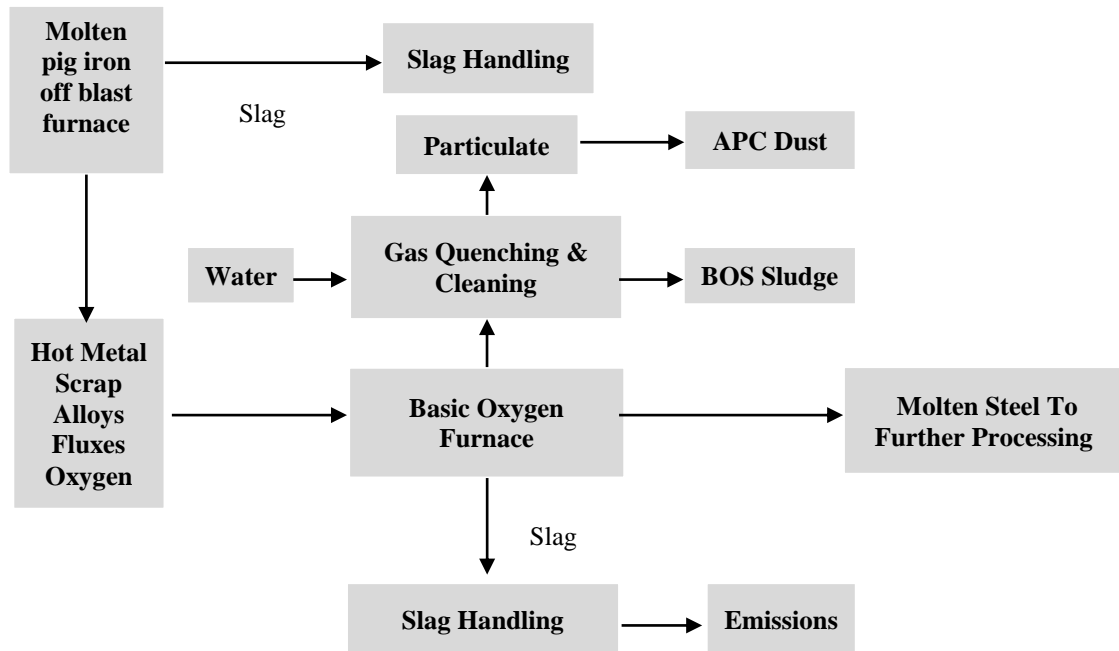
**Figure 2.1: Process flow diagram of steelmaking process** *(Adapted from: Environmental Leadership, 1998)*.

Steelmaking is the term applied to the last stage of refinement in composition of the end product. In addition to removing the carbon and other impurities, the steelmaking process also involves the addition of various alloying elements to give the finished material the combination of properties desired. There are two main processes for making steel in current use. The Basic Oxygen Furnace (BOF) is used for processing most of the nation's pig iron production. The Electric Arc Furnace (EAF) is more generally used for recycled material (Russell and Vaughan, 1976).

In the BOF, atmospheric oxygen is blown through molten metal, either through water-cooled lances inserted from the top of the furnace, or through nozzles located toward the bottom. The oxygen burns off most of the carbon, and the heat of that reaction supplies more than enough energy to maintain the required temperature and the system remains cooled by the addition of more metal to keep the temperature within the desired range (Russell and Vaughan, 1976).

Integrated steel plants generate large amounts of solid wastes which are mainly blast furnace slag, blast furnace flue dust and sludge, steel furnace (LD converter) slags, LD

flue dusts, LD sludges, acetylene sludge, mill scales, etc. Studies and research have indicated that during the production of steel approximately 2-4 tonnes of wastes are being generated per tonne of steel produced, however this is much dependent upon process capacity (Das et al., 2006; Thakur et al., 2000; Yadev et al., 2001).

Regardless of the type of furnace used or grade of steel produced, steel making is accompanied by the emission of a large quantity of dust and sludge which are carried out of the furnace by the exhaust gas. As a result of high temperature, turbulence and exothermic reactions during the steelmaking process, some of the liquid steel formed is ejected into the gaseous phase. In this gaseous phase there are elements which are volatilised from the steelmaking bath. The extent or the degrees to which different elements volatilise from the furnace depend upon their vapour pressures (American Iron and Steel Institute, 2013).

The gases and fumes released during BOF steelmaking are quenched with water to reduce their temperature prior to being treated in air pollution control systems (electrostatic precipitators, bag house filters). The off-gas control systems generate wastewater streams containing suspended solids and metals primarily lead and zinc, but also trace amounts of arsenic, cadmium, copper, chromium and selenium. Standard treatment of this liquid effluent consists of sedimentation in clarifiers or thickeners and also blowdown treatment consists of metal precipitation (Russell and Vaughan, 1976).

The steelmaking process is carried out at temperatures between 1600-1700$^{\circ}$C, virtually all Zn, Pb and Cd present in the charge enter the gaseous phase. Some quantities of iron and alloying elements are also volatilised during the reaction. When the temperature of the gas phase drops in the roof of the furnace and in the ducts conveying the fumed materials oxidise and condense largely as particles which are mechanically carried out of the bath. Interactions of the particles lead to the formation of physically and chemically complex micro- fine agglomerates (Nyirenda et al., 1991). As a result various slags, sludge and waste dusts are produced as by-products in this metallurgical process, Table 2.1 presents wastes that are generated from steel plants.

**Table 2.1: Different types of solid/liquid waste generated from steel plants** *(Source: Das et al., 2006)*.

| Solid/liquid wastes | Hot metal (kg/t) | Source of generation |
|---|---|---|
| Coke breeze | - | Coke oven |
| Nut coke | - | Coke oven |
| Coke dust/sludge | - | Coke oven |
| Blast furnace slag | 340 - 421 | Blast furnace |
| Blast furnace dust/sludge | 28 | Blast furnace |
| Sintering plant sludge | - | Sintering plant |
| LD slag | 200 | Steel melting shop |
| LD sludge | 15-16 | Steel melting shop |
| Lime fines | - | Steel melting shop |
| ACP/GCP sludge | - | Steel melting shop |
| Carbide sludge | - | Acetylene plant |
| Mill scale | 22 | Mills |
| Mill sludge | 12 | Rolling mills |
| Refractory, bricks | 11.6 | Steel melting shop/mills, etc. |
| Sludges/scales | - | Water treatment plant |
| Fly ash | - | Power plant |

In the United Kingdom about 1 million tonnes of basic oxygen steel (BOS slag) slag is produced annually and approximately 10-12 million tonnes of BOS slag is held as stockpiles (personal communication, 2010). U.S. steel production was reported to be 90 Mt for 2001 and 102 Mt for 2000. The International Iron and Steel Institute reported the world pig iron output to be about 577 Mt and crude steel production to be 845 Mt in 2001 (Kalyoncu et al., 1999).

As discussed earlier, uses of iron and steel slags range from building and road construction to waste stabilisation and water remediation. The principal constituents of iron and steel slags are silica, alumina, calcium oxides, and magnesia, which together make up 95% of the composition (Kalyoncu et al., 1999). Minor elements included are manganese, iron, and sulphur compounds, and trace amounts of several other elements are also included. The physical characteristics, such as density, porosity, and particle size, are affected by the processing of the slag or sludge (cooling methods) and their chemical compositions.

As stated before, these wastes usually contain some valuable resources and elements such as iron, zinc, lead, calcium, etc., which can be recovered and reused within in steelmaking process or can be used as raw material elsewhere. They are known as a secondary resource of metals, rather than an end-waste and have been applied as a resource material in many areas such as in civil engineering industry.

Another crucial factor that needs to be considered is that some of these materials contain a notable amount of harmful or heavy metals such as As, Cd, Hg, etc. The release of these metals may cause environmental problems. The conventional method for disposal of steel production waste is dumping. The increasing stockpile of these materials not only occupies huge areas, but also wastes resources (Heavy metals) can potentially have an impact on the environment.

## 2.2.2 Environmental challenges at BOS unit

Related issues:

➢ Capturing and removal of contaminants in the hot and dirty primary off-gas from the BOS converter;

➢ Secondary emissions related to charging and tapping the furnaces;

➢ Control of emissions from ancillary operations such as hot metal transfer, desulphurisation, or ladle metallurgy operations;

➢ Accumulation of slag and sludge wastes;

The environmental practices and environmental standards of iron & steel industry have improved substantially over the last decades. The most important and serious environmental problems are related to the air emissions (dust, heavy metals, compounds, aromatic hydrocarbons, VOCs, SOx, CO and NOx) and the handling of solid wastes.

Currently environmental regulations require the cleaning of wastes before disposal to remove residual metals such as zinc, lead and others. These residual metals can often be found in their oxide forms. However, de-zincing and other metal residual removal

operations require a high capital expenditure to comply with those environmental regulations. The primary wastes collected from BOF in form of sludge or dust are collected either by wet scrubbers or dry electrostatic precipitator or baghouse filters (Environmental Leadership, 1998).

Most BOS/BOF primary gas handling systems are designed to generate plant steam from the water-cooled hood serving the primary system. About half of the systems are open combustion designs where excess air is drawn into the hood of the off-gas exhaust system, allowing carbon monoxide to combust prior to high energy wet scrubbing for air pollution particulate control. Some other methods are suppressed combustion systems where excess air is excluded from the off-gas collection system prior to high energy wet scrubbing for air pollution particulate control, thus suppressing the combustion of carbon monoxide until after scrubbing (Environmental Leadership, 1998; American Iron and Steel, 2013).

Suppressed combustion systems offer the potential for recovery of energy, a practice that is more predominant in Europe and Japan. Secondary emissions related to the charging and tapping the BOF vessel, or emissions escaping the main hood during oxygen blowing, and they can be captured by exhaust systems serving local hoods or high canopy hoods (American Iron and Steel, 2013).

Studies and figures through literature address that over the past years; steel production has increased rapidly and extended, consequently large volumes of by-products and wastes produced. There is also an increasing demand to utilise these waste materials and this pressure in recent years has introduced new technologies which have been expanded, and some of them are still under developing stages in order to improve the recovery rates of slags.

Simple disposal of steel production wastes are not favourable due to occupying land and also increasing the disposal costs (permits, legislations, landfill tax). Thus recycling and utilisation of these wastes has been promoted in the steelmaking industry due to several benefits:

- To save energy indirectly;

- To reduce air emissions;

- To reduce the depletion of earth's limited natural resources;

- To save money in landfill tax.

Waste gas sludge (BOS sludge) needs to be processed before recycling. BOS Sludge from wet scrubbers/clarifiers requires an additional drying step which can be costly. BOS dust and BOS sludge are not listed as hazardous waste. If the zinc content is adequately reduced (below 5%), BOS sludge can be recycled to the blast furnace or BOS vessel after briquetting or pelletising (American Iron and Steel, 2013).

Several processes for recycling the particulate are in use or under development. A number of methods dependent on zinc content have been investigated in relation to recovery of BOS dust or sludge in steelmaking process and they are as follow:

- Sintering; pelletisation and briquetting with low zinc content (American Iron and Steel, 2013);

- Cold bonded agglomeration/pelletising with binders (Robinson et al., 2003);

- Bottom Injection; inserting of BOS dusts into furnaces (Holley, 1985);

- Magnetic hydrocyclones;

- Leaching of BOF dust with concentrated ammonia and $CO_2$ to solubilise zinc in flue dust (Peters, 1978);

- Physical separation; (magnetic separation, froth flotation, size classification);

- BOS dust reduction by BF dust with low zinc content (Mikhail and Turcotte, 1997);

Utilisation of iron and steel slags, dusts or sludge in any application can be revised as a viable option, since the reuse or the recovery of such materials offers economical and environmental related benefits. For example the substitution of steel slags for lime dosing in acid mine drainage remediation not has only been economical but also eliminated two negative impacts on the environment (Simmons et al., 2002).

As noted before, there has been research on steel slag and its uses in the field of AMD treatment. However limited research has focused on the possible environmental impacts of the re-used and recycling steel slags. There are two main potential environmental issues when using steel slags for AMD or other waste water treatment.

Discharge concentration after AMD treatment results in high pH (11-12) and the potential of toxic and heavy metals to leach from the slag matrix which in time results in the surrounding environment (Ziemkiewicz and Skousen, 1998). Steel slags consist of different types of heavy metals, including Sb, Cu, Mn, Mo, Ni, Ag, Tl, Sn, V, and Zn in various concentrations. A typical Toxicity Characteristics Leachate Procedure (TCLP) analysis for steel slag is presented in Table 2.2 (Hamilton et al., 2007).

There is some concern that heavy metals elements may leach from steel slag when it is used in AMD treatment (Fallman et al., 2000; Proctor et al., 2002). This can affect the adsorption rate of heavy metal from AMD solution and create a further environmental problem. The possibility that toxic metals may become mobile in the environment when steel slag is used has been investigated by researchers; however no agreements have been consolidated because there is conflicting research published on this issue (Fallman et al., 2000; Proctor et al., 2002).

**Table 2.2: Typical TCLP analysis of steel slag** *(Source: Hamilton et al., 2007).*

| Element | Amount in steel slag (mg/L) | EPA maximum allowed concentration in leachate (mg/L) |
|---|---|---|
| **Arsenic** | <0.002 | 5.0 |
| **Barium** | 1.4 | 100.0 |
| **Cadmium** | <0.002 | 1.0 |
| **Chromium** | <0.038 | 5.0 |
| **Lead** | <0.004 | 5.0 |
| **Mercury** | <0.0 | 0.2 |
| **Selenium** | <0.003 | 1.0 |

Chaurand et al. (2006) looked at the leachability of Cr and V from Blast Oxygen Furnace (BOS slag) steel slag. It was found that the amount of both Cr and V that leached from the steel slag was dependent on the speciation of the metal. There was less Cr found in the leachate, and the majority of it was in the less toxic form and Vanadium was found to have higher concentrations and was very toxic.

Other studies have reported very low metal concentrations in leachate from steel slag. Gomes and Pinto (2006) performed leaching tests on Electric Arc Furnace (EAF) slag and ladle slag and the purpose was to determine if the age of the slag influenced the rate of metal leaching. Neither the EAF nor the ladle slag violated the "Inert" leach water quality criteria for the tested metals. However, the rate of leaching did change with slag age, with older slag releasing more metals. Although leaching rates increased over time, overall metal concentrations in the leachate remained low. For example, Ca and Mg made up 0.5% of the leachate, while all other metals were below 0.05%.

## 2.2.3 Overview of slags and sludge from steelmaking process

As discussed previously in this chapter integrated iron and steelmaking plants generate large amounts of solid wastes which are mainly blast furnace and steel furnace slags, dusts and sludges. The objective of this section is to briefly revise the recycling and utilisation routes of these waste materials. Efforts have been made on the utilisation of blast furnace and steel slags since these are raw materials for many industries ranging from civil engineering, agriculture sector and wastewater remediation (Das et al., 2006).

### 2.2.3.1 Blast furnace slag

BF slag is produced as iron ore, coke and fluxes are melted together in a blast furnace unit.  During the period of cooling and hardening from its molten state, BF slag can be cooled in several ways to form any of several types of BF slag products such as air cooled slag, expanded (pelletised) and ground granulated blast furnace slag (GGBS) (Mueller et al., 2005).

The physical characteristics, such as density, porosity, and particle size are affected by the cooling rates of the slag and its chemical composition and these are illustrated in Table 2.3. Blast furnace slag can be used directly at the end of the production process, without further processing (apart from size classification) that is an integral part of this production process. This material can therefore be considered to fall outside of the definition of waste.

**Table 2.3: Chemical and physical properties of typical granulated BF slag** *(Manchisi et al., 2013)*.

| Chemical Constituents | | Physical properties | |
|---|---|---|---|
| Oxide | % w/w | Parameter | Value |
| CaO | 44.1 | True density | 2.89 g/cm$^3$ |
| Al$_2$O$_3$ | 10.6 | BET Surface area | 0.769 m$^2$/g |
| Fe$_2$O$_3$ | 0.39 | Porosity | 54.5% |
| MgO | 5.8 | Total pore area | 1.275 m$^2$/g |
| SiO$_2$ | 30.7 | Average pore dia. | 1.336 μm |
| SO$_3$ | 1.98 | Total pore vol. | 0.426 mL/g |

Today blast furnace slag has found a wide application in cement production and is marketed as Portland blast furnace slag cement (PBFS). In the UK, Lafarge Tarmac market all blast furnace slags for Tata steel plant. Since blast furnace slag contains little iron and high calcium oxide content with similar composition of clinker, it can be used along with the clinker and gypsum for the production of cement. Blast furnace slag is basically inorganic in nature as it contains mostly inorganic constituents such as silica, calcium oxide, magnesium oxide and other metal oxides (Francis et al., 2004; Manchisi et al., 2013).

Blast furnace slags are primarily made up of silica, alumina, calcium oxide, and magnesia. Other elements like manganese, iron, sulphur, and trace amounts of other elements make up the rest of the slag. Ground granulated blast furnace slag (GGBS) is

also a by-product of blast furnace unit operations.  GGBS as very fine white powder is produced when molten slag from blast furnace is quenched rapidly using water jets; this produces a granular glassy aggregate with high glass content. The GGBS has already a well-established recycling route and is used as an additive in cement formulations. All blast furnace slags generated at Tata Steel sites in the UK are processed by Tarmac and sold as products for the cement and civil industry.

In XRF analysis as shown in Table 2.4, it can be noted that the CaO content of GGBS is 39.6% which is about twice as much compared to BOS sludge. GGBS is a non-metallic product unlike BOS sludge in which the iron values are very high. In both samples GGBS and BOS sludge, the oxides of calcium, silicon, aluminium and magnesium with low solubility in water make an alkaline solution resulting in high pH.

**Table 2.4: Typical XRF chemical analysis of ground granulated blast furnace slag (GGBS)** *(Courtesy of Hanson LTD, UK).*

| Chemical Composition | $SiO_2$ | $Al_2O_3$ | MnO | CaO | MgO | S | $TiO_2$ | $Al_2O_3$ | $Na_2O$ | $K_2O$ | $SO_3$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **Weight (%)** | 36.76 | 13.38 | 0.60 | 39.56 | 7.33 | 0.98 | 0.75 | 13.38 | 0.32 | 0.54 | 0.08 |

The exact concentrations of elements and moisture content values in samples are much dependent upon their processing history. As in treatment of acid mine drainage, these two samples can be compared to one another in order to find out whether either of the samples show high efficiency in adsorption of heavy metals ions from AMD solutions.

The blast furnace slag can also be used in the preparation of materials such as ceramic glass, silica gel, ceramic tiles, bricks, etc. (Das et al., 2006). Crystalline and amorphous blast furnace slag can also be used as an adsorbent of phosphate from water solutions

and the adsorption kinetics and isotherm measurements confirmed the sorption of phosphorus on crystalline as well as amorphous slags (Kostura et al., 2005).

The adsorption characteristics of blast furnace slag on the removal of lead have been investigated by researchers, and found to be a function of pH. Depending on the experimental conditions 97-98% lead removal can be achieved which is useful for the application of granulated slag for lead removal from industrial waste (Dimitrova and Mehandgie, 1996). For silicate based materials such as BF slags, many researchers and process developers consider metal adsorption process to occur through ion exchange and metal hydroxide/silicate precipitation (Dushina and Aleskovski, 1976), physical adsorption based on ion exchange (Lopez et al., 1995) and mainly sorption through ion exchange and some form of metal silicate precipitation (Dimitrova and Mehanjiev, 1998).

### 2.2.3.2 Blast furnace flue dust and sludge

Blast furnace flue dust is another by-product from the integrated steel plants. The flue dust is a mixture of oxides rejected from the top of the blast furnace; with major constituents including iron oxides and coke fines. It also contains silicon, calcium, magnesium and other minor elements in their oxide forms in lesser quantities. The physical and chemical analysis of the blast furnace flue dust sample obtained from two steel plants of India is given in Table 2.5.

The direct recycling of flue dust is not usually possible due to the presence of compounds such as zinc, lead, cyanides, oil and alkali metals (Ellis et al., 1999). The zinc and lead exist mostly due to the scrap added into the blast furnace. Additionally in some cases the dust contains toxic elements such as Cd, Cr, and As which makes it hazardous and unacceptable for landfill.

As stated in the previous chapter, the presence of such elements particularly Zn has caused many problems and operational difficulties such as refractory failure, scaffold formation in the stack and others (Das et al., 2006).

**Table 2.5: Physical and chemical properties of typical BF flue dust** *(Source: Das et al., 2006).*

| Chemical composition | Sample 1 (%) | Sample 2 (%) |
|---|---|---|
| Carbon | 29.90 | 33.62 |
| $Fe_2O_3$ | 51.10 | 49.50 |
| $SiO_2$ | 6.31 | 8.30 |
| $Al_2O_3$ | 5.12 | 2.54 |
| CaO | 4.90 | 1.96 |
| MgO | 0.88 | 1.33 |
| Pb | 0.024 | 0.019 |
| Zn | 0.042 | 0.028 |
| MnO | 0.58 | 0.02 |
| $K_2O$ | 1.22 | 0.154 |
| $Na_2O$ | 0.47 | 0.07 |
| Fe (T) | 35.7 | 34.62 |
| Bulk density (g/cc) | 1.42 | 1.32 |
| Specific gravity | 2.59 | 2.56 |
| Porosity (%) | 45.17 | 48.53 |

During the production of pig iron in a blast furnace, Zinc-Lead containing sludge is also generated. The sludge particles also contain large amounts of iron and carbon that could be recycled in the furnace. However the zinc content of the sludge is high, thus the Zn input to the blast furnace must be limited due to the problems it can cause.

Several works and studies have been carried out on the recovery of zinc and lead, hydrometallurgical processes in which the sludge is leached under both acid and oxidising conditions have been reported. After the separation of the solids, i.e. carbon and iron from the leaching solution, the latter is passed through an anion exchanger to remove zinc and lead and then recirculated to the reactor (Van-Herck et al., 2000).

In some cases selective leaching by sulphuric acid at low concentration and room temperature, gives significant recovery of zinc (about 80%) (Zeydabadi et al., 1997) and some studies have reported on the use of Ammonium thiocyanate ($NH_4SCN$) solution which is produced by the gas emitted from coke furnace to remove zinc from the blast furnace sludge; ZnO reacts with $NH_4SCN$ and forms $Zn(SCN)_2$ which dissolves easily in water (Cho et al., 1997).

Zinc from zn-bearing blast furnace wastes is also separated by froth flotation and hydrocyclone methods. Experiments have reported that Zn, Pb and other non-ferrous metal contents of blast furnace dust can be removed by wet-classifying the dust in a hydrocyclone separator. The de-zinced, wet-cleaned blast furnace dust containing around 1% zinc is made into mini pellets as sinter raw materials (Uno et al., 1997).

In another work, oxidising-chlorination roasting of blast furnace and steelmaking converter sludges with $CaCl_2$ for the sublimation of Zn and Pb chlorides was carried out. It was observed that the degrees of Zn and Pb chloride sublimation were 99.5 and 98.6% respectively (Shevko et al., 1993).

The use of Waelz kiln (rotary kiln) to reclaim Zn and Pb from blast furnace sludge has also been reported over the past years. The material is premixed in tanks, fed into an impact crusher, pelletised and put into the kiln. Water, hydrate of lime and coke breeze is added as needed since carbon and basicities help de-zincing and reduction of iron oxide. It was possible to volatilise successfully 95% Zn, 95% Pb, 30% sulphur and 30% potassium oxide from a mixture containing 4% Fe, 4.5% Zn, 2% Pb and 7% carbon (Serbent et al., 1975).

The flue dust is generally recycled through sinter making in more advanced countries. The Institute of Gas Technology, USA has developed a fluidised-bed process for recovering direct reduced iron from blast furnace flue dust. Up to 95% of the iron oxides contained in the waste streams could be reduced to elemental iron. The yield of iron depends upon the quantity of iron oxide present in the flue dust and generally ranges from 20 to 30% of the waste stream (Rehmat and Mensinger et al., 1996). In

USA and Canada the BF flue dust and the finer mill-scale are generally recycled through the sintering plant.

An important factor in relation to blast furnace sludge is its adsorption capacity similarly to blast furnace slags. It is proved to purify solutions containing metal ions such as $Cu^{2+}$ from aqueous solutions (Lopez-Delgado et al., 1998). Other studies also report the adsorption of $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$, $Cd^{2+}$, and $Cr^{3+}$ on the BF sludge, this was investigated by determination of adsorption isotherms (Langmuir and Freudlich) and kinetic studies (Lopez et al., 1995). Blast furnace flue dust also has shown ability to remove heavy metal ions from aqueous solutions. BF dust was found to be a good potential adsorbent for divalent copper and lead ions from solutions (Lopez-Delgado et al., 1998).

### 2.2.3.3 Basic oxygen furnace (BOS) steel slag

As stated before in this chapter, the main purpose of the BOS vessel is to convert the molten iron and steel scrap and other additives into high quality steel of defined specifications. During the steelmaking process large quantities of various waste materials containing iron bearing dusts and sludges are generated from pollution control devices such as bag houses, precipitators, clarifiers, scrubbers and dust collectors. Some of these waste materials are typically disposed of as landfill on site and others are returned back into the sinter plant for re-use (American Iron and Steel Institute, 2013). Each year, a great amount of steel slag is produced in the different countries, as shown in Table 2.6.

**Table 2.6: Production of steel slag in the different countries.**

| Country | Steel slag (BOF+EAF) (Million tonnes) | Reference |
|---------|---------------------------------------|-----------|
| Europe | 12 | Motz et al. (2001). |
| USA | 8 | Proctor et al. (2000). |
| Japan | 12.6 | Okumura (1993). |

Steelmaking by-products include Basic oxygen furnace slag (BOF slag), air pollution control dust (BOF dust) and waste treatment plant sludge (BOF/BOS sludge). BOF slag is produced from Basic Oxygen Furnace (BOF steel slag) and Electric Arc Furnace (EAF steel slag) in the steel making. They are about 10–15% by weight of the steel output (Proctor et al., 2000).

**Table 2.7: Chemical composition of steel slag (wt. %)** *(Source: Das et al., 2006).*

| (wt. %) | FeO | CaO | MnO | MgO | SiO$_2$ | P$_2$O$_5$ | Al$_2$O$_3$ | S |
|---|---|---|---|---|---|---|---|---|
| **Sample 1** | 26.30 | 47.88 | 0.28 | 0.82 | 12.16 | 3.33 | 1.22 | 0.28 |
| **Sample 2** | 27.89 | 50.0 | - | 1.50 | 12.0 | 3.35 | 1.58 | 0.30 |

Although the blast furnace slag and steel slag have similar constituents, the proportions are very different. BOF slag is composed of calcium silicates combined with fused oxides of iron, aluminium, calcium and magnesium, Table 2.7 presents the typical chemical properties of steel slag. After molten BOF slag is removed from the furnace, it is cooled and processed to recover the high metallic portions (iron and manganese) for use in the sinter plant or as a flux in the blast furnaces. Some slag may be recycled to steelmaking under certain conditions depending on content composition (Phosphorus removal) (Fregeau-Wu et al., 1993).

In a study it has been reported that use of the magnetic 10-50mm products of the slag processing unit increases the production rate and decrease the coke rate at blast furnace units. No difficulties were found, also 50-500mm magnetic slag was used to replace scrap in the BOF, which has been found effective due to its low cost compared to scrap. Based upon these results and analysis, the use of the -10mm fraction of the slag (4% by weight) in the sinter mix has become a standard practice at Kardemir iron and steel works at Turkey (Topkaya et al., 2004).

As previously stated, steel slag (BOS slag) generated from the basic oxygen furnace has different composition in comparison to other by-products Because of its physical, chemical and mineralogical properties, it can be used as a substitute for aggregates in civil engineering works (road construction, railway ballast and hydraulic protection structures). It is also used an additive in cement kilns, however BOF slag has not reached the same level of utilisation as blast furnace slag. Because of the steel slag large content of free lime and similar composition and mineralogy to Portland cement; there is a great potential for furthering the usage of steel slag in civil and agricultural industry as fertilisers, soil stabilisation or soil conditioner for acidity corrector of the soil (Maslehuddin et al., 2003).

In addition to the use of steel slag in civil and agriculture sectors, it is also used in acid mine drainage treatment. Various researchers including (Ziemkiewicz and Skousen, 1998; Simmons et al., 2002) have identified steel slag as a suitable adsorbent to remediate waters contaminated by acid mine drainage (AMD), since it has proven to have a significant acid neutralising potential that can be exploited to precipitate out the majority of dissolved metals by increasing solution pH (Kim et al., 2008). Batch testing with steel slag and solutions of various heavy metals including iron, zinc, aluminium, copper, and lead showed over 80% removal of aluminium, and over 90% removal of the other metals (Ochola and Moo-Young, 2005).

### 2.2.3.4 Basic oxygen furnace (BOS) flue dust and sludge

The fine solid particles recovered after wet cleaning (i.e., clarifiers) of the gas emerging from BOF reactor in the sludge form are termed as waste gas sludge or BOF/BOS sludge. The BOS dust (BOF dust) and BOS sludge collected from dry dust precipitators and wet scrubbing systems represent two of the three largest wastes typically land-disposed by iron and steel plants. Together with slag and water treatment plant sludge, these wastes present more than 93% of all wastes stored, recycled or disposed *(Environmental Leadership 1998)*.

X-ray diffraction analysis and studies report that the major phase in BOF flue dust is iron oxides (magnetite & hematite) whereas blast furnace flue dust is a carbon rich waste material. The BOF (BOS) sludge contains high quantities of iron and lime (CaO) and it may be suitable for recycling in the sinter plant subjected to its zinc content. The chemical analysis of typical sludge generated at a steel plant is shown in Table 2.8.

A detailed and scientific investigation is important to establish the scope of the problems associated with recovering dusts and sludges and proposed utilisations must be carefully evaluated. The following obstacles hinder the recycling BOF sludge (Das et al., 2006):

➢ High moisture content (35-40%) (this makes the sludge sticky and form agglomerates, therefore it must be optimally dried and made handleable);

➢ High Zinc content is a major barrier to direct recycling, as it causes operational difficulties such as resulting in extra coke consumption or affecting the permeability of the mix in the furnace.

➢ Available dust collection facilities (The amount of dust to be collected increases with every additional recycling step);

➢ Size distribution and energy requirements;

➢ The method of charging recycled material to the furnace (e.g. to the sinter machine, bottom injection to the furnace (Holley et al., 1985).

**Table 2.8: Chemical analysis of BOF sludge samples generated at a steel plant** *(Source: Das et al., 2006).*

| Chemical constituents | Sample 1 (%) | Sample 2 (%) |
|---|---|---|
| FeO | 79.58 | 76.93 |
| $Fe_2O_3$ | 2.79 | 1.43 |
| $SiO_2$ | 0.71 | 1.97 |
| $Al_2O_3$ | 0.32 | 0.95 |
| CaO | 8.9 | 10.59 |
| MgO | 0.38 | 0.38 |
| MnO | 0.10 | 0.24 |
| P | 0.101 | 0.126 |
| Fe (Total) | 64.12 | 61.0 |

BOF dust and sludge generally contain high iron content (70-80%) and between 0.3 and 12% zinc on a dry basis dependent upon processing route. Most of the sludge and dusts containing small amounts of zinc (less than about 1%) could be recycled through sinter plants and the recycling is generally influenced by the analysis of the waste material (Nyirenda et al., 1991).

Studies and research demonstrate that in direct use of steel plant wastes, most agglomeration processes in use are essentially sintering, pelletisation and briquetting. Briquetting necessitates the use of organic (molasses) and inorganic (clays) binders which can be used to recycle such waste materials. Converting such wastes into briquettes will significantly reduce the operating costs of the plant and it also brings environmental benefits.

It is important to process the fine powder into agglomerates or pellets with certain physical and mechanical strength characteristics, e.g. high temperature strength, similar to those of iron-ore pellets used as blast furnace feed.

Mikhail and Turcotte (1997) carried out experiments by utilising the carbon rich BF dust as a reductant for the BOF dust, with the potential benefit of utilising two major by-product residues to generate a value-added recyclable material. The reduction of BOF dust by BF dust in different atmospheres (air, helium and $CO_2$) was conducted using thermal analysis and Fourier transform infrared spectroscopy. The results demonstrate that the reduction was found to be most extensive in the inert atmosphere (Helium). A complete metallisation of iron oxides, the main components of the BOF dust in a mixture with 50% BF dust, takes place when the mixture is heated to $1300^{o}C$. Such mixtures when cold bonded or pelletised could represent iron rich agglomerates viable for recycling back to the iron and steelmaking units and hence the recovery of valuable iron units.

Processes such as electrothermic, half-shaft, flash furnace, high temperature reduction technologies have shown the ability to process flue dust, yielding slags which are environmentally friendly for disposal. The cost for such processing is off-set by the

value of the recovered zinc product, which requires that the feed of at least 15-20% Zn, however new processes will need to breakthrough to challenge the existing ones (Nyirenda et al., 1991).

Carbothermic reactions trials have also been carried out by researchers where waste sludge oxides without addition of coal under a nitrogen atmosphere are converted into metallic iron. The results report that increasing the weight ratio of sludge, size of samples, carbon content, density of sample or reaction temperature could increase the reduction rate (Chen et al., 1992).

However in all strategies for processing BOF/BOS sludge, physical separation has played little or no role due to the size distribution and the association of the contained ferrous and non-ferrous components. Chapter 4 in this thesis presents findings and conclusions on the physical separation on BOS sludge for further study.

Overall the decision to process the dusts and sludge separately, leads to new processing alternatives. Many facilities and processes have been developed and modified for treating fine-grained wastes (e.g. rotary hearth furnace). The Criteria for the choosing the optimal method are influenced by factors such as:

➢ Capital and labour cost;

➢ Energy consumption;

➢ Rate of harmful components reduction;

➢ Possible pre-treatment methods;

➢ Treatment capacity and productivity.

## 2.3 Acid Mine Drainage (AMD) Treatment

### 2.3.1 Shortcomings and possible solutions

Organic contaminants can degrade in the environment, however most heavy metals in the environment do not undergo microbial or chemical degradation, and therefore total amounts accumulate and persist for long periods of time. Treatment processes for metal-contaminated wastewater include chemical precipitation, membrane filtration, ion exchange, adsorption, coagulation/co-precipitation and adsorption (Gupta and Ali, 2002; Apak et al., 2002).

Adsorption is a process by which the heavy metal contaminants are removed from aqueous solution through sorption onto the surface of a material. Adsorption is one of the most popular methods for the removal of heavy metals from wastewater or AMD solutions. There is growing research interest in the use of waste products/ by-products of steel industry as inexpensive adsorbents. Common inorganic wastes that have been suggested include fly ash, blast furnace slag, steel furnace slag, red mud and water treatment sludge, lignite, natural and synthetic zeolites (Bailey et al. 1999; Gupta and Ali, 2002; Babel and Kurniawan 2003; Zhou and Haynes, 2010; Motsi et al., 2010; Kim et al., 2008; Simmons et al., 2002; Mohan and Chander, 2001; Manchisi et al 2013).

Although many studies have reported the metal sorption characteristics (e.g. adsorption isotherms, kinetics, effects of pH, temperature, adsorbent dosage) of individual waste materials for one or sometimes several metals, the relative adsorption capability of different materials under the same operational parameters has not commonly been reported.

As a result, it is not clear on which waste materials research should be concentrated. In addition, the ease of desorption of metals from low-cost adsorbents and the regeneration capability of adsorbents are not well documented. Regeneration ability is an important characteristic of materials in terms of an adsorbent since once they become saturated, it is suitable to remove the contaminant metals and reuse the adsorbent and be able to repeat this over a number of cycles. However in some cases regeneration cannot be

selected as a suitable option as the objective would be to recycle and the recovery of all the wastes accumulated as landfill e.g. stockpile of BOS sludge on a steel plant site.

The formation of acid mine drainage (AMD) and its discharge into the environment surrounding abandoned mines is likely to cause serious environmental pollution. AMD is a problem because of the increasing number of closed mines. The pumps, which currently keep these mines dry, are being switched off and groundwater is returning to its pre-mining industry levels leading to AMD (Azapagic et al., 2004; Mack and Gutta, 2009).

The treatment, or the prevention, of such pollution is costly and requires high maintenance. Related issues with AMD originating from abandoned mines to nowadays have been carried in an inconsistent path because of liability concern and the fund has come from the public purse via the Environment Agency and Coal Legal Authority in the UK.

The problem with treatment is that there is no recognised, environmentally friendly, route to deal with AMD. The standard treatment has been to deal with lime which produces a waste material (ochre). Such wastes must be disposed of in a nearby tailings dam if possible or in landfill. The many technologies proposed for treatment of acid mine drainage, are usually as expensive and always more complex than liming. Liming is not sustainable for every UK mine due to the requirement costs for lime, disposal space and plant operations (Bone et al., 2003).

Predictions of release of dissolved metals from mine sites suggest that sulphide oxidation and the release of dissolved heavy metals will continue for many years. Stabilisation, treatment and optimisation processes of these sites can be very costly, therefore an alternative and cost effective solution or process are constantly sought in order to neutralise AMD.

There are a number of AMD treatment technologies such as passive and active treatment. The selection of method is based upon the concentration of heavy metals in the solution, volumes and the cost of treatment. There is no shortage of choice when it

comes to choosing an active treatment method for AMD water; however each process has a number of advantages and disadvantages.

The drawbacks of some of these AMD technologies include maintenance problems, large volumes of sludge and cost. However unused BOS sludge as a waste itself in large volumes may have potential to minimise metal toxicity in AMD and hence be sold as a functional adsorbent for AMD treatment by steel producers.

If adsorption is the selected method for the removal of heavy metals, waste gas sludge (BOS sludge) can be considered as an ideal adsorbent due to its lime free content and its physical properties. The objective of this section in this chapter is to discuss the acid mine drainage issue, its sources, environmental impact, prevention and the use of low cost waste materials such as BOS sludge to treat another problem known as AMD.


## 2.3.2 Sources and formation of Acid Mine Drainage

Mining activities can expose a significant amount of mineral deposits and sulphide minerals including pyrite ($FeS_2$). Mining activities bring these deposits to the surface where they are crushed to release valuable minerals such as zinc, copper, gold and others. Hence large amounts of pyrite become exposed to surface conditions where air and water accelerate the oxidation of the pyrite to produce AMD *(USEPA, 1994)*. Acid mine drainage (AMD) is highly acidic with a pH range of about 2-3 and contains elevated concentrations of iron, toxic metal ions and other heavy metal contaminants which can cause damage to the environment (Bone et al., 2003).

In the case of abandoned mines, water can enter the mines through a number of ways including via mine faults, galleries and adits from the surface as rainwater or from groundwater (National Rivers Authority, 1999). If this water is not pumped out within a certain period of time AMD will be formed due to the reaction of water and the exposed sulphide minerals (mostly $FeS_2$) deep in the mine (World Coal Association, 2010; Singer and Strumm, 1970).

**Figure 2.2: AMD Effluent discharging downstream of an abandoned coal mine, Aberbaiden Colliery, South Wales.**

(**Reprinted from:** http://cdn.environment-agency.gov.uk/scho0508bnzs-e-e.pdf)

An example of this is Wheal Jane Mine Cornwall, which in 1992 was flooded, because the water drainage pumps were switched off, resulting in an adit failure and hence generating and discharging of AMD into the surrounding environment (Hallberg and Johnson, 2003). The legally and environmentally acceptable concentrations for heavy metals discharges were exceeded by many orders of magnitude due to this release of AMD into the Carnon River and the surrounding waterways.

Table 2.9 shows the water quality in the Carnon River, initially when AMD was discharged in 1992, the water quality in 1995 and the legal discharge concentrations from mines according to the Environmental Quality Standard (EQS). Mine discharges rather than watercourses may not have to meet EQS standards (Bone et al., 2003) as such metal and mine waste is dealt with on a case by case basis (Griffiths et al., 2005) by insurance of consent limits by regulatory bodies such as the Environmental Agency. The concentrations in 1995 are drastically lower than those in 1992; nevertheless the concentrations are still higher than the legal requirement for waste water discharges into the environment, hence treatment is still required.

**Table 2.9: Chemical Quality of Wheal Jane Mine AMD.**

| | Jan 1992 [a] | 1995 [b] | EQS values [c] | Wheal Jane consent limits [c] |
|---|---|---|---|---|
| **pH** | 2.6-3.1 | 3.5 | 6-9 | 4-10 |
| **Aluminum** | 170-197 | 30 | 0.01-0.025 | 10.0 |
| **Arsenic** | 26-29 | 9 | 0.05 | 0.1 |
| **Cadmium** | 1.4-1.9 | 1 | 0.005 | 0.04 |
| **Copper** | 14-18 | 1.5 | 0.028 | 0.08 |
| **Iron** | 1720-1900 | 300 | 1.0 | 5.0 |
| **Manganese** | 11-25 | 12 | 0.03 | 1.0 |
| **Zinc** | 1260-1700 | 120 | 0.5 | 2.5 |

[a] *Hamilton et al., 1994,* [b] *Dobbs-Smith et al., 1995,* [c] *Bone, 2003.* ***Except pH, all values are expressed as mg/l.***

Heavy metals found in AMD such as aluminum, copper, lead, nickel, zinc etc, exist in association with pyrite. There are varieties of metal sulphides that may release metal ions into AMD. However the major cause of AMD formation is the accelerated oxidation of iron pyrite (FeS2) and other minerals. The pyrite oxidation process has been extensively studied by other researchers and can be summarised by the following reaction sequence (Singer and Strumm, 1970).

$$FeS_2 + 3.5O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad 1$$

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

$$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3(s)\downarrow + 12H^+ \qquad 3$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad 4$$
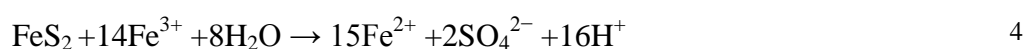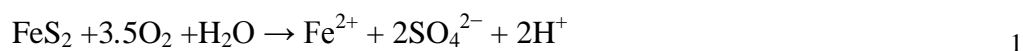
Pyrite reacts with oxygen and water, producing ferrous iron ($Fe^{2+}$) and sulphuric acid by reaction (1). The second stage the ferrous iron is further oxidized by oxygen (oxidation of $Fe^{2+}$ to $Fe^{3+}$) by reaction (2). The third stage corresponds to the hydrolysis of $Fe^{3+}$ with water to form a ferric hydroxide precipitate and the pH of the solution has decreased as acid production increases, which is promoted by the pH-dependent reaction (3). The fourth step is defined as the oxidation of additional pyrite by $Fe^{3+}$ according to reaction (4), resulting in more acid production.

Reaction (4) can be catalysed by bacteria, most notably *Thiobacillus Ferroxidans*. The pyrite oxidation is controlled by bacterial species that have definite pH growth range and pH growth optimum. The conversion of $Fe^{2+}$ to $Fe^{3+}$ in the overall pyrite reaction sequence has been described as the 'rate determining step', which can be greatly accelerated by bacterial action. The overall reaction for the formation of AMD is thus:

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 16H^+ + 8SO_4^{2-} \qquad\qquad 5$$

The primary factors that determine the rate of acid generation are (Akcil and Koldas, 2006; McGinness et al., 2009; Valenzuela et al., 2005):

➢ pH;
➢ Temperature;
➢ Oxygen content of the gas phase, if saturation is less than 100%;
➢ Oxygen concentration in the water phase;
➢ Degree of saturation with water;
➢ Chemical activity of $FeS_2$;
➢ Surface area of exposed metal sulphide;
➢ Chemical activation energy required to initiate acid generation;
➢ Bacterial activity.

Other metals usually found in AMD water, such as lead, copper, aluminum, zinc, cobalt, cadmium etc., occur since they exist in the rocks with pyrite. For instance, there are several of other metal sulphides that may release these metal ions into solution (Costello, 2003; Younger et al., 2002):

Chalcopyrite: $CuFeS_2$ (s) + 4 $O_2$ (aq) $\rightarrow Cu^{2+}$ (aq) + $Fe^{2+}$ (aq) + $SO_4^{2-}$ (aq) $\qquad$ 6

Sphalerite: $ZnS$ (s) + 2 $O_2$ (aq) $\rightarrow Zn^{2+}$ (aq) + $SO_4^{2-}$ (aq) $\qquad$ 7

Galena: $PbS$ (s) + 2 $O_2$ (aq) $\rightarrow Pb^{2+}$ (aq) + $SO_4^{2-}$ (aq) $\qquad$ 8
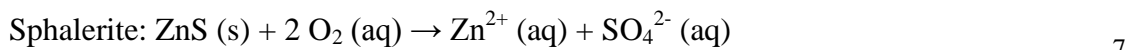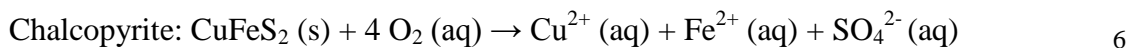
The formation of AMD is complex due to a number of factors, such as the presence and type of activating micro-organisms, type of sulphide and non-sulphide minerals present, solution pH, temperature and the availability of oxygen, nutrients and water. These factors can be varied from region to region, thus influencing the pH, metals content and amount of AMD produced. (Steffen et al., 1989; Sanchez et al., 2005) The chemical composition of several representative AMD solutions from different regions is given in the Table 2.10.

**Table 2.10: Typical composition of Acid Mine Drainage.**

| Component | U.K,Wheal Jane Mine [a] | Spain, Rio Tinto River [b] | Spain,Odiel River [b] | Norway, Storwartz Mine |
|---|---|---|---|---|
| pH | 2.6- 3.1 | 2.89 | 3.76 | 6.5 |
| Fe | 1720- 1900 | 123 | 4.9 | 1.60 |
| Cu | 14-18 | 15.7 | 5.4 | 0.06 |
| Al | 170-197 | 66.5 | 32.8 | 0.03 |
| Zn | 1260-1700 | 24.1 | 11.5 | 2.13 |
| Mn | 11-25 | 6.8 | 8.1 | 1.35 |
| Ni | - | 0.135 | 0.145 | - |
| As | - | 0.147 | 0.004 | - |
| Co | - | 0.476 | 0.269 | - |
| Pb | - | 0.121 | 0.045 | - |

[a]*Hamilton et al., 1994,* [b] *Nieto et al., 2007. **Except pH, all values are expressed as mg/l.***

## 2.3.3 Environmental impact of Acid mine Drainage

A vast majority of pollution of water is caused by humans. Mining companies have come and gone, leaving mines abandoned and disused to collect water. Two major types of mining are surface and underground mining. Surface mining is the mining of coal and other minerals that are close to the surface of the earth (giving easier access to such minerals). Underground mining is used to access minerals deep down in the earth

through tunnels made specifically to enter certain areas deep inside a mine (World Coal Institute, 2010).

A major problem with inactive mines (closed mines) is that they are the leading cause of Acid Mine Drainage (AMD). Underground water must be pumped out continually for mining to continue otherwise the water flows over the rocks and becomes toxic (World Coal Institute, 2010). Acidic water from inactive mines also runs into streams and rivers, causing a series of chemical reactions which are threats to the surrounding environment and still the responsibility for treating acid mine drainage is the crucial issue.



**Figure 2.3: A Lake polluted with acid and toxic wastes, resulting in disruption of surrounding environment, Canada.**

**(Reprinted from:** http://whaton.uwaterloo.ca/s06_amd.html).

Drainage water from AMD is initially clear but turns a vivid orange colour as it undergoes neutralisation because of the precipitation of iron oxides and hydroxides. This precipitate is often called ochre, it is very fine and it is a low density unstable solid material. In conditions where flowing water carries these toxic materials, they can be easily transported and deposited, covering large surface areas (Modis et al., 1998).

As discussed before, AMD with low pH (2-4) contains sulphuric acid and high amounts of dissolved metals such as copper, aluminum, lead, iron and zinc which generally make acid mine drainage extremely toxic to most organisms and surrounding environment. These contaminants are not biodegradable and tend to accumulate in the ecosystem, causing various problems. AMD widely affects the stream physically and ecologically. Iron precipitate blankets the stream consequently affecting the surrounding environment drastically (Earl and Callaghan, 1998). The dissolved iron as precipitate ferric hydroxide can be absorbed by the organisms in the water or by the animals that drink the water; iron in high quantities can cause them to become ill and die (Fripp et al., 2000).

Dissolved heavy metals not only increase the toxicity of AMD but act as metabolic poisons. These heavy metals hold back the growth of aquatic organisms. The contained heavy metals can precipitate out of solution as hydroxides; these consume dissolved oxygen reducing the oxygen available for aquatic organisms (Hoehn and Sizemore, 1977).

The presence of copper was found to be more toxic than other metals. Copper slows down the decomposition of organic matter, hence affecting the soil condition (Lide, 1997). Zinc and lead are also threats as they cause blood and reproductive disorders in animals (Wong et al., 1977).

The presence of ferric hydroxide in the water can also reduce sunlight penetration because of the state of the contaminated water. A decrease in sunlight causes distortion in the photosynthesis in plants. While tolerant species may be able to survive the harsh conditions generated by AMD such as lack of oxygen, extremely acidic pH, and high metal concentrations, sensitive species cannot survive and the aquatic cycle is significantly affected (Koryak et al., 1972).

The pH of AMD can be as low as 2; this is an important factor in determining its environmental impact. The lower the pH, the more sever the effect of AMD on plants, aquatic and animal life. The acidity is caused when the hydrogen ($H^+$) ions are released into the water during oxidation steps that have been outlined in the previous section within this chapter. These reactions can sometimes occur many years after a mine has been shut down. Once in the waterways, the sulphuric acid extensively lowers the pH of the streams and rivers. Virtually causing major damage to ecosystem that cannot handle the stress of the acidity levels.

## 2.3.4 Remediation and prevention of Acid Mine Drainage

It appears that the only method to prevent acid mine drainage is to stop new mining completely, however this is not likely to occur. The best approach of controlling acid mine drainage is to preclude its formation in the first instance. Such techniques are known as collectively as source control and the main barrier in terms of implementing such methods are the high costs involved. Figure 2.4 outlines different methods that have been practiced to prevent AMD water.

Numerous treatments exist to solve the problem of AMD, including non-limestone treatments and limestone treatments. Traditionally, the treatment of AMD consists in the neutralisation with limestone ($CaCO_3$) or similar materials, resulting in the precipitation of Fe and other metal hydroxides as well as gypsum ($CaSO_4$) (Hallberg and Johnson, 2005). However Grout injections and wetlands are treatments that do not utilise limestone (Fripp et al., 2000).



**PREVENTION**

- Flooding/sealing of underground mines
- Underwater storage of mine tailings
- Land-based storage in sealed waste heaps
- Blending of mineral wastes
- Total solidification of tailing
- Application of anionic surfactants
- Microencapsulation (coating)
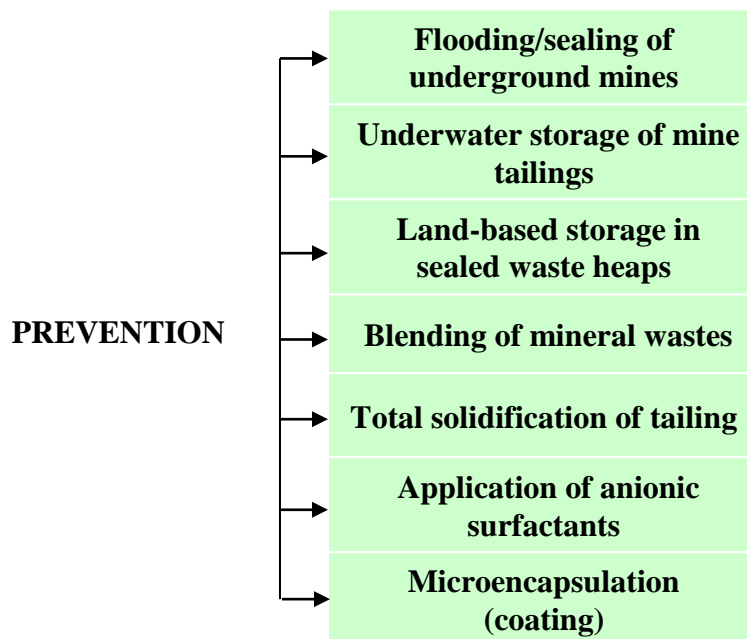
**Figure 2.4: Different methods that have been considered to prevent or minimise acid mine drainage water** *(Source: Hallberg and Johnson, 2005).*

The AMD treatments that involve limestone are limestone dumping and limestone leach beds. Limestone dumping involves introducing massive quantities of limestone into a stream affected by AMD in order to increase the pH. Limestone leach beds consist of a pond that is filled with limestone and water (clean source). The limestone dissolves in the water to make it alkaline. Once the water is alkaline, a channel directs it from the leach bed to the stream, so the limestone treated water gradually enters the stream of AMD (Fripp et al., 2000).

Lime neutralisation remains by far the most widely applied treatment method. This is largely due to the high efficiency (90-95%) in removal of dissolved heavy metals combined with the fact that lime costs are low in comparison to alternatives. Lime treatment essentially consists of bringing the pH of the raw water to a point where the metals of concern are insoluble.

Lime dissolution is the first step of the neutralisation process. For large treatment systems, quicklime is used. This lime must first be hydrated (slaked) and is normally fed to the process as slurry. The hydrated lime then dissolves to increase pH. The minimum pH required to complete precipitation of heavy metal ions are presented in Table 2.11. The two following equations illustrate the lime dissolution reactions:

$$CaO + H_2O \Rightarrow Ca(OH)_2 \qquad\qquad\qquad\qquad 9$$

$$Ca(OH)_2 \Rightarrow Ca^{2+} + 2OH^- \qquad\qquad\qquad\qquad 10$$

**Table 2.11: Minimum pH values required for complete precipitation of heavy metal ions as hydroxides** *(Source: Brown et al., 2002)*.

| Heavy Metals | Minimum pH |
|---|---|
| $Cu^{2+}$ | 7.2 |
| $Fe^{3+}$ | 4.3 |
| $Zn^{2+}$ | 8.4 |
| $Mn^{2+}$ | 10.6 |

In extreme cases where the pH of the stream is found to be very low due to the presence of AMD, slags from steelmaking process can be used instead of limestone. As discussed

before these wastes consist of calcium oxide (CaO). For example in a bed of slag, the calcium oxide disassociates to produce calcium ($Ca^{2+}$) and oxygen ($O^{2-}$) ions.

The oxygen ions react with the water in the slag bed to produce hydroxide ($OH^-$), which is a strong base. The increased pH then provides hydroxide ions which combine with the dissolved metals to produce precipitates. The following equations show some of the precipitation reactions with different metals:

$$Cu^{2+} + 2OH^- \Rightarrow Cu(OH)_2 \qquad\qquad 11$$

$$Fe^{2+} + 2OH^- \Rightarrow Fe(OH)_2 \qquad\qquad 12$$

$$Fe^{3+} + 3OH^- \Rightarrow Fe(OH)_3 \qquad\qquad 13$$

$$Pb^{2+} + 2OH^- \Rightarrow Pb(OH)_2 \qquad\qquad 14$$

$$Zn^{2+} + 2OH^- \Rightarrow Zn(OH)_2 \qquad\qquad 15$$

$$Al^{3+} + 3OH^- \Rightarrow Al(OH)_3 \qquad\qquad 16$$

$$Co^{2+} + 2OH^- \Rightarrow Co(OH)_2 \qquad\qquad 17$$
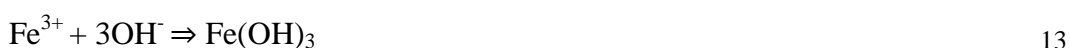
There are several of AMD treatment technologies such as passive and active treatment. The selection of method is based upon the concentration of heavy metals in the solution and the cost of treatment. Preventing the formation or the migration of AMD from its source is generally considered to be the feasible option, although it may not be practical in many locations, and in such cases, it is required to collect, treat, and discharge mine water under process specifications.

There are many options available in treating AMD, which can be categorised into those that use either chemical or biological mechanisms to neutralise AMD and remove metals from solution (Feng et al., 2000; Mohan and Chander 2001; Chartrand and Bunce 2003; Santos et al., 2004; Gibert et al., 2005; Johnson and Hallberg, 2005; Mohan and Chander, 2006; Motsi et al., 2010).
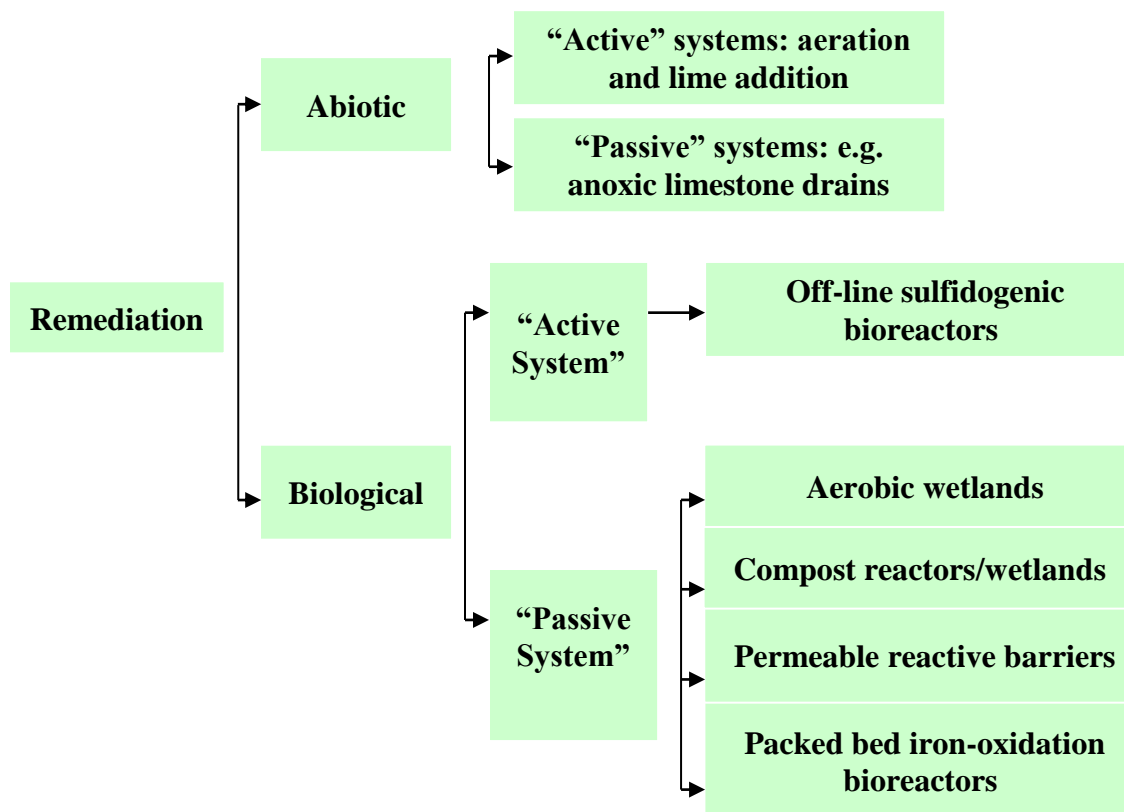
**Figure 2.5: Biological and abiotic strategies for remediating acid mine drainage water** *(Source: Johnson and Hallberg, 2005)*.

As Figure 2.5 addresses, both abiotic and biological systems include those that are classified as active (i.e., require continuous inputs of resources to sustain the process) or passive methods (i.e., require relatively little resource input once in operation). Active treatment requires the use of chemical treatment (addition of a chemical neutralising agent) systems to buffer acidity and passive treatment allows naturally occurring chemical and biological processes to carry out the treatment in a controlled system outside of the receiving polluted effluent (Coulton et al., 2003; Ziemkiewicz et al., 1997; Fripp et al., 2000).

The most widespread method for treating AMD is active treatment, which involves the addition of a chemical − neutralising agent (Coulton et al., 2003). As with any treatment methods there are a number of advantages and disadvantages involved, some of these are summarised in Table 2.12.

**Table 2.12: Advantages and disadvantages of active treatment** *(Source: Bone et al., 2003)*.

| Advantages | Disadvantages |
|---|---|
| Precise process control system | Capital and operating cost |
| Fast removal of acid and heavy metals | Expensive chemicals used |
| Track record and available expertise | Sludge disposal |
| Consistent effluent quality | High energy consumption |

The addition of an alkaline material to AMD will raise its pH, accelerating the rate of chemical oxidation of ferrous iron and causing most of the dissolved metals to precipitate out as hydroxides or carbonates. Table 2.13 shows the chemicals that are used in active treatment of AMD.

**Table 2.13: Chemicals for acid neutralisation, coagulation/flocculation, and oxidation.**
*(Source: Skousen et al., 1998)*

| NAME | CHEMICAL FORMULA | COMMENTS |
|---|---|---|
| **Acid Neutralisation** | | |
| Limestone | $CaCO_3$ | Used in anoxic limestone drains open limestone channels. |
| Pebble Quick Lime | $CaO$ | Very reactive, needs metering equipment. |
| Soda Ash Briquettes | $Na_2CO_3$ | System for remote locations, but expensive. |
| Caustic Soda | $NaOH$ | Very soluble, can be in solid or liquid form, but cheaper in liquid form. |
| Fly Ash | $CaCO_3, Ca(OH)_2$ | Neutralisation value varies with each product. |
| Hydrated Lime | $Ca(OH)_2$ | Cost effective reagent, but requires mixing. |
| Ammonia | $NH_3$ or $NH_4OH$ | Very reactive and soluble |
| **Coagulants/Flocculants** | | |
| Alum (aluminium sulphate) | $Al_2(SO4)_3$ | Acidic material, forms $Al(OH)_3$ |
| Copperas (ferrous sulphate) | $FeSO_4$ | Acidic material, usually slower reacting than alum. |
| Ferric Sulphate | $Fe_2(SO4)_3$ | Ferric products react faster than ferrous. |
| Sodium Aluminate | $NaAlO_2$ | Alkaline coagulant |
| **Oxidants** | | |
| Calcium Hypochlorite | $Ca(ClO)_2$ | Strong oxidant |
| Sodium Hypochlorite | $NaClO$ | Strong oxidant |
| Calcium Peroxide | $CaO_2$ | Trapezes, an acid neutraliser. |
| Hydrogen Peroxide | $H_2O_2$ | Strong oxidant |
| Potassium permanganate | $KMnO_4$ | Very effective, commonly used. |

At present in the UK, a number of technologies have been practically applied to the AMD problem e.g. at Wheal Jane Mine. The active treatment process starts with the addition of 5 % lime slurry to the *AMD*, in order to increase its pH to about 9.5 as illustrated in Figure 2.6. The mixture is then aerated in aeration tanks installed with a diffuser at their base. The product of the aeration tanks is pumped to the clarifiers where it is mixed with flocculants to assist settling. The settled sludge is about 30 – 40 % solids, this sludge is disposed of at a tailing pond (Whitehead et al., 2005). A removal of 3,200 tonnes of metal to the tailings dam at a removal efficiency of 99.2% is achieved.
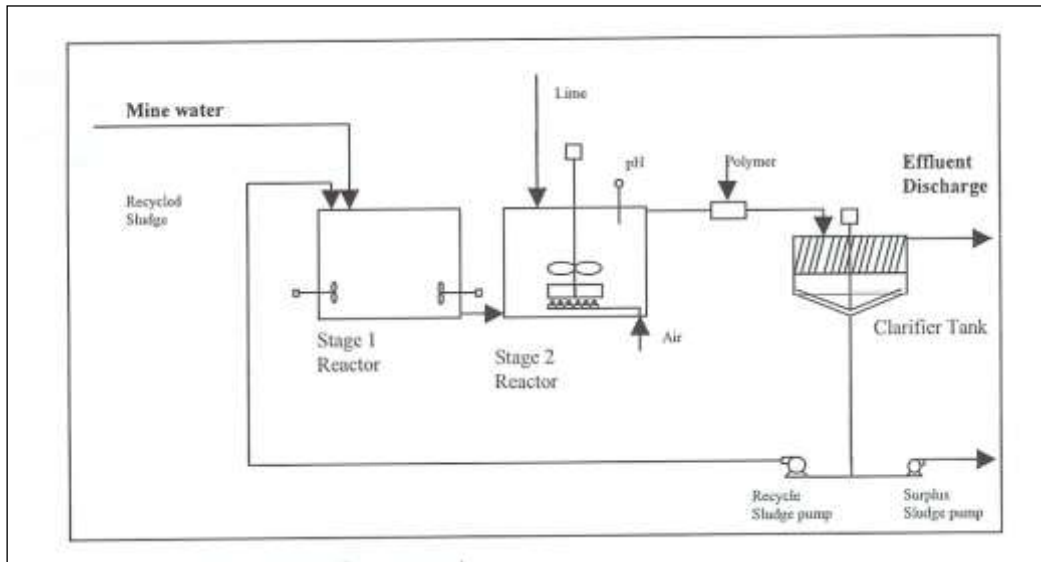


**Figure 2.6: Wheal Jane active treatment plant** *(Adapted from: Whitehead et al., 2005)*.

Since the early 1990s, passive treatment systems have been developed to treat AMD; these require only sporadic maintenance, which greatly reduces long term costs. Passive treatment technologies take advantage of naturally occurring chemical and biological reactions in a controlled environment to treat AMD with minimal operational or maintenance cost (Gazea et al., 1996; Johnson and Hallberg, 2005). The primary passive technologies include aerobic and anaerobic wetlands; anoxic limestone drains (ALD), limestone ponds, open limestone channels (OLC), vertical flow reactors and settling ponds (Johnson and Hallberg, 2005).

A pilot passive treatment plant was constructed at Wheal Jane Mine to determine the effectiveness of this technique in providing a cost effective alternative to the expensive active treatment method. The constructed passive treatment plant consisted of three individual wetland circuits which differ only in the pre – treatment, that is, pH control of the inflowing *AMD*. The three systems incorporate a limestone treatment tank, a series of aerobic cells, anaerobic cell and rock filters (Swash and Monhemius, 2005; Whitehead et al., 2005; Hallberg and Johnson, 2003), as shown in Figure 2.7.
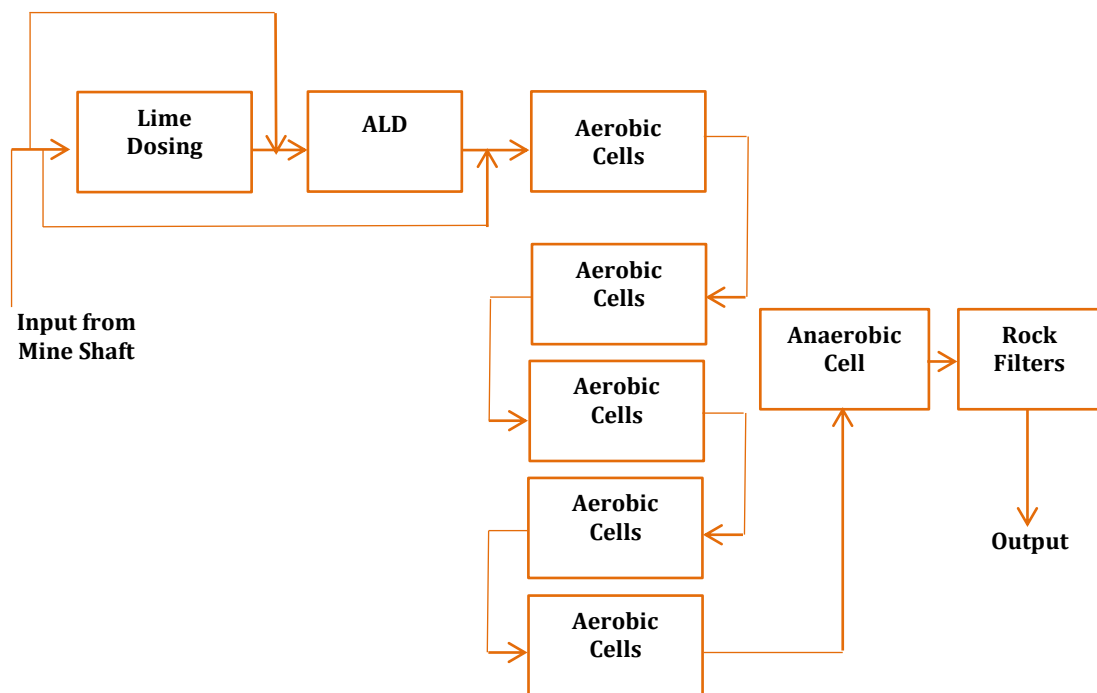


**Figure 2.7: Simplified process flow diagram for the passive treatment plant at Wheal Jane Mine** *(Source: Whitehead et al., 2005)*.

As discussed above The Wheal Jane pilot passive treatment plant considered of three separate treatment system, although all three of the systems had the same principal treatment:

➢ Aerobic cells- reed beds (iron removal);
➢ Anaerobic cells (zinc, copper, cadmium, iron removal);
➢ Aerobic rock filters (manganese removal)

The systems varied in the methods of pre-treatment to raise pH prior to mine water entering the aerobic cells:

➢ Lime dosing system(to raise the pH of AMD without the removal of excess iron)
➢ Lime free system (no pre-treatment)
➢ Anoxic limestone drain system (to remove dissolved oxygen from AMD; to reduce the formation of iron hydroxide)

The passive treatment plant was only able to treat 6 litres of AMD per second, which is far less than the volume needed to be treated (about 330 L/s). This meant that if passive treatment was to be employed more land had to be used, but the land area available in the Carnon Valley was not adequate to accommodate a full scale passive treatment plant (Environmental Agency, 2007). Furthermore, passive systems are generally less controllable and consistent than active treatment plants. Thus, the active treatment plant is the main method for AMD treatment at Wheal Jane.

Choosing methods to use to remediate AMD is dependent by a number of environmental and economic factors. Sometimes the actual environmental cost of a remediation system is not immediately apparent. One such cost is the amount of fossil fuel energy needed to transport liming materials, often long distances from source to mine sites, for instance at Wheal Jane mine in Cornwall, where the lime is transported from a site in the Midlands of England.

Fundamentally legislation is likely to become the dominant factor in determining which remediation system can be used in any situation. The sustainability of any remediation system is a factor that is becoming increasingly critical in decision making. One of the problems is that products of AMD remediation have not been looked at as a resource.

There are technologies that have the potential to extract and retain valuable metals from AMD treatment in order to offset the treatment costs by bringing revenue from by-products of AMD treatment process (McGinness et al., 1999). The basic idea is to:

➢ Produce "grey" water from AMD which may have industrial usage, like being used as a source water for a pump storage electricity generating facility;

➢ Choice of selectivity of certain metals and concentration from AMD until they reach a commercial grade which may be profitable;

➢ Proposals to make building materials from AMD sludge e.g brick;

➢ Generating a by-product from AMD treatment process that has a commercial value, and thus can be sold, for example iron oxide from AMD can be sold to a paint company as a pigment.

The appropriate choice is site-dependent and should be based on the specific treatment challenges. For example, if sludge disposal volume is an important concern, HDS (High density sludge) process or Geco Process should be selected. For improved lime efficiency, the Geco or Staged-Neutralisation process should be considered. If capital investment is a concern and a large area is available, then perhaps pond treatment would be an effective treatment option (McGinness et al., 1999).

Overall there are a number of acid mine drainage treatment procedures, however these are considered to be outside of the scope of this study and the main focus is on adsorption of acid mine drainage which is particularly an effective technique and fits into active treatment category. Natural materials that are available in large quantities or waste residues from industrial operations such as steelmaking process have potential as inexpensive adsorbents (Bailey et al., 1999).

## 2.3.5 Adsorption of Acid Mine Drainage

Adsorption is involved in many natural, physical, biological, and chemical systems, and is widely used in different industrial applications. Adsorption is becoming a popular method for the removal of heavy metals from the AMD (Omer et al., 2003). Natural materials, waste and residue products from industrial or agricultural activities have excellent potential as an economic adsorbent for heavy metal removal from AMD solution.

Adsorption is the process of attraction or diffusion of molecules from a bulk fluid (gas or liquid) to an exposed solid surface (Richardson et al., 2002). The efficiency of diffusion process depends upon the selectivity, molecular structure of the adsorbent for a particular fluid and other factor as outlined below:

➢ Chemical composition of adsorbent;

➢ Mechanical strength and porosity;

➢ Particle size distribution;

➢ Surface area & exothermic properties.

There are two types of adsorption processes; these are physical and chemisorption. Physical adsorption occurs when a solute is bound to the solid surface via weak van de Waals forces or dipole interactions. Physical adsorption is considered fast and reversible. Chemisorption is usually a slow and irreversible chemical reaction that generates strong bonds between the adsorbate and adsorbent at the exposed surface.

The primary requirements for an economic and commercially attractive adsorbent are listed below: (Richardson et al., 2002; Ruthven et al., 1984)

➢ The adsorbent must have a large internal surface area, this is mainly manifested by porous material;
➢ This surface area should be accessible through pores large enough to allow certain molecules passage during adsorption, that is it should be highly selective;
➢ The adsorbent should be easy to regenerate (if needed);
➢ The adsorbent should be mechanically strong, enough to withstand bulk handling and vessel vibrations;
➢ There should not be any rapid exhausting (that is, loss of adsorptive capacity) of the adsorbent due to continual recycling.

**2.3.5.1 Examples of adsorbents used for removal of heavy metals**

As some methods have a number of shortcomings, which are high land utilisation, production of large secondary solid waste, high capital and operating costs, hence alternative methods need to be developed. There are number of inorganic adsorbents that have been used in AMD treatment. Some of these include steelmaking wastes, zeolites (natural & synthetic), activated carbon, lignite, natural clinker, coal fly ash, red mud, water treatment sludge and many others. These functional materials can alternatively be stored inexpensively in cleaning water particularly for acid mine drainage purposes.

The use of natural zeolite has gained attention among researchers and this is mainly because of its sorption properties which provide a combination of ion exchange and molecular sieve properties. In a study it is reported that the uptake efficiency of heavy metal ions ($Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$) from synthetic AMD solution has been 80%, 95%, 90% and 99% of $Fe^{3+}$, $Mn^{2+}$, $Zn^{2+}$ and $Cu^{2+}$ respectively from solutions (Motsi et al., 2010).

Adsorption rate and capacity also depend upon adsorbent dose, solution initial concentration and other process parameters. A number of researchers have shown the feasibility of using natural zeolite to adsorb heavy metals under different experimental conditions like temperature, pH, concentration and agitation speed (Zamzow et al., 1990; Erdem et al., 2004; Motsi et al., 2010).

Among the various techniques recognised, ion exchange has been thought to be efficient and economically feasible as a wastewater treatment operation. For instance in a study at India, anion exchange resins were used for the removal of copper from aqueous solution. The adsorption process, which is basically pH dependent in the case of AMD treatment, shows maximum removal of copper in the pH range 2-6 and the uptake of copper by the ion exchange resins was reversible and therefore has good potential for the removal of copper from acid mine drainage water (Gaikwad et al., 2009).

The use of lignite in AMD treatment has also received increasing interest. Lignite possesses a high oxygen content, which is fixed in carboxyl and hydroxyl groups. These groups are the active centres of the ion exchange. Hence the lignite materials can be used as alternative cation exchangers (Jochova et al., 2004). Another investigation reports that adsorption capacity of Fe(II), Fe(III) and Mn(II) in multi-component aqueous systems showed 100% efficiency (Mohan and Chander, 2006). This demonstrated the advantage of lignite as an adsorbent on a large scale for the removal and recovery of metals from acid mine drainage.

In a study, the adsorption capacity of some inorganic solid wastes (air-cooled blast furnace (BF) slag, water-quenched BF slag, steel furnace slag, coal fly ash, coal bottom ash, water treatment (alum) sludge and seawater-neutralised red mud) for $Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$ and $Cr^{3+}$ was determined (Zhou and Haynes, 2010). Results indicated that all materials had the ability to remove metal cations from aqueous solution and their relative abilities were partially pH dependant and adsorption increased greatly with increasing pH.

Water treatment sludge was also as effective as the slags and red mud; however bottom fly ash was the least effective sorbent. For $Zn^{2+}$, $Cd^{2+}$ and $Cu^{2+}$, percentage adsorption was generally greater at 10 mg/l than 100 mg/l aqueous solution. While for $Pb^{2+}$ and $Cr^{3+}$, there was little difference in percentage adsorption between the 10 mg/l and100 mg/l levels (both near 100% adsorption). The high alkalinity present in blast furnace and steel slags (due to hydrolysis of calcium silicates) and red mud (due to the presence of residual NaOH) results in them having 100% adsorption rates of all respective metal ions.

### 2.3.5.2 Using waste gas sludge (BOS sludge) to treat Acid Mine Drainage

Recycling of BOS sludge waste is a challenge as explained earlier in this chapter, separate processing is commonly counted as an economically unfavourable solution. Since steelmaking slags appear to have a number of applications in removal of heavy metals from aqueous solutions, exploiting steel wastes as different types for treating

acidic solutions such as AMD in a manner which minimises the volumetric generation of sludge or slag for disposal on steel sites is recently gaining more attention.

In recent years, several batch studies on the adsorption of heavy metal ions using iron/steelmaking slags and other industrial wastes as functional sorbents have been published; however the studies are limited and inconsistent and the adsorption mechanisms are yet to be understood fully in detail. Thus BOS sludge can be considered as an alternative solution for the treatment of AMD and the factors that make BOS sludge an ideal candidate are as follow:

➢ High Availability;

➢ Presence of exchangeable cations (neutralising potential ability);

➢ Low cost (implementation methodology);

➢ Favourable structure and adsorptive properties (high surface area and porosity);

➢ More effective and efficient compared to existing adsorbents.

The literature review and examples of materials demonstrate that extensive expertise has been accumulated in an attempt to recover metals from acidic solutions such as AMD. The need to focus on adsorption topic is obvious and hence laboratory investigations must be conducted to introduce the use of a novel sorbent and to extend the knowledge of utilisation of steel wastes under adsorption techniques and methods towards acid mine drainage treatment.

# CHAPTER 3

# MATERIALS AND METHODS

## 3.1 Introduction

This study aimed at evaluating the use of waste gas sludge (BOS sludge) to clean up AMD solutions. This chapter describes in detail the methods and materials used in the characterisation and performance of BOS sludge and other steel slags as potential adsorbents in the process of AMD treatment. Some of the methods used include kinetic studies, the effect of thermal pre-treatment of adsorbent, effect of initial solution pH and solution concentration, adsorbent mass and reactor studies. The preparation and analysis of different solutions used in this research are also discussed; synthetic solutions containing desired heavy metals were used to simulate actual AMD solutions and also real AMD from Wheal Jane mine was also used.

## 3.2 Materials and Sample Preparation

### 3.2.1 Synthetic solutions and other chemicals

Synthetic single and mixture component solutions of $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ were prepared from analytical grade $[Fe(NO_3)]_3.9H_2O$, $Cu(NO_3)_2.3H_2O$, $Mn(NO_3)_2.3H_2O$ and $Zn(NO_3)_2.6H_2O$ respectively (Fisher Scientific, UK). The metal concentrations were in the range of 5, 10, 20, 40, 100, 120 and 140 mg/l of all metals in synthetic AMD solution which were prepared by mixing desired concentrations in a litre of distilled water. The synthetic solution was used to observe the behaviour of each cation in the presence of competing cations, that is, the other 3 cations and also to determine the capacity of BOS sludge and other steel slags as an adsorbent.

Sulphuric acid was used for desorption and regeneration tests in this research; the acid concentration used was 2 % (wt) $H_2SO_4$. Sodium chloride (NaCl) solution, 20 mg/l was also prepared and used in desorption and regeneration tests.

Real AMD from Wheal Jane mine was collected in 25 litre sealed containers. The real AMD was used to determine the effectiveness of BOS sludge and other adsorbents in treating actual AMD and results were compared to synthetic AMD solutions.

Standard solutions for metal analysis using the atomic absorption spectrometer (AAS) were prepared from standard metal solutions from Fischer Scientific. The range of standards used was 1-140 mg/l dependent upon the concentration of AMD solution used in the process.

In this study pelletising tests were performed, *Bentonite clay* was used as a binder for the sorption process and this was provided by the School of Chemical Engineering; University of Birmingham, UK. Encapsulated BOS tests were also carried out using geotextile membranes; which these were supplied by the School of Civil Engineering; University of Birmingham.


## 3.2.2 Characterisation of BOS sludge and other materials

In this study BOS sludge (also known as waste gas sludge) was utilised as the principle adsorbent and granulated blast furnace slag, blast furnace flue dust and ground granulated blast furnace slag samples also tested for comparison purposes. These samples were supplied by Tata Steel plant in Port Talbot (UK, South Wales). The samples were used in their natural state ("as received") with no chemical modifications, unless stated. The BOS sludge was originally in slurry lump form; samples were then left out open in air temperature to dry up naturally before use.

### 3.2.2.1 Adsorbent particle size

Particle size classification of the samples was carried out using sieve screens. The sieves were manually used when needed and mechanically vibrated using a vibratory shaker for 40 minutes which was adequate for efficient separation to take place. Typical particle size range of naturally dried BOS sludge used in this study was 0.18 to 9.1mm, unless stated otherwise.

### 3.2.2.2 Scanning Electron Microscopy (SEM) & EDS

The surface morphology of BOS sludge was studied using a scanning electron microscope, Philips XL-30 Environmental SEM-FEG. This particular microscope is also fitted with an Oxford Inca 300 EDS system. EDS, stands for Energy Dispersive Spectroscopy; it is an analytical technique used for the elemental and chemical composition analysis of a sample.

The dried samples were gold coated in a vacuum chamber in order to make them conductive, to enable better scanning and analysis. The gold coating is very thin; otherwise the definition of the sample will be compromised. Samples were placed on a brass disc/stage using sticky carbon tape. The gold coating of the samples and the sticky carbon tape were used to prevent the accumulation of surface charge on the sample during analysis. Samples were placed into a vacuum chamber of the microscope and analysed using different magnifications. Samples that were analysed using SEM are BOS sludge (feed), magnetic BOS and non-magnetic BOS and the Inca scanning software was used to study the samples' surface morphology and for data analysis.

### 3.2.2.3 X-Ray diffraction (XRD) and X-Ray Fluorescent (XRF)

Mineralogical analysis of the BOS sludge samples was carried out using X-Ray Diffraction (*XRD*). Chemical analysis to determine the chemical composition of the samples was obtained by X-Ray Fluorescence (*XRF*) these analytical procedures were carried out by the supplier of the BOS sludge samples, Tata Steel; BOS unit in Port Talbot (UK, South Wales).

### 3.2.2.4 Magnetic separator

Feed BOS, non-magnetic BOS and magnetic BOS samples were obtained using by magnetic separation using a magnachute and wet high intensity magnetic separator (Model: L.I.R.1.4 Rapid Magnetic) As discussed in the previous chapter BOS samples as steel wastes are known to be ferromagnetic due to high iron content. Magnetic separations have been carried out in order to separate the non-magnetic metals such as Zn, Pb and Cu from the rest of the metals present in the BOS sludge. In this process 50 g of the homogenous BOS sample was weighed using an analytical balance and was mixed with water to be made as slurry; this was then fed into both separators. The magnetic and non-magnetic samples collected were dried and analysed.

### 3.2.2.5 Froth flotation separator

A froth flotation cell (Model: Denver LF6797A; rpm: 1425) was used to separate metal content such as Fe and Zn by exploiting differences in their surface chemistry. Hydrophilic particles disperse in suspension while as hydrophobic phases attach to air bubbles and are then removed in the froth phase. Froth flotation tests were carried out using Teefroth as a frothing agent (to give a stable froth) and a collector for iron phases (Cytec) was recommended by Cytec industries, samples were then collected, dried and analysed.

Each sample was initially attacked with 50% v/v Hydrochloric Acid. When dissolution of all soluble material was complete the solution was oxidised with drop wise additions of concentrated Nitric Acid, any insoluble residue was filtered and reserved. The insoluble residue was ashed and fused in a eutectic mixture of Sodium and potassium Carbonates. The resultant mass was dissolved in dilute Hydrochloric Acid and the solution added to the acid soluble fraction. The combined solutions from each sample were analysed for Iron and Zinc by inductively Coupled Plasma Optical Emission Spectroscopy.

### 3.2.2.6 Surface area (BET)

Surface area measurements for the BOS sample and thermally treated BOS were determined by Nitrogen adsorption fitted to the BET equation (Brunauer, 1943), using the TRISTAR 3000 apparatus from Micromeritics. BET analysis provides precise specific surface area evaluation of BOS by nitrogen multilayer adsorption measured as a function of relative pressure using a fully automated analyser. The technique encompasses external area and pore area evaluations to determine the total specific surface area in $m^2/g$ yielding important information in studying the effects of surface porosity and particle size. These tests were carried out by the Department of Chemistry at the University of Warwick.

### 3.2.2.7 Other physical characteristics

Other physical properties namely porosity, moisture content and density of BOS sludge samples were measured. The density of the BOS sample was determined using a helium gas pcynometer from Micromeritics, model AccuPyc II 1340. The porosity of BOS sample was measured using a mercury porosimeter, Micromeritics, AutoPore (IV).

## 3.3 Experimental procedure

### 3.3.1 Batch Adsorption Studies for Synthetic and Wheal Jane AMD

Batch adsorption tests were carried out using different quantities of BOS sludge and other adsorbent samples (BF slags) mixed with solutions containing the desired concentration of heavy metal ions as synthetic solutions or using real AMD (Wheal Jane AMD). The mixtures were agitated in 200 ml plastic bottles over a tumbling mill at 110 rpm and then the solutions were filtered and analysed using the AAS.

### 3.3.1.1 Kinetic Studies

The mass of BOS sludge and other materials used was in a range of 4, 8, 16, 20 and 24g in a constant volume (200 ml) of either synthetic or real AMD solutions containing

different metal ions, at different concentrations. The agitation time was specified for 180 minutes (accumulative time). Some sorption experiments were carried out in duplicates in order to observe the reproducibility of the results. The errors in analysing the cations between duplicate experiments are presented for each section in the relevant chapter.

### 3.3.1.1.1 Effect of adsorbent particle size

The effect of adsorbent particle size on the kinetics of the process was also investigated. Three different sizes were used; $1 - 1.4$ mm, $3.4 - 7.6$ mm, $7.6 - 9.1$ mm and BOS slurry as received. Different ranges of adsorbent dosage at the required particle size was mixed with 200 ml AMD solution of the appropriate single or multi component mixture solution for 180 minutes and liquid samples were collected at regular intervals and analysed.

### 3.3.1.1.2 Effect of solid/liquid ratio

Different masses were used in this study, ranging from 4, 8 16, 20 and 24 g of BOS sludge and other adsorbents. The mixture was agitated and the samples were taken at regular intervals for AAS analysis. The particle size of BOS sludge used was dependent upon the process mode and parameters selected.

### 3.3.1.1.3 Effect of initial solution pH

The solution pH was varied as follows: 3.5 and 4.5 $\pm$ 0.1 (based on data for typical AMD sites) for the synthetic AMD solutions. Solution pH was adjusted using 2 % (wt) $H_2SO_4$, Synthetic solutions of single component solution AMD containing of 40 (mg/l) each of $Zn^{2+}$ and $Fe^{3+}$ from calibration standard solutions were prepared. 200ml of each single component synthetic solution was then contacted with 8g, 16g and 24g of BOS sludge samples respectively for the treatment of synthetic AMD.

Wheal Jane AMD solution was also contacted with 24g of BOS sample and the solution pH was varied using NaOH from the initial pH (2.8) to 3.5 and 4.5 to investigate the

influence of pH variation in relation to removal of heavy metals. The pH of each sample was measured using a Microprocessor pH meter (Hanna PH211).

### 3.3.1.1.4 Effect of initial metal solution concentration

The effect of initial metal concentration of synthetic AMD solution on the removal of heavy metals by 16 g of BOS samples of size of $1 - 1.4$mm were investigated using single component solution concentrations ranging from 5, 10, 20, 40, 100, 120 and 140 mg/l. The experiments were run for 180 minutes.

### 3.3.1.1.5 Effect of agitation

Agitation or mixing of the AMD and BOS used in this study was carried out using two methods. The first method was carried out in a 200 ml bottles over a tumbling mill rotating at a speed of 110 rotations per minute. The second method was carried out using a mechanical agitator in a reactor vessel at different speeds (20 and 45 rpm) which was sufficient to allow suspensions of the BOS.

### 3.3.1.1.6 Effect of competing cations

Acid mine drainage normally contains more than one cation, it is a mixture of different cations and toxic elements for example $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$, $Zn^{2+}$, $Pb^{2+}$, $Cr^{3+}$ etc. Tests were performed to investigate the influence of the presence of other cations on the adsorption capacity of BOS sludge for each of the cations. Two Multi-component solutions containing equal concentrations of 40 and 100 mg/l containing of $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ were made and contacted with BOS sludge for 180 minutes. The effect of single component solution on the removal of selected heavy metals by 16 g of BOS samples with size of $+1$mm, $- 1.4$mm were compared to the results of multi-component solutions using 16 g of BOS sample with the same particle size.

### 3.3.1.1.7 Equilibrium Adsorption Isotherms

Equilibrium isotherm experiments were conducted by mixing 16 g of BOS sample with 200 ml single component solutions. The range of initial metal concentration was from

5–140 mg/l. The particle size of adsorbent used was +1mm, $-$ 1.4 mm. The mixtures were agitated for 180 minutes, until equilibrium was reached and then the solution was filtered and analysed using the AAS.

### 3.3.1.1.8 Thermal pre-treatment of adsorbent

A furnace used for heating BOS sludge at $200^\circ C$ for 60 minutes in an air atmosphere; 24 g of thermally treated BOS sludge was contacted with Wheal Jane AMD solution for 180 minutes; the mixture was agitated using a tumbling mill (110 rpm) in a 200ml bottle; samples were collected at regular intervals and analysed.

### 3.3.1.1.9 BOS Regeneration tests

200ml of Wheal Jane solution was contacted with 24 g of BOS sludge for 180 minutes; samples filtered and the BOS separately contacted with NaCl and $H_2SO_4$ for 20 minutes. The regenerated sample was contacted again with 200 ml of AMD for 180 minutes under agitation and the samples were collected at regular intervals and analysed.

### 3.3.1.1.10 pelletising

24 g of particle size of +1mm–1.4mm sieved BOS sample were made as pellets using water and binder (Bentonite clay). Pellets were heated up to $400^\circ C$ for 90 minutes in a furnace and the pellet samples were contacted with 200 ml of Wheal Jane AMD for 180 minutes and agitated using a tumbling mill. The solution was then filtered and analysed using the AAS.

### 3.3.2 Treatment of synthetic acid mine drainage

The objective of this study is similar to those in batch tests to treat synthetic acid mine drainage under different operating conditions. Thus synthetic solutions containing a mixture of $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ at different concentrations were made up. Two main methods were investigated, these are batch and semi-continuous.

### 3.3.2.1 Batch experiments using encapsulated method

24 g of BOS sludge with size of 180 – 250 μm was charged into a geotextile membrane as an *'encapsulated product'* and was contacted with 200ml of multi-component synthetic AMD solution at desired concentrations (40 mg/l). Samples were contacted for 180 minutes and agitated using a tumbling mill.

### 3.3.2.2 Semi-continuous experiments using reactor tank

The reactor is a basic cubic tank constructed of rigid Perspex with length of 25.5cm, height 20cm and width of 22cm with working capacity of 11L. The AMD solution is pumped at a specified flow rate each time through an inlet distributor. Although the reactor was a Perspex tank it was well resistant to the acidic nature of AMD. The solution was pumped through an inlet in an upward flow direction into the tank via pipelines using a peristaltic pump and in the case of mixing mode; a three bladed impeller was placed inside the reactor tank for agitation using a speed regulator. The impeller bottom clearance is kept one-fourth of the tank volume, Figure 3.1 illustrates the reactor assembly for AMD treatment used in this study.

The agitated vessel was provided with a lid on the top of the tank with a slot up to the centre, which allows the shaft of impeller to pass through the lid. The lid prevented any splashing of liquid during agitation. Two baffles were provided in the tank, which inhibit the formation of vortex during agitation. A metal grid with attached geotextile membrane was also used at the bottom of the tank to support the weight of the BOS sludge and more importantly to provide adequate residence time and necessity space for the AMD solution to gradually channel through the BOS sludge bed.

The solution then cascades down and settles into another tank (settling tank) through a layer of filter membrane inside and eventually drains out through an outlet drain pipe (diameter of drain pipe,1.5cm). The purpose of the settling tank was to allow solid suspensions to settle, thus to prevent the chances of adsorbent particulates diffusing through the final neutralised water, See Appendix C for photographs of the unit.

An analysis sample of solution was collected at regular time intervals throughout the process and the final concentration of the heavy metal ions in the solution was then determined using the AAS. The results based on this study were used to propose a design of a passive AMD treatment reactor vessel with comparable flow rates used at the Wheal Jane pilot passive treatment plant.
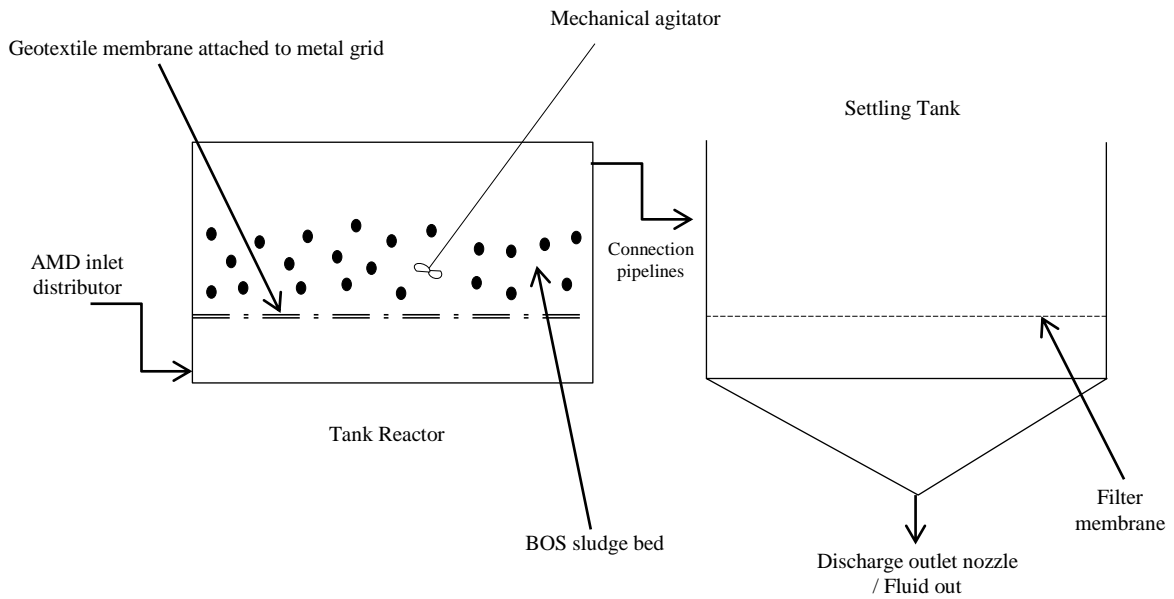


**Figure 3.1: Simplified sketch of reactor assembly for AMD treatment used in this study.**

### 3.3.2.2.1 Effect of adsorbent mass on process efficiency

Different masses of BOS sludge and blast furnace flue dust were used in this study, ranging from 2-6 kg dependent upon the investigation criteria. The mixtures were agitated and the samples were taken at regular intervals for AAS analysis. The particle size of BOS sludge used was also dependent upon the process mode and parameters selected.

### 3.3.2.2.2 Effect of initial solution concentration on process efficiency

The effect of initial solution concentration on the removal of the cations from synthetic AMD solution by BOS samples were investigated using different concentrations of 5 and 20 mg/l in 40L of synthetic AMD solution.

### 3.3.2.2.3 Effect of particle size on process efficiency

The effect of adsorbent particle size on the kinetics of the process was also investigated. Three different size ranges were used; 0.18-0.5mm and 1–1.4mm and BOS slurry as received. The experiments were run ranging from 200 to 400 minutes and in some tests for 50 hours. Samples were collected at regular intervals for each experiment run and analysed using the AAS.

### 3.3.2.2.4 Effect of mixing on process efficiency

Agitation or mixing of the synthetic solutions and the BOS samples used in this particular study was carried out using a mechanical agitator attached to a speed regulator, where two different speeds were used; those are 20 and 45 rpm.

## 3.4 Sample Analysis

Samples collected from the different experiments were analysed using an atomic absorption spectrometer (AAS), [Model 751, Instrumentation Laboratory, USA]. The AAS uses an air –acetylene flame and single element hollow cathode lamps. The AAS is generally used to analyse relatively low metal concentrations and hence dilution of some of the samples was sometimes necessary. The AAS was calibrated using standard solutions of the respective metals in the range 1 – 140 mg/l. Distilled water was used for all dilution purposes and for filtering samples, syringe and micro filters with a 0.2μm membrane were used.

Specific sorption experiments were carried out in duplicate in order to observe the reproducibility of the results and the mean value was used. The errors in analysing

copper, iron, zinc and manganese was approximately ±6.65%, 6.67%, 5.77% and 5.59% respectively. A detailed explanation of how the AAS works is given in Appendix A.

# CHAPTER 4

# CHARACTERISATION OF BOS SLUDGE

## 4.1 Introduction

The mineral phases, chemical properties and physical strength of sorbents and many other materials are affected by the size distribution, shape and structure of their particles and most importantly processing history. The characterisation of BOS sludge is studied in this chapter. Particle characterisation reveals information on the physical and chemical nature of BOS sludge particles, which can be related to its ability to remove heavy metal ions from solutions such as AMD. Different analytical techniques were used in this study; these include scanning electron microscopy (SEM), X – Ray Fluorescent (XRF), energy dispersive X-ray analysis (EDS) and surface area determination using BET (BET stands for Brunauer, Emmett, and Teller, the three scientists who optimised the theory for measuring surface area (Brunauer et al., 1938)). Zinc and iron distribution analysis was undertaken by EDS on BOS sludge samples concentrated using froth flotation and magnetic separation methods. The result of wet chemical analysis from Port Talbot Tata Steel Plant (Wales, UK) is also presented and evaluated.

## 4.2 Scanning Electron Microscopy (SEM)

A scanning electron microscope (SEM) was used to observe the sample surface. The SEM is an instrument that produces a largely magnified image by using electrons instead of light to form an image. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down onto the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample. The electrons interact with the atoms that make up the sample producing signals that contain information about the

sample's surface morphology and topography and composition. Detectors collect these X − Rays, backscattered electrons, and secondary electrons and convert them into a signal that can be displayed as a greyscale SEM image on a computer.

## 4.2.1 Results and discussion of characterisation using SEM

Figure 4.1 below is a Scanning Electron Microscopy-Energy Dispersive Spectroscopy (SEM-EDS) showing macro-porosity surface structure with elemental composition. Figure 4.2 shows micrographs of "as received" BOS sludge samples obtained from SEM analysis at different magnifications showing clearly a large number of pores on the BOS surface.
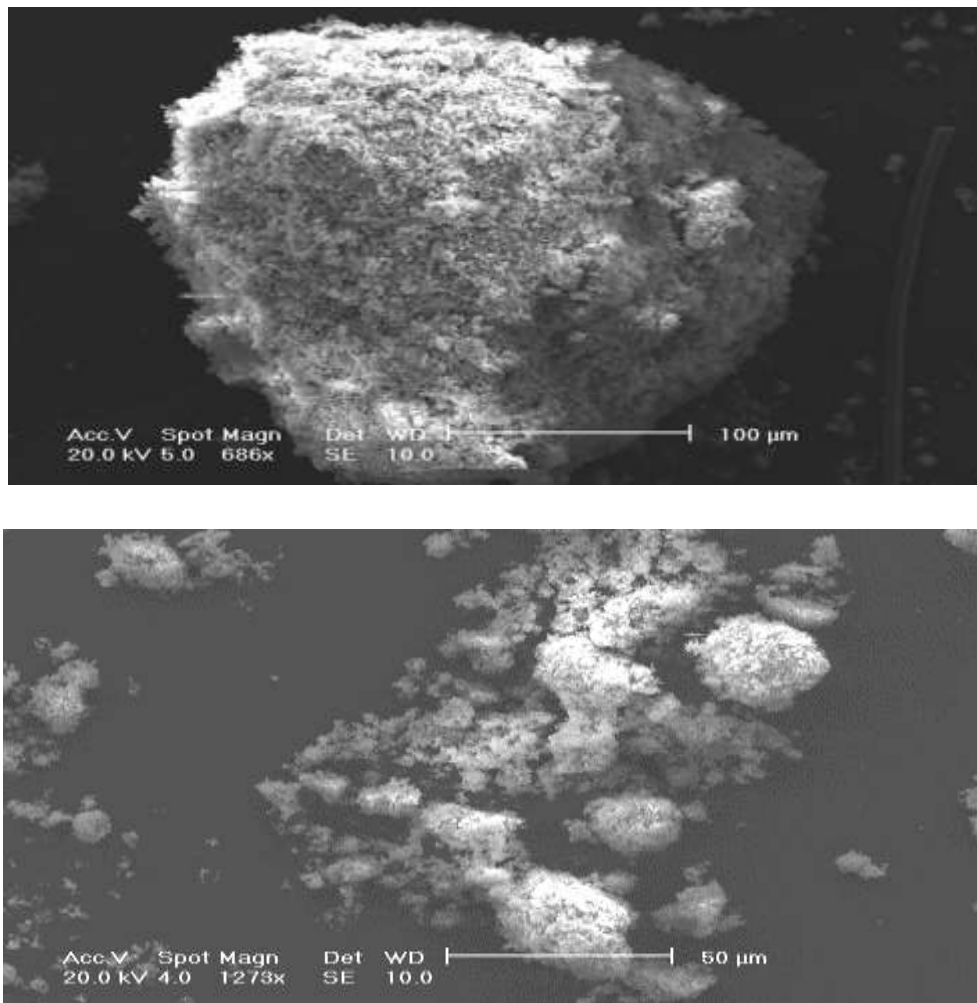




**Figure 4.1: SEM Micrographs of BOS sludge for +1mm,-4mm BOS size fraction.**

**(a)**
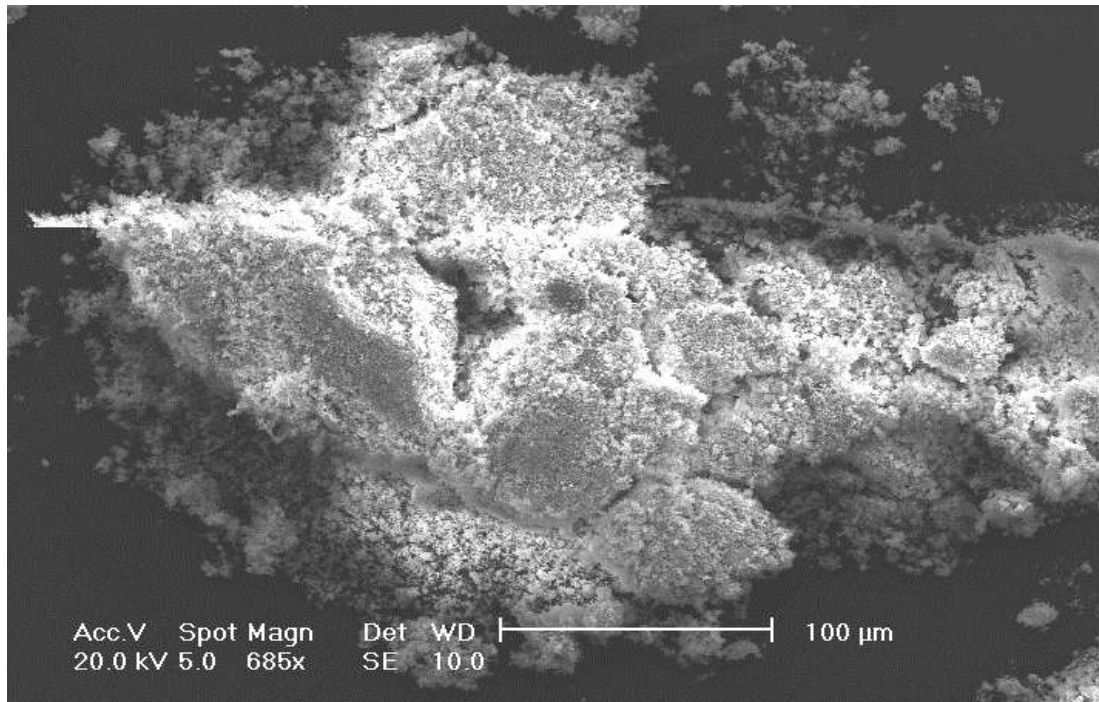


**(b)**
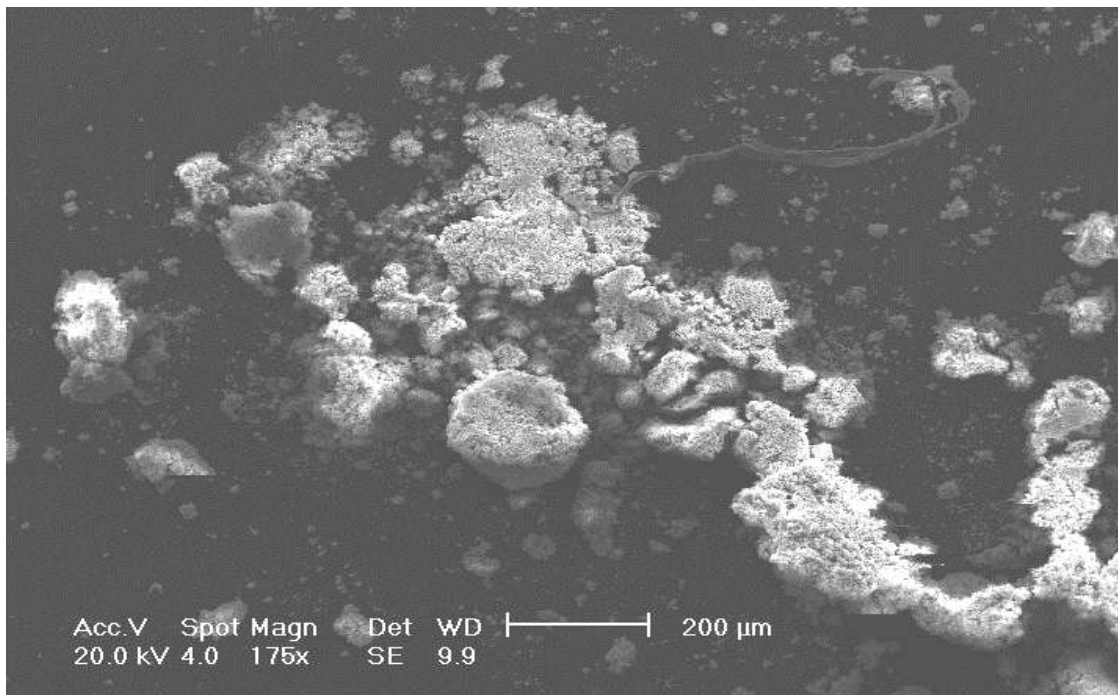


**Figure 4.2: SEM Micrographs of BOS sludge (as received) at different magnifications: (a) x685 and (b) x175.**

From EDS analysis of BOS surface in the Figure 4.3, it can be observed that zinc is evenly distributed and dispersed in BOS sludge and appear as frankelite ($FeZn_2O_4$) and can be described as a mirror image of iron particles. Calcium elements are also visibly shown as clusters in the BOS sludge sample, this is due to BOS high free lime content.



Fe Ka1

Zn Ka1

Si Ka1

Ca Ka1

O Ka1
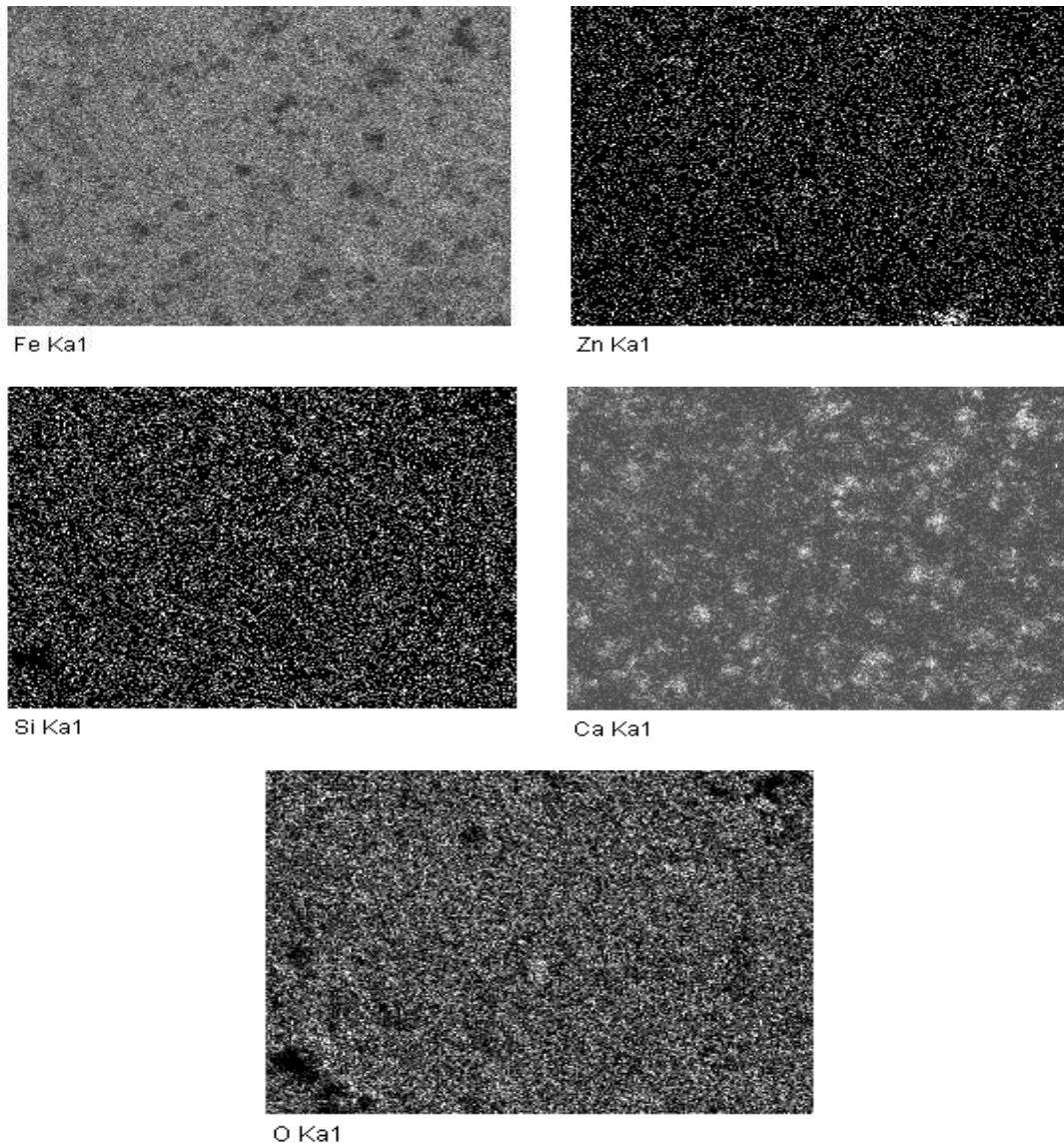
**Figure 4.3: SEM Micrographs; Elemental Dot-mapping of BOS sludge illustrating structure and dispersion profiles.**

## 4.3 Energy Dispersive Spectroscopy (EDS)

The scanning electron microscope used in this study was also fitted with an EDS system, which means it could also perform energy dispersive spectroscopy. EDS is an analytical technique used to identify the elemental composition of a sample based on the emission of characteristic X – Rays by the sample when subjected to a high energy beam of charged particles such as electrons or protons (Goldstein et al., 2003), See Table 4.1.

The most important aspect is that x-rays generated from any particular element are characteristic of that element, and as such, can be used to identify which elements are actually present under the electron probe. An electron beam was directed onto different parts of the samples in order to obtain a more accurate analysis. Typical analysis data and scanning method illustrations is shown in Figure 4.4.

**Table 4.1: EDS analysis of BOS sludge (as received) showing the elemental composition and predominant exchangeable cations.**

| Spectrum | O | Mg | Si | Ca | Mn | Fe | Zn | Total |
|---|---|---|---|---|---|---|---|---|
| Spectrum 1 | 23.29 | 0.86 | 0.77 | 5.07 | 1.18 | 63.47 | 5.37 | 100.00 |
| Spectrum 2 | 20.12 | 0.89 | 0.72 | 7.41 | 1.10 | 64.86 | 4.91 | 100.00 |
| Spectrum 3 | 24.50 | 1.88 | 1.04 | 6.61 | 1.98 | 56.36 | 7.64 | 100.00 |
| Spectrum 4 | 22.77 | 1.60 | 1.10 | 6.88 | 0.93 | 59.86 | 6.87 | 100.00 |
| Spectrum 5 | 25.54 | 1.11 | 0.97 | 6.71 | 0.99 | 58.43 | 6.26 | 100.00 |
| Spectrum 6 | 23.73 | 0.64 | 0.69 | 4.77 | 1.93 | 62.71 | 5.54 | 100.00 |
| **Mean** | **23.33** | **1.16** | **0.88** | **6.24** | **1.35** | **60.95** | **6.09** | **100.00** |
| **Std. deviation** | 1.85 | 0.48 | 0.18 | 1.06 | 0.48 | 3.27 | 1.02 | |
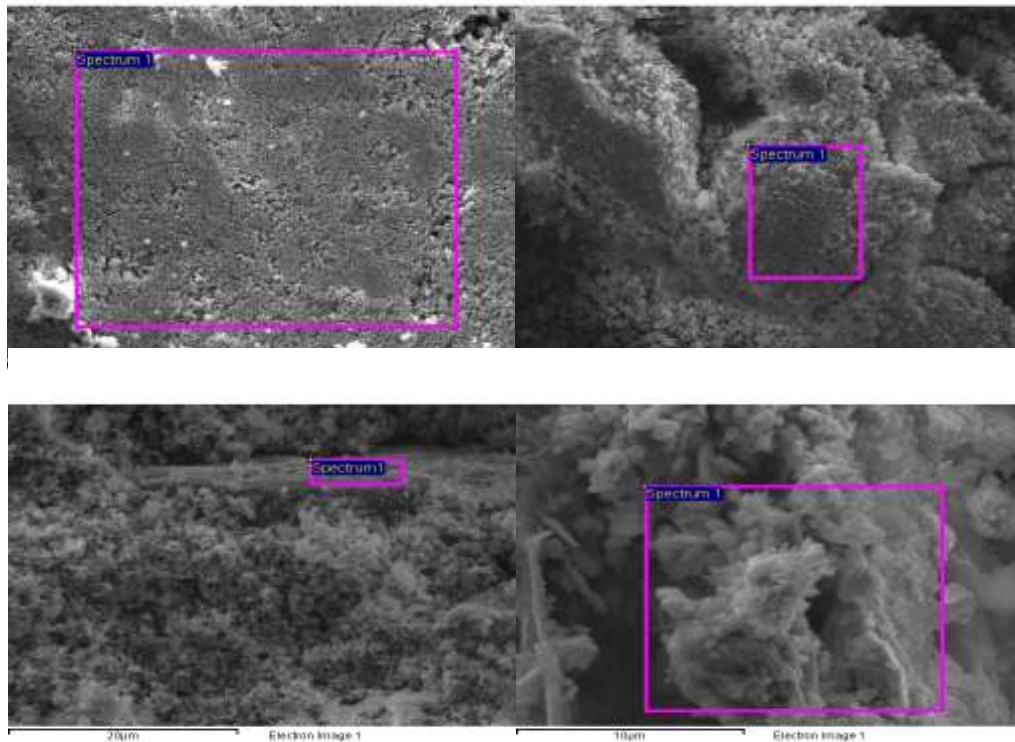
**Figure 4.4: Illustrations of scanning method for BOS sludge samples during EDS analysis.**

## 4.4 Iron and zinc analysis after magnetic separation

Magnetic separation is based on a three-way competition between magnetic forces, other external forces such as gravitational or inertial forces, and inter-particle attractive and repulsive forces. The combination of these forces determines the outcome of any given magnetic separation and is much affected by the nature of the feed such as size distribution, magnetic susceptibility and other physical and chemical characteristics. In this study magnetic separation trials carried out include:

➤ Ferromagnetic Fraction [0.04Tesla] (Low intensity magnetic separation)

➤ Paramagnetic Fraction [1Tesla] (High intensity magnetic separation)

➤ Diamagnetic Fraction

Magnetic separation has been conducted in order to separate non-magnetic metals such as zinc in the BOS sludge by exploiting the differences in the respective magnetic properties. The separation was carried out using a magnachute and wet high intensity magnetic separator. All samples were dried in an oven (80°C, air temperature) in the laboratory over a two day period, the resultant residue samples were sent for chemical analysis at Guardian Laboratories [Midlands] Limited and compared to the data obtained by EDS analysis at Birmingham University mineralogy laboratories.

**Table 4.2: Comparison of EDS analysis and wet chemical analysis showing iron and zinc fractions by magnetic separation.**

| Samples | Zn %w/w | Fe (Total) %w/w |
|---|---|---|
| **Diamagnetic BOS fraction[2]** | 3.45 | 49.27 |
| **Diamagnetic BOS fraction[1]** | 1.35 | 17.59 |
| **paramagnetic BOS fraction[2]** | 4.22 | 56.27 |
| **paramagnetic BOS fraction[1]** | 8.64 | 55.34 |
| **Ferromagnetic BOS fraction[2]** | 4.11 | 60.34 |
| **Ferromagnetic BOS fraction[1]** | 4.54 | 64.31 |
| **BOS sludge feed fraction[2]** | 3.75 | 57.00 |
| **BOS sludge feed fraction[1]** | 5.37 | 63.47 |

*[1] Bham Laboratory analysis [2] Guardian laboratories analysis.*

As shown in Table 4.2, comparison of the EDS and wet chemical analysis data shows some differences. This is to be expected as the chemical analysis takes a bulk sample (2-5 grams) for dissolution whilst the EDS scans single particles. It appears that Fe is slightly concentrated in the magnetic fractions and zinc remains at high levels relatively in all fractions. Despite zinc being attracted more towards paramagnetic fraction, the trend show that the zinc particles are dispersed, distributed and bonded within other magnetic elements in the samples which make it complex for any physical separation method to be successful. The zinc seems to follow iron and is lower in non-magnetic fraction and the results also reveal that zinc is not present as discrete ZnO phase and

possibly zinc vapour as a surface coating on all particles in BOS sludge is occurring, therefore the possibility of separating it via mineral processing technology is remote. The zinc content in the non-magnetic via chemical analysis is 3.45% which is too high for recycling through the blast furnace.

Froth flotation method has been investigated in this study on a small laboratory scale for the recovery of zinc particles present in the BOS sludge samples. It was expected that the zinc phase report to the froth phase rather than in the non-floated fraction. Chemical analysis of the froth phase indicated low iron content but no significant change in zinc level. This indicates that the Ca/Si particles are being floated by the Zn and Fe are closely associated and not liberated. The results of the flotation cell studies are shown in Table 4.3.

**Table 4.3: EDS analysis of flotation cell studies on iron and zinc fractions.**

| Fractions | iron %w/w | zinc %w/w |
|---|---|---|
| **Non-Floated fraction** | 64.2 | 4.3 |
| **Floated fraction** | 35.8 | 3.1 |

From the results of size classification as presented in Table 4.4, it can be concluded that the values of iron are similar at each size range and zinc values also remain constant throughout. This confirms that the zinc metal is dispersed within the ferrous elements in the BOS sludge samples and evenly distributed across all size ranges of BOS sludge.

**Table 4.4: Chemical analysis showing iron and zinc content obtained by size classification.**

| Fractions | Units | Total Iron | Total Zinc |
|---|---|---|---|
| BOS +38μm | % w/w | 64.9 | 4.0 |
| +38μm,-53μm | % w/w | 65.4 | 4.1 |
| +53μm,-106 μm | % w/w | 66.3 | 3.9 |
| +106μm,-180 μm | % w/w | 67.0 | 4.0 |
| BOS+180μm | % w/w | 65.8 | 4.1 |

## 4.5 X–Ray Fluorescence analysis

X–Ray fluorescence (XRF) is the emission of characteristic "secondary" (or fluorescent) X– Rays from a material that has been excited by bombarding with high-energy X– Rays or gamma rays. When primary X–Rays from an X − Ray tube or a radioactive source strikes a sample, the X–Ray can either be absorbed by the atom or scattered through the material.

The process in which an X–Ray is absorbed by the atom by transferring all of its energy to an innermost electron is called the "photoelectric effect." During this process, if the primary X–Ray had sufficient energy, electrons are ejected from the inner shells, creating vacancies. These vacancies present an unstable condition for the atom. As the atom returns to its stable condition, electrons from the outer shells are transferred to the inner shells and in the process give off a characteristic X–Ray whose energy is the difference between the two binding energies of the corresponding shells. Because each element has a unique set of energy levels, each element produces X–Rays at a unique set of energies, allowing one to non-destructively measure the elemental composition of a sample.

The results of chemical analysis performed using XRF are presented in Table 4.5. The predominant exchangeable cations for the BOS sludge were found to be $Fe^{2+}$, $Ca^{2+}$, $Zn^{2+}$, $Mn^{2+}$ and this is in agreement with the results obtained using EDS analysis.

Chemical analysis and reviewed studies in Chapter 2 also report that major phases in BOS samples are iron oxides and high quantities of lime (CaO).

XRF analysis reveals that the sample used in this research is enriched with calcium and iron. It is evident from the analysis as shown in Table 4.5 that the iron is mostly present in divalent form due to the reduction during the reactions occurring in the process. Due to very high iron and appreciable amount of CaO, BOS sludge is a good raw material for recycling to iron and steel units however, this is much dependent on zinc removal from the BOS sludge before considering feasible recycling options.

**Table 4.5: Typical XRF chemical analysis of BOS sludge slurry obtained from Port Talbot Tata Steel Plant; BOS unit.**

| Chemical composition | Weight (%) |
|---|---|
| FeO | 23.95 |
| $SiO_2$ | 2.60 |
| $Al_2O_3$ | 1.62 |
| $H_2O$ | 12.9 |
| MnO | 1.41 |
| CaO | 13.11 |
| MgO | 1.7 |
| Zn | 3.1 |
| Pb | 0.08 |
| C | 2.08 |
| Metallic Fe | 20.3 |
| Fe (Total) | 49.43 |

The Zn, Fe, CaO and other phases are distributed in all size fractions. Hence separation of zinc and iron by simple physical separation methods is not possible. However more detailed and continuous experimental work needs to be undertaken under different separation methods in order to establish a much greater understanding of the elemental analysis of this particular material as it has a very complex structure.

## 4.6 Other particle characteristics

The other characteristics of BOS sludge that were investigated are listed in Table 4.6. The density of BOS sludge was determined using a helium gas pcynometer from Micromeritics, model AccuРус Ц 1340. The density of dry BOS sludge was calculated to be 4.2693 $g/cm^3$, and the standard deviation was 0.0069 $g/cm^3$.

**Table 4.6: Physical properties of BOS sludge used in this study, compared with other adsorbents.**

| Physical properties | This Study | Motsi et al., 2010 | Gaikwad., et al 2009 | Das et al., 2006 | Manchisi et al., 2013 |
|---|---|---|---|---|---|
| Sorbents | BOS sludge | Natural zeolite | Anionic exchange resin | Blast furnace flue dust | Granulated Blast furnace slag |
| Surface area; $m^2g^{-1}$ | 16.95 | 15.879 | --- | --- | 0.769 |
| Porosity (%) | 74.2548 | 47.63 | --- | 45.17 | 54.5 |
| Exchange capacity; meq $ml^{-1}$ | --- | --- | 1.10 | --- | --- |
| Density; $g/cm^3$ | 4.2693 | 2.2751 | --- | 1.42 | 2.89 |
| Moisture content (%) | 19.21 | 9.41 | 40.0 | --- | --- |
| Specific gravity | --- | --- | --- | 2.59 | --- |
| Average pore dia. (μm) | 1.665 | --- | --- | --- | 1.336 |
| Total pore area; $m^2g^{-1}$ | 1.289 | --- | --- | --- | 1.275 |
| Physical form | Black slurry | Buff microporus crystal | Spherical beads | Black fine particles | Coarse particles |

[*]Surface area measurement of BOS, error $\pm0.005m^2g^{-1}$

The porosity of BOS sludge and thermally treated BOS sludge samples were measured using a mercury porosimeter. The porosity of BOS sludge was 74.2 %. Surface area measurements were determined by Nitrogen adsorption fitted to the BET equation (Brunauer, 1943), using the TRISTAR 3000 apparatus from Micromeritics. Moisture content of fresh BOS sludge was also determined by measuring a known mass of BOS

sludge and drying it in an oven at 200ºC. The mass of the sample was continuously monitored and when the mass was constant the samples were removed from the oven and final weight measured. It was found that the moisture content was 19.21 % (w/w).

Recycling of BOS sludge is a challenge as explained in this section, because of complexity encountered in separation of zinc from iron content and also other physical limitations of BOS sludge. As discussed in chapter 2, steelmaking slags appear to have a number of applications in removal of heavy metals from aqueous solutions. Therefore BOS sludge can be considered as an alternative remedy for the treatment of actual AMD and the prominent factors that make BOS sludge an ideal candidate are its neutralising capacity (exchangeable cations) and its favourable adsorptive properties (high surface area and porosity).

# CHAPTER 5

# TREATMENT OF SYNTHETIC AMD WITH BOS SLUDGE AND OTHER ADSORBENTS

## 5.1 Introduction

The first objective of this chapter is to assess whether the BOS sludge is effective in the removal of metals from synthetic AMD solution. Kinetic studies are important because they provide information about the process dynamics, these studies are essential in the design and operation of any adsorption unit in AMD remediation. Kinetic studies also help to evaluate the suitability of any material as a potential adsorbent in removing pollutants from solution (Connors, 1990).

The rate of adsorption process is dependent upon essential factors such as adsorbent particle size, initial metal concentration, initial solution pH, adsorbent dosage, mixing regimes and many others. This study investigates the adsorption efficiency of $Fe^{3+}$, $Cu^{2+}$, $Zn^{2+}$ and $Mn^{2+}$ using BOS sludge as an adsorbent as a function of different factors in treating synthetic acid mine drainage.

Equilibrium studies were also investigated in this chapter, these studies generally involve the determination of the adsorption capacity of a given material, this is important in accessing the potential of any material as an economic and commercially feasible adsorbent. The material is contacted with the solute until equilibrium is achieved. The adsorption equilibrium is a dynamic concept achieved when the rate at which molecules are adsorbed onto a surface is equal to the rate at which they are desorbed (Richardson et al., 2002).

Therefore the main objective of the equilibrium studies was to determine the maximum capacity of BOS sludge towards copper, iron, zinc and manganese removal under the studied conditions. Experimental data were also fitted to conventional adsorption mathematical isotherm models, Freundlich and Langmuir models. These were used to predict the adsorption performance of BOS sludge.

The studies of adsorption equilibrium are important in determining the effectiveness of adsorption; however, it is also important to identify the types of adsorption mechanism in a given system. A number of kinetic models were identified and used to describe the uptake process/mechanism. The models used in this investigation are pseudo first order, pseudo second order, Elovich model, Weber-Morris model and Vermeulen's approximation which were applied to the experimental data in order to analyse the rate limiting steps between single and multi adsorbates systems.

## 5.2 Experimental procedure

The potential of BOS sludge as an adsorbent for the treatment of acid mine drainage was determined using batch experiments under different experimental parameters. For the effect of initial concentration, 16g of BOS samples were contacted with different concentrations of single component solutions ranging from 5 – 140 mg/l. For other experiments, the synthetic AMD was a mixture of all four heavy metals in one solution that is $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ at a concentration of 40 and 100 mg/l for each cation. A comparison was carried out for the removal of each metal ion from synthetic AMD solution (sAMD) by different samples.

All batch adsorption tests for kinetic studies on the adsorption of heavy metal ions were carried out in 200ml of sAMD solution. The mixtures were agitated using the tumbling mill rotating at a speed of 110 rotations per minute. The samples were withdrawn during each experiment at predetermined time intervals and filtered and the filtrate was analysed for heavy metal ions using the AAS.

The percent adsorption (%) was calculated using the equations:

$$\% \, Adsorption = (C_i - C_f) \, / \, C_i \, x \, 100, \qquad\qquad [5.1]$$

Where, $C_i$ and $C_f$ are the concentrations of the metal ions in the initial and final solutions respectively.

The amount of metal adsorbed from aqueous solution at time t, was determined by the following equation:

$$q_t = m_s \, /m = (C_o - C_t)(V/m), \qquad\qquad [5.2]$$

Where $q_e$ is the amount of heavy metal ions adsorbed at any time, mg/g adsorbent; $m_s$ is the mass of metal adsorbed, mg; m is the adsorbent mass, g; $C_o$ is the initial concentration of heavy metal ions, mg/l; $C_t$ is the liquid- phase concentration of heavy

metal ions at any time, mg/l; V is the volume of solution from which adsorption occurs, L.

The equilibrium amount of metal adsorbed from aqueous solution was determined by the following equation:

$$q_e = m_s/m = (C_o - C_e)(V/m), \qquad\qquad [5.3]$$

Where $q_e$ is the amount of heavy metal ions adsorbed at equilibrium, mg/g adsorbent; $m_s$ is the mass of metal adsorbed, mg; m is the adsorbent mass, g; $C_o$ is the initial concentration of heavy metal ions, mg/l; $C_e$ is the liquid- phase concentration of heavy metal ions at equilibrium, mg/l; V is the volume of solution from which adsorption occurs, L.

The distribution coefficient/ratio can also be calculated as follows:

$$K_d = q_e/C_e \ (ml/g) \qquad\qquad [5.4]$$

The percent adsorption and $K_d$ are related as follows:

$$\% \ Adsorption = 100K_d / K_d + V/m \qquad\qquad [5.5]$$

Where, V is the volume of the solution (ml) and m is the mass of the adsorbent (g). The distribution coefficient is important because it implicitly indicates the selectivity, capacity and affinity of an ion for ion exchange.

## 5.3 Results and discussion

### 5.3.1 Factors that affect the rate of metal adsorption

There are a number of parameters that affect the rate of adsorption. These include adsorbent dosage (grams/litre), adsorbent particle size and surface area, initial solution pH and metal concentration, solution temperature, different mixing regimes and the presence of competing cations.

#### 5.3.1.1 Effect of initial metal concentration on metal recovery

The effect of initial concentration was investigated by contacting 16g of BOS sample with different concentrations of single component solutions ranging from 5 − 140 mg/l as illustrated in Table 5.1. An increase in metal concentration of the solution generally results in an increase in the amount of heavy metals adsorbed (q (mg/g)), See Figure 5.1.
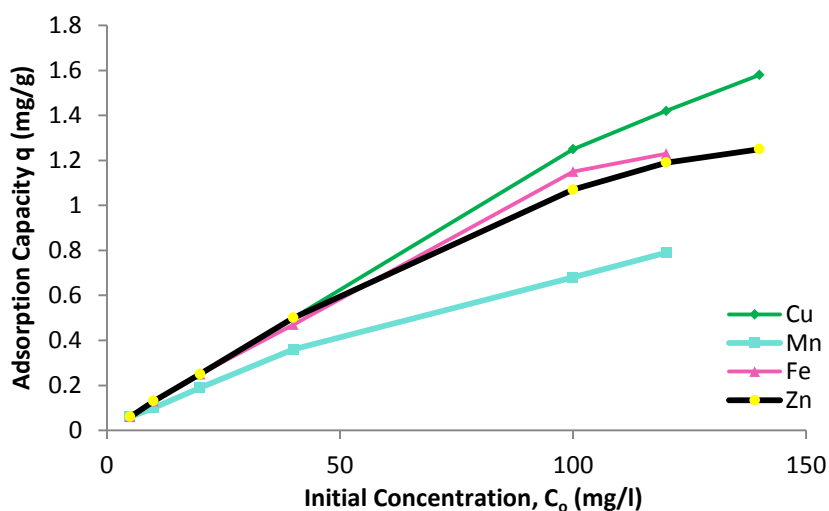


**Figure 5.1: Comparison of Adsorption capacities of $Cu^{2+}$, $Mn^{2+}$, $Fe^{3+}$ and $Zn^{2+}$ onto 16g of BOS: 200ml single component solutions**

The results in Table 5.1 show that the amount of heavy metals adsorbed by BOS at equilibrium is dependent upon the initial metal concentration. The increase in the amount of metal adsorbed as initial solution concentration increases is due to an increase in the concentration driving force between the reactants. Table 5.1 also reveals

that an increase in initial concentration not only results in an increase in the amount adsorbed (qe) but a decrease in the efficiency of BOS for the removal of heavy metal from solutions.

**Table 5.1: Effect of initial solution concentration on the adsorption capacity of BOS sludge; 200ml solution; particle size: +1mm,-1.4mm; total contact time: 180 minutes.**

| Heavy metals | Initial Concentration, $C_o$ (mg/l) | Percentage Adsorbed (%) | Amount Adsorbed, qe (mg/g) | Distribution Coefficient ratio, $K_d$ (ml/g) |
|---|---|---|---|---|
| **Copper** | 5 | 100.00 | 0.06 | - |
| | 10 | 100.00 | 0.13 | - |
| | 20 | 100.00 | 0.25 | - |
| | 40 | 100.00 | 0.50 | - |
| | 100 | 99.74 | 1.25 | 4.81 |
| | 120 | 94.36 | 1.42 | 0.21 |
| | 140 | 90.55 | 1.58 | 0.12 |
| **Manganese** | 5 | 89.44 | 0.06 | 0.11 |
| | 10 | 80.65 | 0.10 | 0.05 |
| | 20 | 77.13 | 0.19 | 0.04 |
| | 40 | 72.54 | 0.36 | 0.03 |
| | 100 | 54.21 | 0.68 | 0.01 |
| | 120 | 52.67 | 0.79 | 0.01 |
| **Iron** | 5 | 100 | 0.06 | - |
| | 10 | 100 | 0.13 | - |
| | 20 | 100 | 0.25 | - |
| | 40 | 93.60 | 0.47 | 0.18 |
| | 100 | 91.98 | 1.15 | 0.14 |
| | 120 | 82.00 | 1.23 | 0.06 |
| **Zinc** | 5 | 100.00 | 0.06 | - |
| | 10 | 100.00 | 0.13 | - |
| | 20 | 100.00 | 0.25 | - |
| | 40 | 100.00 | 0.50 | - |
| | 100 | 85.91 | 1.07 | 0.08 |
| | 120 | 79.73 | 1.19 | 0.05 |
| | 140 | 71.68 | 1.25 | 0.03 |

Hence the BOS becomes an inefficient sorbent at higher concentrations, the reason being at low concentrations the ratio of surface active sites to total metal ions in the solution is high and thus more metal ions can interact with BOS particles and thus being removed from the solution. However at higher concentrations the BOS can easily become saturated and hence a decrease in the amount adsorbed is exhibited.

This can be observed by the general decreasing trend in the percentage adsorption of the four heavy metals, See Figure 5.2. This is in agreement with other researcher's studies on the effect of initial concentration on the uptake of heavy metals by different inorganic adsorbents (Motsi et al., 2010; Sprynskky et al., 2006; Manchisi et al., 2013).
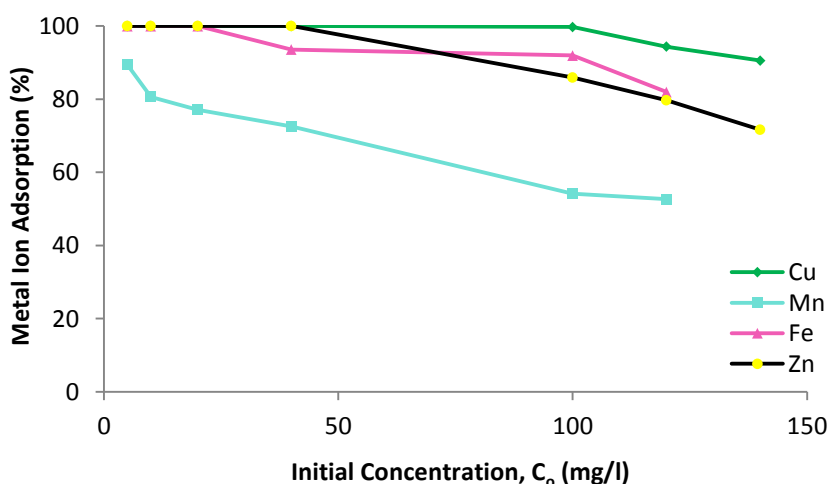


**Figure 5.2: Comparison of the adsorption of heavy metal ions from single component solutions onto 16g of BOS: 200ml single component solutions.**

The distribution coefficient, $K_d$, can be used as a measure of the selectivity, capacity and affinity of an ion for ion exchange with the BOS. If the distribution coefficient of an ion is large then that indicates that more of that ion is adsorbed from solution by BOS. An example of this is shown in Table 5.2 in which the adsorption of the cations by BOS forms the following order $Cu^{2+}>Fe^{3+}>Zn^{2+}>Mn^{2+}$.

**Table 5.2: Distribution coefficients of $Cu^{2+}$, $Mn^{2+}$, $Zn^{2+}$ and $Fe^{3+}$ onto 16g of BOS in 200ml of single component solution at 120 mg/l.**

| Heavy metal ions | Distribution coefficient $(K_d)$ ml/g |
|---|---|
| $Cu^{2+}$ | 0.21 |
| $Mn^{2+}$ | 0.01 |
| $Zn^{2+}$ | 0.05 |
| $Fe^{3+}$ | 0.06 |

## 5.3.1.1.1 Adsorption isotherms

Adsorbent capacity and degree of affinity are determined by fitting experimental data to the Langmuir and Freundlich adsorption isotherms. There are several isotherm equations for analysing experimental adsorption equilibrium parameters. Adsorption isotherms also known as equilibrium data are the fundamental requirements for the design of adsorption systems, the most common being Langmuir and Freundlich models. The adsorption of heavy metals from solution by BOS was fitted to both the Langmuir and Freundlich isotherm models.

The Langmuir isotherm is a theoretical isotherm developed in 1916. It is an empirical isotherm derived from a proposed kinetic mechanism. It is based on the following assumptions (Richardson et al., 2002; Langmuir et al., 1918):

➤ The surface of the adsorbent is uniform, that is, all the adsorption sites are equal;
➤ Adsorbed molecules do not interact;
➤ All adsorption occurs through the same mechanism and the energy of adsorption is the same all over the adsorbent surface;
➤ At the maximum adsorption, only a monolayer is formed: molecules of adsorbate do not deposit on other, already adsorbed, molecules of adsorbate, only on the free surface of the adsorbent.

A basic assumption of the Langmuir theory is that sorption takes place at specific homogenous sites within the adsorbent. It is then assumed that once a metal occupies a site, no further adsorption can take place at that site. Theoretically, therefore a saturation value is reached beyond which no further sorption can take place. The saturated monolayer curve can be represented by the expression:

$$q_e = q_m \, b_L \, C_e \, / \, 1 + b_L \, C_e \qquad\qquad [5.6]$$

A well know linear form of the Langmuir equation can be expressed as:

$$C_e / q_e = C_e / q_m + 1/q_m b_L \qquad\qquad [5.7]$$

Where,

$q_e$ is the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg/g),

$C_e$ is the equilibrium concentration of the adsorbate (mg/l),

$q_m$ is related to the maximum adsorption capacity (mg/g),

$b_L$ is the Langmuir adsorption coefficient, this constant is related to energy of adsorption (L/mg).

There are a vast number of researchers who have used the Langmuir and Freundlich adsorption isotherm models to establish the most appropriate correlation for the equilibrium curves for the removal of heavy metals from aqueous solution using different inorganic adsorbents, (Kim et al., 2008; Motsi et al., 2010; Sprynskyy et al., 2006; Erdem et al., 2004; Lopez et al., 1995; Lopez-Delgado et al., 1998).

The effect of isotherm shape has been discussed with a view to predicting whether an adsorption system is favourable or unfavourable (Weber and Chakravorti, 1974). A dimensionless separation factor has been proposed (Hall et al., 1966), $R_L$, as an essential feature of the Langmuir isotherm model and is defined as:

$$R_L = 1/(1+ b_L.C_{ref})$$ [5.8]

Where,

$C_{ref}$ is the reference fluid-phase concentration of adsorbate (mg/l) and $b_L$ is the Langmuir constant. For a single adsorption system, $C_{ref}$ is usually the highest fluid-phase concentration encountered. Value of $R_L$ indicates the type of adsorption accordingly as shown in Table 5.3.

**Table 5.3: Type of isotherm according to the value of** $R_L$ (*Source: Zawani et al., 2009*)

| Value of $R_L$ | Type of Isotherm |
|---|---|
| $0 < R_L < 1$ | Favourable |
| $R_L > 1$ | Unfavourable |
| $R_L = 1$ | Linear |
| $R_L = 0$ | Irreversible |

The Freundlich isotherm is commonly used to describe adsorption characteristics for a heterogeneous surface. This model assumes that as the adsorbate concentration increases, the concentration of adsorbate on the adsorbent surface also increases and correspondingly, the sorption energy exponentially decreases on the completion of the sorption centres of the adsorbent and derived empirically in 1912 (Metcalf and Eddy, 2003), the Freundlich isotherm can be expressed as:

$$q_e = K_F C_e^{(1/n)}$$ [5.9]

Where, $q_e$ is the amount of solute adsorbed per unit mass of adsorbent at equilibrium (mg/g) and $C_e$ is the equilibrium concentration of the adsorbate (mg/l),

$K_F$ and n (1/n= $n_F$) are empirical Freundlich constants that are dependent on experimental conditions. $K_F$ is the constant related to overall adsorption capacity (mg/g) and 1/n is the constant related to surface heterogeneity (dimensionless). The linear form of the Freundlich was used to find the constants:

$$\text{Log } q = \log K_F + n_F \log C_e \qquad\qquad [5.10]$$

Freundlich isotherm constant $n_F$ indicates the heterogeneity factor. In the literature, $n_F$ values lower than 1 indicates good adsorption implying a material with relatively heterogeneous binding sites (Papageorgiou et al., 2006). BOS can be a heterogeneous adsorbent due to its porous nature. The adsorption of heavy metals from solution by BOS was fitted to both the Langmuir and Freundlich isotherm models, as shown Table 5.4.

**Table 5.4: Langmuir and Freundlich Adsorption Isotherm model parameters for heavy metal ion adsorption from solution by BOS.**

| Heavy metals | $Cu^{+2}$ | $Fe^{+3}$ | $Zn^{+2}$ | $Mn^{+2}$ |
|---|---|---|---|---|
| **Langmuir Adsorption Isotherm (Parameters)** | | | | |
| $b_L$ (L/mg) | 3.19 | 0.231 | 0.245 | 0.066 |
| $q_m$ (mg/g) | 1.588 | 1.507 | 1.385 | 0.953 |
| $R^2$ | 0.9958 | 0.9726 | 1.0 | 0.9693 |
| $R_L$ | 0.002 | 0.035 | 0.028 | 0.112 |

| Heavy metals | $Cu^{+2}$ | $Fe^{+3}$ | $Zn^{+2}$ | $Mn^{+2}$ |
|---|---|---|---|---|
| **Freundlich Adsorption Isotherm (Parameters)** | | | | |
| $K_F$ (mg/g) | 0.0975 | 0.0334 | 0.007 | 0.0122 |
| $n_F$ | 0.4593 | 0.5916 | 0.9899 | 0.1174 |
| $R^2$ | 0.6023 | 0.6153 | 0.92 | 0.9615 |

The Langmuir model gave a much better fit of the experimental results compared to the Freundlich adsorption isotherm, as shown in Figure 5.3. The $R_L$ values which are important characteristics of the Langmuir isotherms indicate that adsorption systems are favourable ($0 < R_L < 1$) for all heavy metal ions and hence the choice of Langmuir model is confirmed, See Table 5.4. According to the Langmuir adsorption model, the values of $q_m$ follow the sequence: $Cu^{2+} > Fe^{3+} > Zn^{2+} > Mn^{2+}$.

The Freundlich adsorption isotherm is usually used to fit experimental data over a wide range of concentrations. This isotherm gives an expression of encompassing the surface heterogeneity and the exponential distribution of active sites and their energies. As discussed before, the Freundlich isotherm constant $n_F$ indicates the heterogeneity factor, Table 5.4 shows that $n_F$ values are lower than 1, however this model was not effective in describing the equilibrium data.

The difference in adsorption capacity of the BOS for the heavy metal ions may be due to a number of factors which include hydration diameters, hydration enthalpies and solubility of the cations. The hydration radii of the cations are: $rHZn^{2+} = 4.30$Å, $rHFe^{3+} = 4.57$Å, $rHCu^{2+} = 4.19$Å and $rHMn^{2+} = 4.38$Å (Nightingale, 1959). The smallest cations should ideally be adsorbed faster and in larger amounts compared to the larger cations. Moreover, adsorption should be described using hydration enthalpy, which is the energy that permits the detachment of water molecules from cations and thus reflects the ease with which the cation interacts with the adsorbent. Therefore, the more a cation is hydrated the stronger its hydration enthalpy and the less it can interact with the adsorbent (Amarasinghe and Williams, 2007). This is a very important factor as BOS contains a certain amount of moisture content and thus this can have an effect on overall adsorption capacity of heavy metal ions.

The hydration energies of the cations are: -2010, -1955, -1760 and -4265 kJmol-1 for $Cu^{2+}$, $Zn^{2+}$, $Mn^{2+}$ and $Fe^{3+}$ respectively (Marcus, 1991; Nightingale, 1959). According to the hydration diameters the order of adsorption should be $Cu^{2+} > Zn^{2+} > Mn^{2+} > Fe^{3+}$ and according to the hydration enthalpies the order should be $Mn^{2+} > Zn^{2+} > Cu^{2+} > Fe^{3+}$.

95
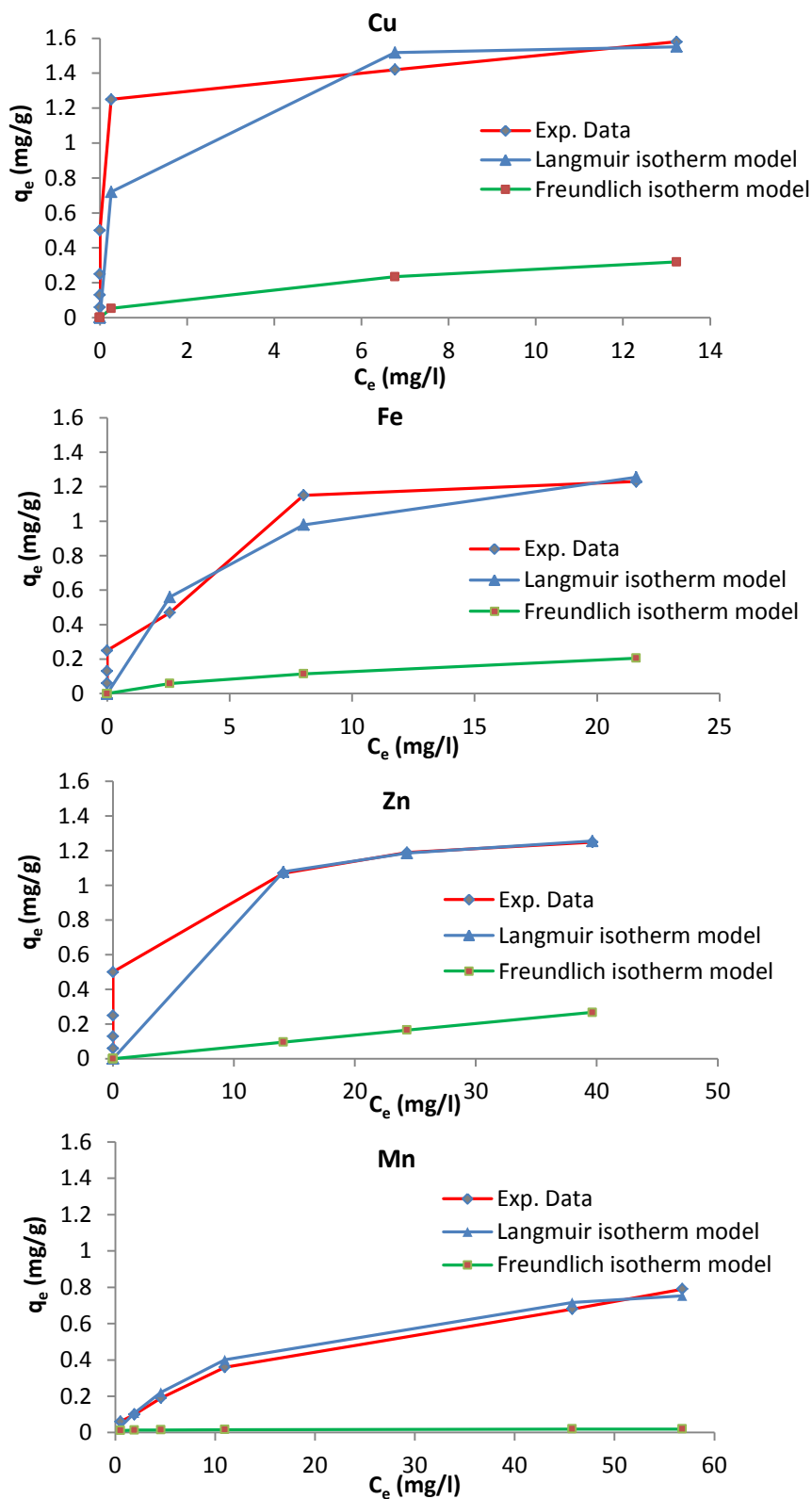
**Figure 5.3: Adsorption Isotherms of heavy metal ions described by Langmuir and Freundlich models.**

The series according to the hydration diameters and enthalpy are different from the experimentally obtained series which are $Cu^{2+}>Fe^{3+}>Zn^{2+}>Mn^{2+}$. The differences in the series are the crucial indicators, as they reveal adsorption is not necessarily the only mechanism involved responsible for the removal of heavy metal ions from solution; precipitation of the metal hydroxides, ion exchange due to exchangeable cations ($Ca^{2+}$, $Mg^{2+}$) on BOS surfaces can have a substantial and major impact in the treatment process by BOS samples.

## 5.3.1.2 Effect of competing cations on metal recovery

In practice, industrial wastewater or particularly acid mine drainage contain a mixture of many different heavy metal ions. These metal ions could have tendency to affect the efficiency of an adsorbent in treating the acidic solutions via competing for active sites in the adsorbent. Experiments were carried out to investigate the influence of the presence of competing cations on the individual adsorption of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ from a solution containing a mixture of all four metal ions, by BOS sample. For this effect, 16 g of BOS was mixed with 200 ml of single and multi-component solutions for 180 minutes with two different initial metal concentrations (40 and 100mg/l). Figure 5.4 compares adsorption of each heavy metal ion from both single and multi-component solutions.

Figure 5.4 shows that the adsorption of $Zn^{2+}$ and $Mn^{2+}$ reduced in multi-component solution (mixed solution). Adsorption of $Cu^{2+}$ was not affected by the presence of competing ions, this may be because one of the mechanisms responsible for removal of $Cu^{2+}$ cations from solution is thought to be precipitation (Dimitrova et al., 1996; Dimitrova and Mehandgiev, 1998, 2000; Feng et al., 2004; Kim et al., 2008). The same effect of precipitation of $Fe^{3+}$ was also observed by Motsi et al. (2010) and Moreno et al. (2001) when zeolites as sorbents were used for AMD treatment.

Interestingly, the adsorption of $Fe^{3+}$ was increased in multi-component solutions compared to their single component solutions at both initial metal concentrations (40 and 100 mg/l); an increase of 5.2% was obtained at 100 mg/l. This indicates that different adsorption mechanisms may be involved in the adsorption of each cation from solution. This effect is analysed under kinetic modelling later in this chapter.
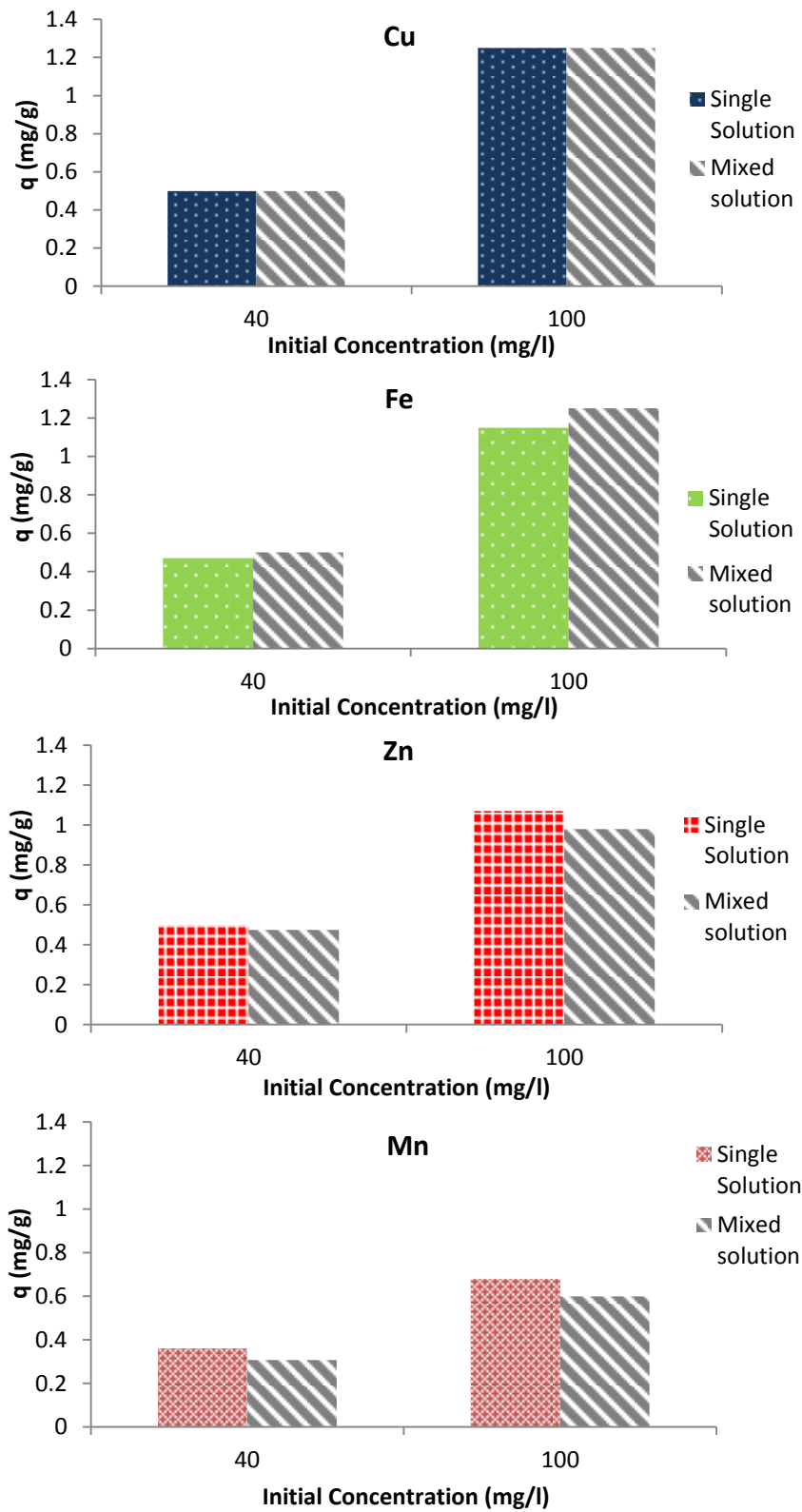
**Figure 5.4: Comparison of the adsorption capacity of BOS for copper, iron, zinc and manganese from single and multi-component solutions.**

## 5.3.1.3 Effect of adsorbent dosage level on adsorption

Batch experiments using synthetic AMD were carried out for this purpose. A series of kinetic experiments at different adsorbent masses of BOS sample (4, 8, 16, 20 and 24g) were performed using fixed initial multi-metal concentrations for the respective cation, as shown in Table 5.5. These experiments were carried out in duplicate and the concentrations given are average values. The percent standard deviation between two duplicate samples when analysing for iron, copper, manganese and zinc was ±1.2%, 1.1%, 1.1% and 1.5% respectively. For comparison, the same batch experiments using synthetic AMD were also conducted using ground granulated blast furnace slag (GGBS) samples, an alternative solvent for AMD, as presented in Table 5.6.

**Table 5.5: Effect of BOS mass on the removal of heavy metals from synthetic AMD solution ($C_o$: 40 mg/l) at pH 1.48, $20^o$C.**

| Heavy metal ions | Adsorbent Mass (g) | Percentage Adsorption (%) | Amount Adsorbed, $q_e$ (mg/g) | Residual liquid-phase at equilibrium, $C_e$ (mg/l) |
|---|---|---|---|---|
| Copper | 4 | 51.23 | 1.03 | 19.51 |
| | 8 | 100 | 1.0 | 0 |
| | 16 | 100 | 0.5 | 0 |
| | 20 | 100 | 0.4 | 0 |
| | 24 | 100 | 0.333 | 0 |
| Iron | 4 | 44.75 | 0.895 | 22.10 |
| | 8 | 75.00 | 0.75 | 10 |
| | 16 | 100 | 0.50 | 0 |
| | 20 | 100 | 0.40 | 0 |
| | 24 | 100 | 0.333 | 0 |
| Zinc | 4 | 0 | - | - |
| | 8 | 0 | - | - |
| | 16 | 95.03 | 0.475 | 1.99 |
| | 20 | 97.93 | 0.392 | 0.83 |
| | 24 | 99.70 | 0.332 | 0.12 |
| Manganese | 4 | 0 | - | - |
| | 8 | 0 | - | - |
| | 16 | 61.68 | 0.308 | 15.33 |
| | 20 | 66.05 | 0.265 | 13.58 |
| | 24 | 73.15 | 0.244 | 10.74 |

**Table 5.6: Effect of GGBS mass on the removal of heavy metals from synthetic AMD solution ($C_o$: 40 mg/l) at pH 1.48, $20^oC$; particle size: dp<180μm.**

| Heavy metal ions | Adsorbent Mass (g) | Percentage Adsorption (%) | Amount Adsorbed, $q_e$ (mg/g) | Residual liquid-phase at equilibrium, $C_e$ (mg/l) |
|---|---|---|---|---|
| Copper | 4 | 100 | 2.0 | 0 |
| | 8 | 100 | 1.0 | 0 |
| | 16 | 100 | 0.5 | 0 |
| | 24 | 100 | 0.33 | 0 |
| Iron | 4 | 99.50 | 1.99 | 0.2 |
| | 8 | 99.50 | 0.995 | 0.2 |
| | 16 | 98.25 | 0.49 | 0.7 |
| | 24 | 100 | 0.33 | 0 |
| Zinc | 4 | 92.50 | 1.85 | 3.0 |
| | 8 | 98.75 | 0.99 | 0.50 |
| | 16 | 100 | 0.5 | 0 |
| | 24 | 100 | 0.33 | 0 |
| Manganese | 4 | 17.50 | 0.35 | 33.0 |
| | 8 | 46.25 | 0.463 | 21.5 |
| | 16 | 82.50 | 0.413 | 7.0 |
| | 24 | 96.25 | 0.321 | 1.5 |

For both sets of samples (BOS and GGBS), it is evident that an increase in adsorbent mass resulted in an increase in the adsorption of the heavy metals. An increase in adsorption rate is because as adsorbent mass increases more adsorption sites are available per unit mass of adsorbent added. The amount of metal adsorbed per unit mass of BOS at equilibrium is lower. The equilibrium uptake capacity ($q_e$) was found to decrease with an increase in the dosage of the adsorbents, See Figure 5.5.

For BOS sample, in the case of $Cu^{2+}$ and $Fe^{3+}$ adsorption increasing the adsorbent dosage from 8 to 24g and 16 to 24g respectively had no effect on the adsorption rate and this is because the metal ions were adsorbed instantaneously. The plots of the percentage of metal removal from sAMD against time for different adsorbent dosages are also presented in Figure 5.6.
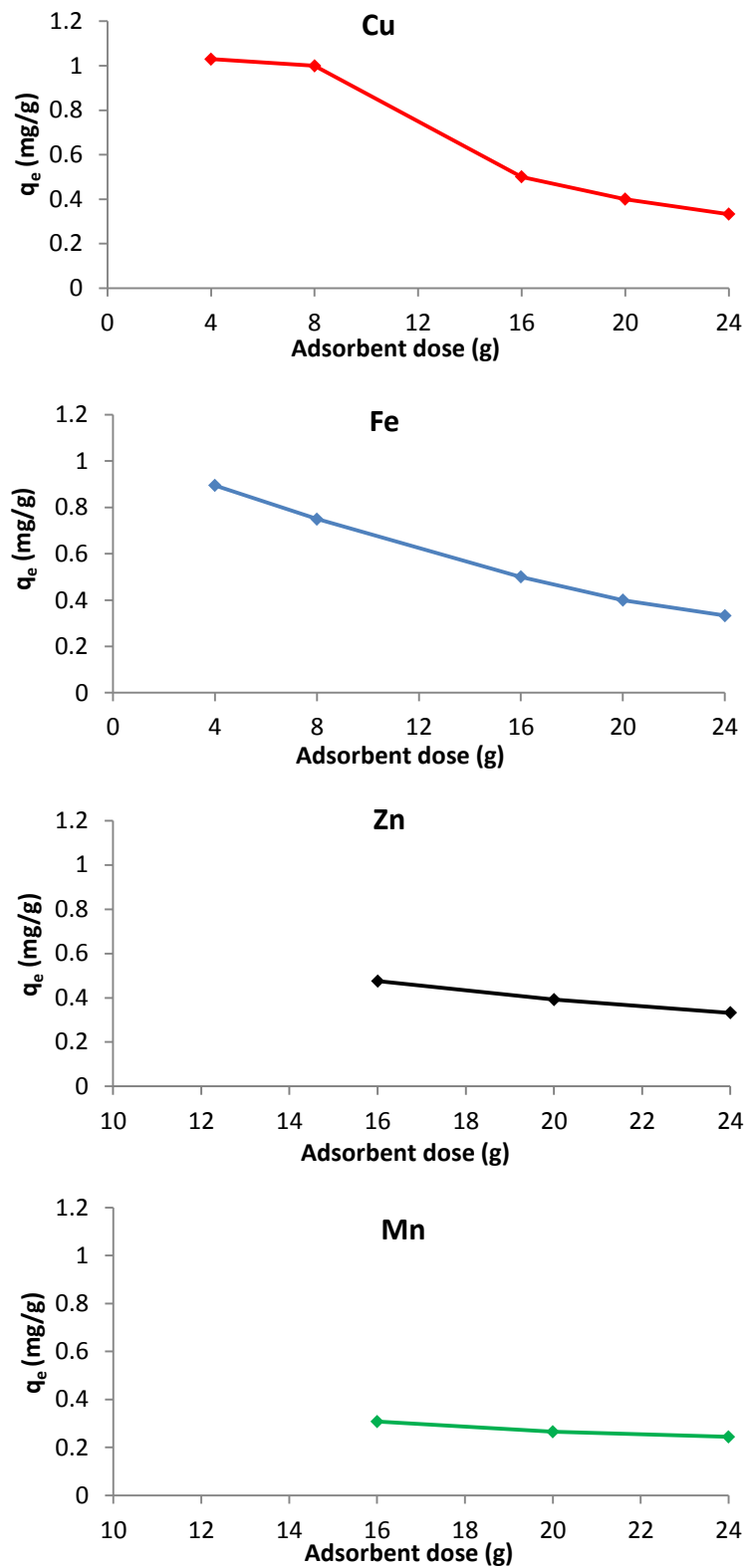
**Figure 5.5: The equilibrium metal uptake capacity ($q_e$) from synthetic AMD (sAMD) solution using different dosages of BOS.**

The final concentrations of heavy metal ions also decrease with an increase in BOS and GGBS dosages; this is because with an increase in mass/dosage there is an introduction of more adsorption sites which adsorb more heavy metal ions from the solution. Although the both samples show extensive potential to be effective adsorbents, it is evident that GGBS shows a greater efficiency of uptake of heavy metals from sAMD solution compared to BOS (See, Table 5.6), particularly in the adsorption of $Mn^{2+}$. The reason for this can be due to the fineness of GGBS particles which ultimately results in larger surface area for adsorption, chemical composition of this particular slag (higher %w/w of $Ca^{2+}$) and also being non-metallic based slag with almost negligible moisture content.

The removal of heavy metal ions from aqueous solution is a complicated process, combination of ion exchange and adsorption and is likely to be accompanied by precipitation of metal hydroxide complexes on active sites of the BOS's surface. Manganese removal from the Wheal Jane chemical precipitation plant has proved problematic. Manganese is a difficult metal to remove from acidic solution, as it exhibits high solubility over a broad pH range (4.5-8) and the chemical oxidation of manganese is kinetically very slow, (Bamforth et al. 2006). Manganese hydrolysis contributes to the acidity of AMD solution (Hallberg and Johnson, 2003).

$$Mn^{2+} + \frac{1}{2} O_2 + H_2O \rightarrow MnO_2 + 2 H^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots 5.11$$

In terms of $Mn^{2+}$ uptake by BOS sample, only 16, 20 and 24g fractions had the capacity to remove $Mn^{2+}$ from solution. The results in Tables 5.5 and 5.6 confirm that the decrease in metal uptake value (mg of metal/g of sample) is essentially due to the splitting effect of concentration gradient between the adsorbate and the adsorbent throughout the reactions. In general, any adsorbent contains considerable amounts of accessory phases that partly dissolve during the reaction, which may explain the sudden increase or decrease in metal concentration and hence the reason the release rate of these elements is controlled by the dissolution of the adsorbent.

The Wheal Jane Mine water maximum consent limit for copper, iron, zinc and manganese in discharge water are 0.08, 5.0, 2.5 and 1.0 mg/l respectively. From the results, it is evident that both BOS and GGBS were able to treat $Cu^{2+}$, $Fe^{3+}$ and $Zn^{2+}$ within the maximum consent limit requirement.

The plots of the percentage of metal removal from sAMD against time for different adsorbent dosages are presented in Figure 5.6. The adsorption of heavy metal ions from sAMD solution onto BOS is a heterogeneous process. The experimental results show a rapid adsorption rate followed by a slower rate or little change in the percentage of removal metal ion over time.

Mass transfer resistance is high for smaller adsorbent dosages. Efficiency of adsorption was high and selective for $Cu^{2+}$, $Fe^{3+}$ and $Zn^{2+}$ but moderate towards $Mn^{2+}$. $Mn^{2+}$ adsorption is low which probably requires longer residence time under these conditions. Within the first 15min, the adsorption sites are available and the cations interact with free adsorption sites across high concentration gradient. Thus higher rate of adsorption is observed for copper, iron and zinc. Manchisi et al., (2013) also found that the efficiency and adsorption rates for $Fe^{2+}$, $Cu^{2+}$, $Mn^{2+}$, $Cd^{2+}$ and $Co^{2+}$ increased with an increase in mass of adsorbent when blast furnace slag was used as a sorbent for similar treatment of synthetic AMD to this study.

From SEM/EDS analysis of BOS sludge and observed high pH values, it is possible that ion exchange process, adsorption and precipitation may be the major mechanisms involved as proposed in several studies (Dimitrova et al., 1996; Dimitrova and Mehandgiev, 2000; Feng et al., 2004; Manchisi et al., 2013; Kim et al., 2008).
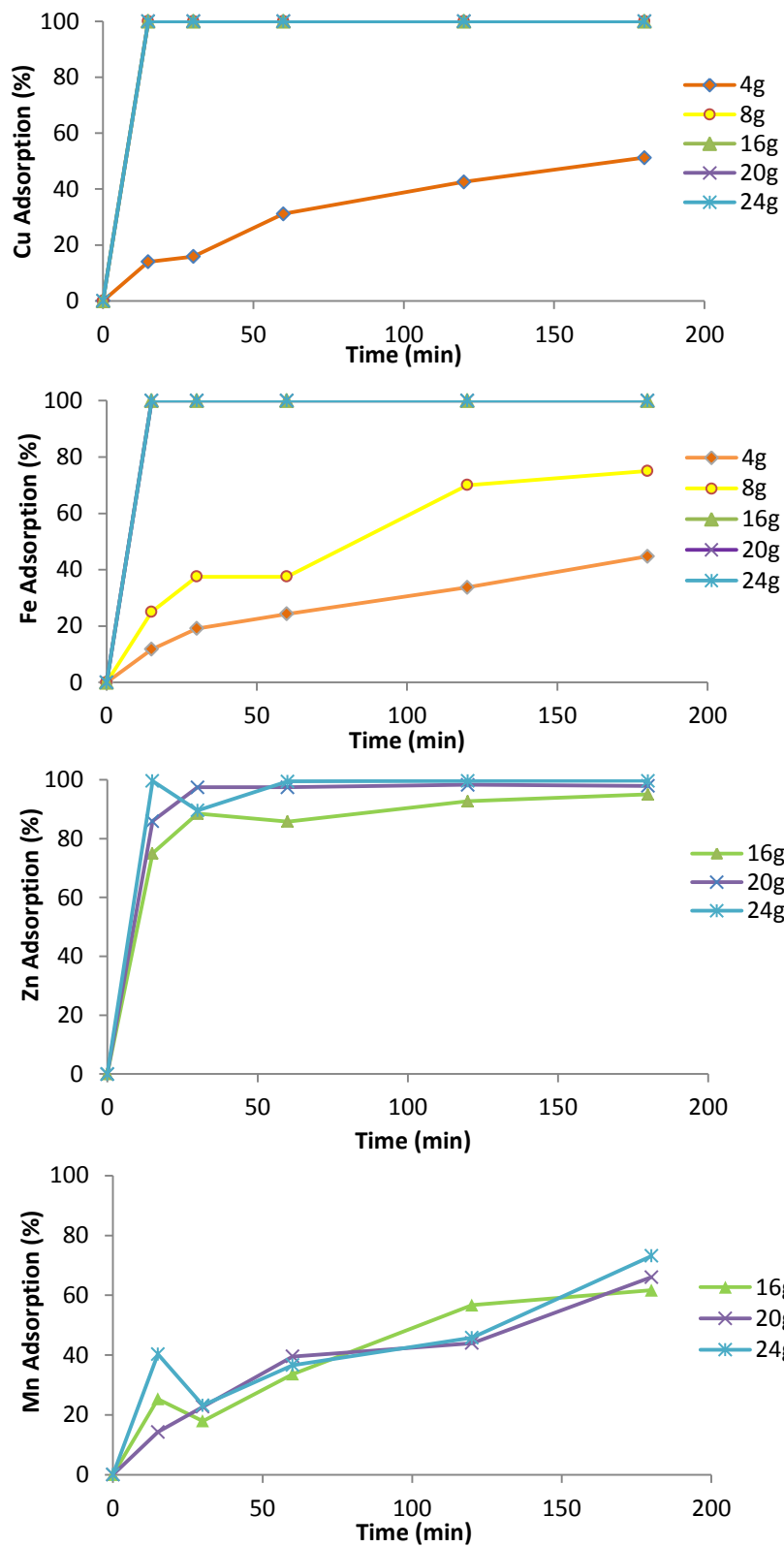
**Figure 5.6: The Effect of BOS mass on the adsorption of copper, iron, zinc and manganese from synthetic solution.**

A high pH promotes adsorption possibly by precipitation and/or ion exchange processes. As discussed in previous chapters steel slags contain quicklime or calcium oxide (CaO). In AMD treatment the calcium oxide disassociates to produce calcium ($Ca^{2+}$) and oxygen ($O^{2-}$) ions. The oxygen ions react with the water in the slag to produce hydroxide (OH-), which is a strong base as reactions show below.

$$CaO \rightarrow Ca^{2+} + O^{2-}$$

5.12

$$O^{2-} + H_2O \rightarrow OH^-$$

5.13

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

5.14

This is in agreement with various researchers including (Kim et al., 2008; Ziemkiewicz and Skousen, 1998; Simmons et al., 2001; Ochola and Moo-Young, 2005; Manchisi et al., 2013, Zhou and Haynes, 2010, Chen et al., 2011) whom have also identified BF/steel slags as a suitable candidate to remediate waters contaminated by acid mine drainage, since such materials proved to have a significant acid neutralising potential that can be exploited to precipitate out a majority of dissolved metals by increasing solution pH.
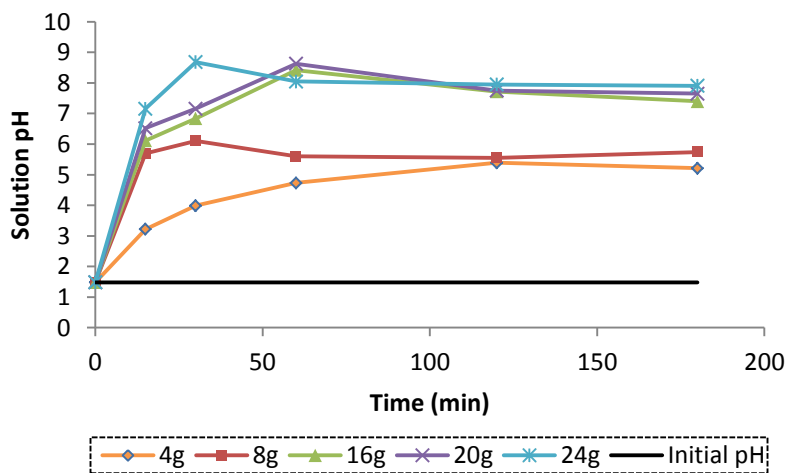


**Figure 5.7: The Effect of BOS mass on suspension pH (200ml solution mixture); particle size +1mm,-1.4mm; pH 1.48 (initial pH).**

The first stage of adsorption could potentially correspond to ion exchange of calcium oxide ($Ca^{2+}$) in the BOS pores and the acidic composition of AMD solution (neutralisation reaction). Zhou and Haynes, (2010) found that the residual alkalinity present in blast furnace and steel slags which have similar elemental composition to BOS sludge (due to hydrolysis of calcium silicates) and red mud (due to the presence of residual NaOH as base) results in them having substantial adsorption capacity for metal cations from waste waters.

As discussed before, the driving force for adsorption is the concentration difference between the bulk solution and the solid-liquid interface. This is initially very high in the first 15 min which results in a higher adsorption rate. However after the initial period slow adsorption is achieved due to slower diffusion of cations and their occupation on active sites onto the BOS surface, thus it can be concluded that saturation point is achieved as the concentration gradient decreases.

The pH of the solution in contact with BOS or other samples used in this study impacts on their ability to remove metals since the acidic solution can influence both the exchanging ions interactions and the structure of samples as these materials are highly alkaline (presence of quicklime). The results indicate that the heavy metal uptake capacity increased considerably as contact time increased (that is tending toward equilibrium) and also it is observed that adsorption capacity increased with an increase in the value of pH for each dosage.

Huifen et al. (2011) discovered that the results for the removal of $Cu^{2+}$ and $Zn^{2+}$ in multi-component wastewater was dependent upon pH when using steel slag, the removal rates of $Zn^{2+}$, $Cu^{2+}$ were 99.24%, 99.1% respectively. In another study under batch experiments with steel slag and synthetic solutions containing of various heavy metals including iron, zinc, aluminium, copper, and lead; 80% removal of aluminium, and over 90% removal of the other metals were achieved (Ochola and Young, 2005).

**5.3.1.4 Effect of particle size on metal adsorption**

The extent and the rate of adsorption is related to the available surface area of the adsorbent, typically the larger the surface area of the adsorbent, greater is the adsorption rate. The surface area of a fine solid adsorbent is usually related to its particle size. The smaller the particle size, the greater is its surface area (Richardson et al., 2002).

Therefore, increasing the external surface area by reducing the adsorbent particle size, results in an increase in the number of available sites for metal uptake (Inglezakis et al., 1999). The effect of particle size on the rate of sorption was investigated using two sieved BOS samples. The samples had the following particle size distribution: +1mm,-1.4mm and +3.35mm,-7.6mm. The use of very fine particles was avoided as it can cause difficulty ( at filtration stage) in solid-liquid batch tests.

The results in Figure 5.8 indicate that decreasing the particle size of BOS provided a higher heavy metal removal rate and efficiencies for $Zn^{2+}$ and $Mn^{2+}$ removal with an increase of 3.8% and 3.3% for $Zn^{2+}$ and $Mn^{2+}$ respectively (99.7% of $Zn^{2+}$ and 73.2% of $Mn^{2+}$) and this is due to an increase in BOS surface area. The initial rates of all metal ions were rapid because of high mass transfer rates based on high concentration gradient of adsorbates across pores in BOS. However as contact time increases there is a decrease in the degree of the effect of particle size on adsorption rates and particle size distribution becomes less significant to removal levels because free adsorption sites and concentration gradient decrease. In the encapsulated method study later in this chapter, the effect of particle size will be investigated further.

Vadapalli et al., (2007) found a similar trend in their work on AMD as the reaction between fly ash and AMD solution was more rapid and more efficient in removing heavy metals (to achieve neutral pH) for the sample containing a higher percentage of fines compared to the standard normal fly ash size range. Manchisi et al., (2013) also found that adsorption rates and capacity increased when a very fine size fraction (dp <45μm) of blast furnace slag was employed in AMD treatment; adsorption was 62% for $Mn^{2+}$ and 100% for $Fe^{2+}$ and $Cu^{2+}$.
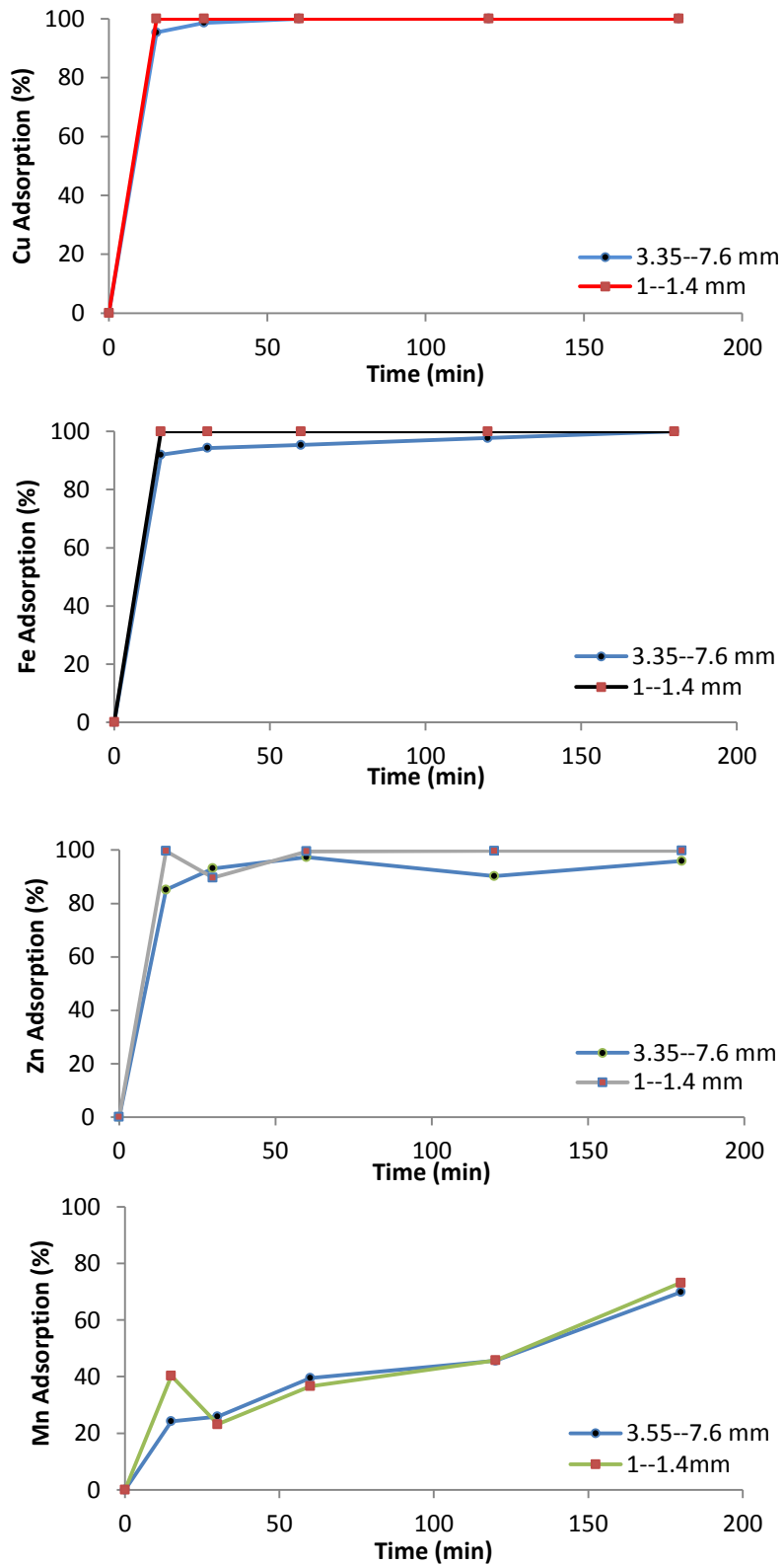
**Figure 5.8: Effect of particle size on the adsorption of copper, iron, zinc and manganese from synthetic solution.**

## 5.3.1.5 Effect of initial solution pH

Adsorption to particle surfaces and hydroxide precipitation are thought to be the principal metal immobilisation mechanisms for AMD remediation. To achieve optimal adsorption it is necessary to increase the pH of the system. Using adsorbents which possess capacity to neutralise acidic water, the pH increase could be achieved instantaneously, without any addition of chemicals such as NaOH, CaOH and $CaCO_3$.

The sorption capacity and reactivity of slags in this case BOS sludge depend on pH in the aqueous solutions (Dimitrova and Mehandgiev, 1998; Yan et al., 1999). The pH level of aqueous solution is an important variable for the adsorption of metal ions on the adsorbents. Solution pH influences both the BOS surface heavy metal binding sites and the chemistry of heavy metal ions in sAMD solution. However few studies have been reported on this effect related to the removal of heavy metal ions from aqueous solutions using steel slag and little is known about the influence of solution pH.

The kinetics of this reaction was investigated by monitoring the pH at three different adsorbent dosages. Synthetic single component solutions of 40mg/l concentration each of $Zn^{2+}$ and $Fe^{3+}$ (these two heavy metal ions were selected as they have two of the highest concentrations in AMD at Wheal Jane Mine) were contacted with BOS samples. The solution pH was varied from their initial value (starting pH) to 3.5 and 4.5. Figures 5.9-5.11 indicate that pH level increases as contact time increases for each adsorbent dosage. The quicklime in BOS dissolves in acidic water to increase pH. The two following equations illustrate these reactions:

$$CaO + H_2O \Rightarrow Ca(OH)_2 \qquad\qquad 5.14$$
$$Ca(OH)_2 \Rightarrow Ca^{2+} + 2OH^- \qquad\qquad 5.15$$
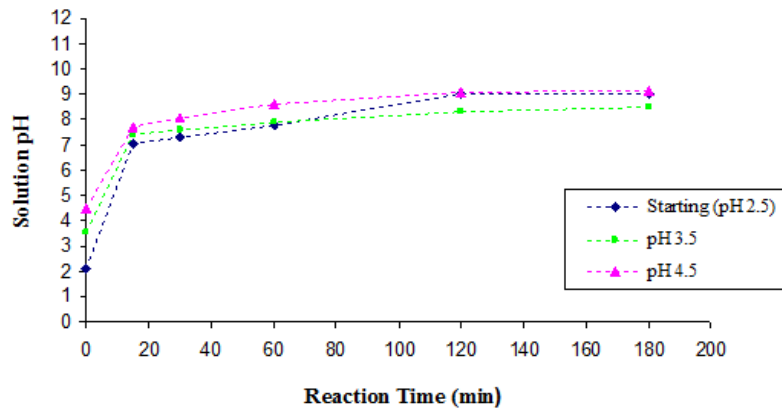
**Figure 5.9: Change in solution pH as adsorption proceeds (200ml single iron component solution; 8g BOS; particle size +1mm,-1.4mm).**
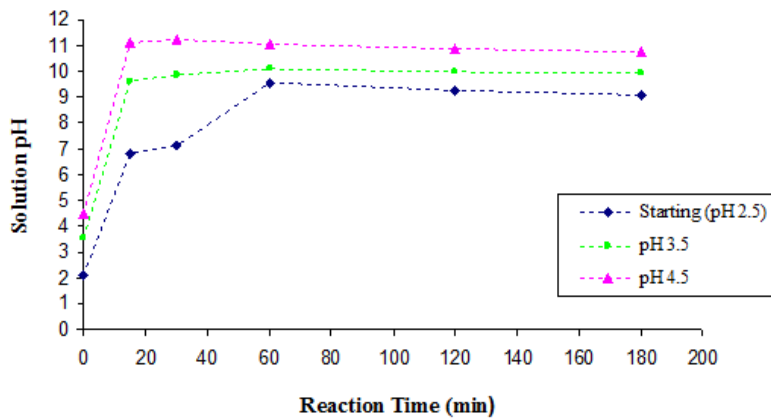


**Figure 5.10: Change in solution pH as adsorption proceeds (200ml single iron component solution; 16g BOS; particle size +1mm,-1.4mm).**



**Figure 5.11: Change in solution pH as adsorption proceeds (200ml single iron component solution; 24g BOS; particle size +1mm,-1.4mm).**

**Table 5.7: Minimum pH values required for complete precipitation of heavy metal ions as hydroxides** *(Source: Brown et al., 2002)*.

| Heavy Metals | Minimum pH |
|:---:|:---:|
| $Cu^{2+}$ | 7.2 |
| $Fe^{3+}$ | 4.3 |
| $Zn^{2+}$ | 8.4 |
| $Mn^{2+}$ | 10.6 |

The increased pH then provides hydroxide ions which combine with the dissolved metals to produce precipitates, as shown in Table 5.7. The following equations show the precipitation reactions with the two selected metals:

$$Fe^{3+} + 3OH^- \Rightarrow Fe(OH)_3 \qquad \text{(complete precipitation at pH 4.3)} \dots\dots\dots\dots\dots\dots 5.16$$

$$Zn^{2+} + 2OH^- \Rightarrow Zn(OH)_2 \qquad \text{(complete precipitation at pH 8.4)} \dots\dots\dots\dots\dots\dots 5.17$$

Metal precipitation processes such as Wheal Jane precipitation plant is operated by controlling pH to a typical set point of 9.5, metals such as iron (Fe), zinc (Zn), and copper (Cu) are precipitated, other metals such as nickel (Ni), manganese (Mn) and cadmium (Cd) require a higher pH, in the range of 10.5 to 11 to effectively precipitate the hydroxides (Aube and Zinck, 1999; Aube et al., 1999). Despite pH effect on precipitation, the effect of initial metal concentration on precipitation must not be excluded.

For adsorption properties of steel slags, researchers reported the removal of heavy metals from wastewaters using slag (Dimitrova and Mehandgiev, 1998). The major removal mechanisms are adsorption and precipitation as following (Dimitrova and Mehandgiev, 2000; Dimitrova et al., 1996):

**Adsorption**

$$>Si-OH \dots H-O-H [Me(OH_2)_3]^{2+} \Longleftrightarrow >Si-OMe + H_3O^+ \qquad \dots\dots\dots\dots\dots\dots 5.18$$

**Precipitation**

$$Me^{2+} + OH^- \leftrightarrow Me(OH)^+ + OH^- \leftrightarrow Me(OH)_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots 5.19$$
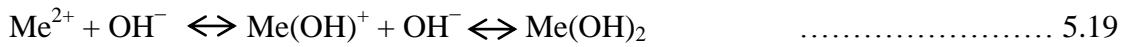
Adsorption could be slow at low pH because heavy metals compete with hydrogen ions below pH 4.0 (Dimitrova and Mehandgiev, 1998). The adsorption of heavy metals in acidic solutions can be described by Eq. (5.18), heavy metals may not precipitate below pH 4.0. The precipitation of heavy metals in neutral and alkaline solutions can be described by Eq. (5.19). However, the relative contribution of two mechanisms to the removal of heavy metals has not been well reported.

While BOS sludge is added to an acidic solution which contains ferric ions, rapid formations of hydroxyl complexes take place. The rate at which these steps evolve depends upon temperature, $Fe^{3+}/OH$ ratio, solution pH, iron concentration, ionic strength and also in this particular case the effect of leaching of cations from BOS into solution. The mechanism by which a soluble entity is transformed into a solid precipitate is very complicated and not well understood (MEND Treatment Committee, 1991). A potential route for iron hydrolysis is given below:

$$2Fe^{3+} + 2H_2O \longrightarrow Fe_2(OH)_2^{4+} + 2H^+ \qquad \ldots\ldots\ldots\ldots\ldots\ldots 5.20$$
Or
$$Fe^{3+} + 2H_2O \longrightarrow FeO.OH + 3H^+ \qquad \ldots\ldots\ldots\ldots\ldots\ldots 5.21$$

For 8g BOS sample on iron adsorption, Figure 5.12 shows that as the solution pH is increased from 2.5 to 4.5, iron uptake by BOS also increases remarkably for the first 15min. From 30min to 120min for all pH values during reactions a non-stable zone is identified which mainly indicates the dissolution of the previously captured iron cations and re-precipitation of $Fe^{3+}$ ions throughout the reaction and this particularly apparent for pH 3.5. The final ion concentrations after 180 min for all pH 2.5, 3.5 and 4.5 were 1.56, 1.40 and 1.0mg/l respectively.
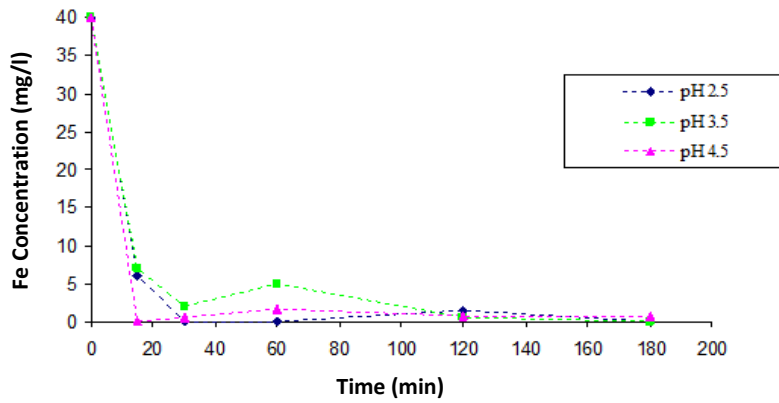
**Figure 5.12: Effect of initial solution pH on the adsorption capacity of BOS (200ml single iron component solution; 8g BOS; particle size +1mm,-1.4mm).**
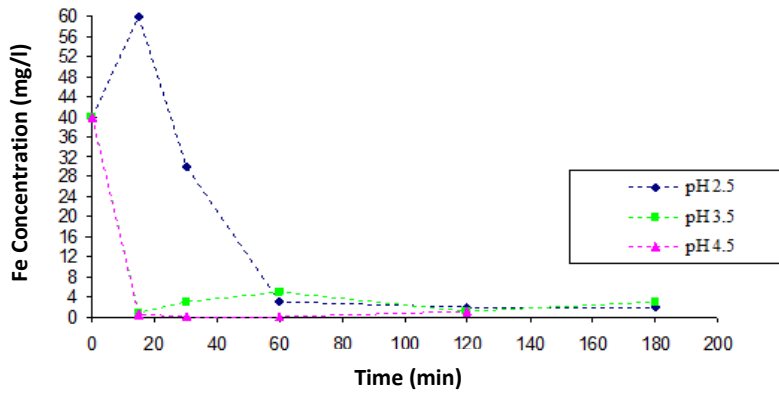


**Figure 5.13: Effect of initial solution pH on the adsorption capacity of BOS (200ml single iron component solution; 16g BOS; particle size +1mm,-1.4mm).**
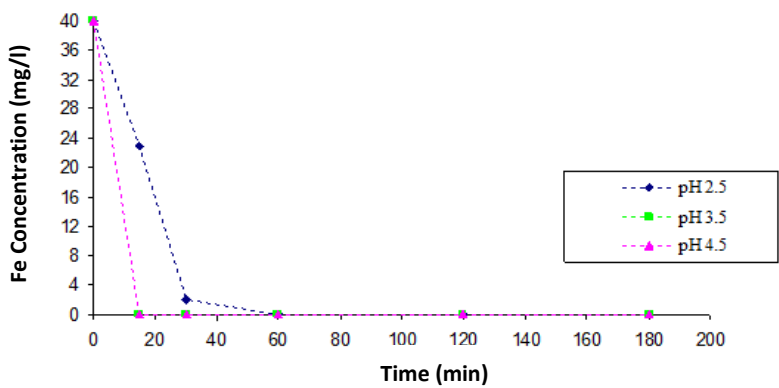


**Figure 5.14: Effect of initial solution pH on the adsorption capacity of BOS (200ml single iron component solution; 24g BOS; particle size +1mm,-1.4mm).**

For 16g BOS sample on iron adsorption, Figure 5.13 exhibits that the initial stage for pH 2.5 for the first 15min corresponds to a high iron leaching from BOS sample into sAMD solution to about 60mg/l, thereafter all the dissolved ions were precipitated out. The same leaching effect was also found for pH 3.5 but not as extensive as pH 2.5. However, for pH 3.5 and 4.5 the driving force for adsorption, was initially very high and hence resulted in a higher adsorption rate. The final metal ion concentration after 120 min for pH 4.5 was in the region of 1.2mg/l and final concentration for pH 2.5 and 3.5 were 2.56mg/l and 3.74mg/l respectively.

24g BOS sample on iron adsorption as shown in Figure 5.14 shows that as solution pH is increased from 2.5 to 3.5 and 4.5 iron metal uptake for the first 15min also increases very rapidly for pH 3.5 and 4.5. It is evident that after first 15min for pH 2.5 the metal ion adsorption percentage was 40.6% and whilst for pH 3.5 and 4.5 after 15min the adsorption percentage was 100%. It can also be observed that there is a steady rate between 60 to 180 min for all pH and adsorption rate consequently is 100% for all pH values at the end of the experiment.
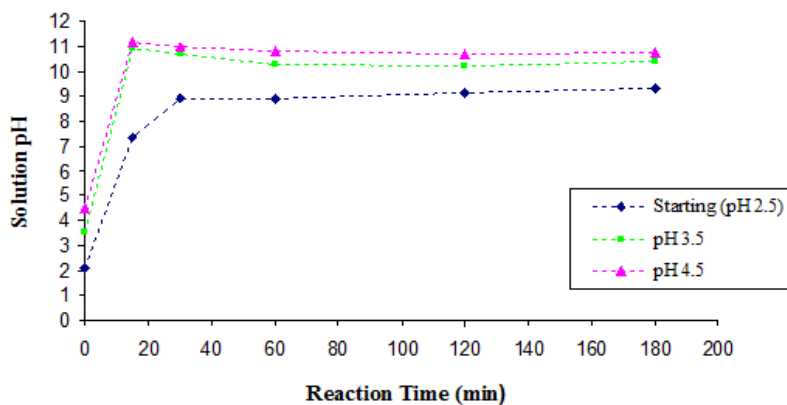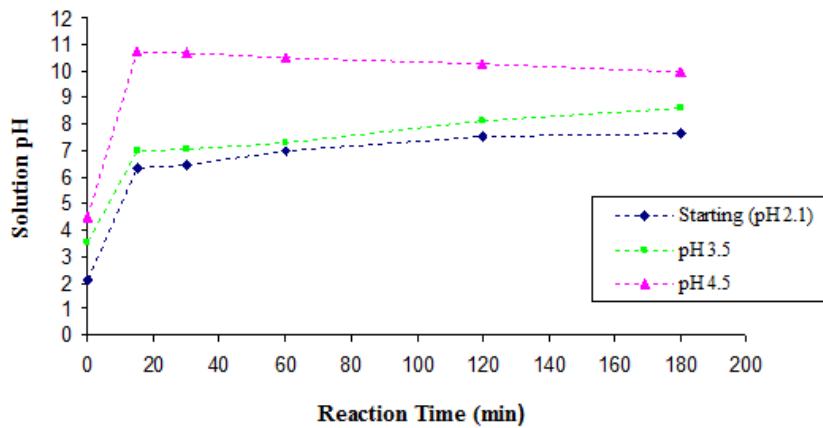


**Figure 5.15: Change in solution pH as adsorption proceeds (200ml single zinc component solution; 8g BOS; particle size +1mm,-1.4mm).**
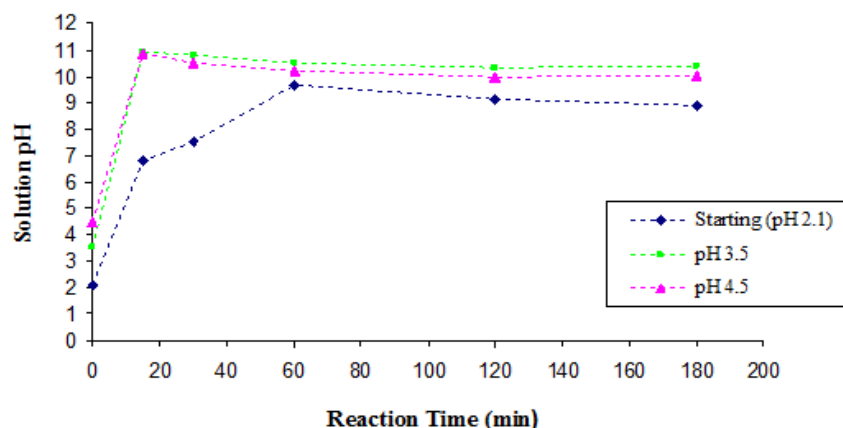
**Figure 5.16: Change in solution pH as adsorption proceeds (200ml single zinc component solution; 16g BOS; particle size +1mm,-1.4mm).**
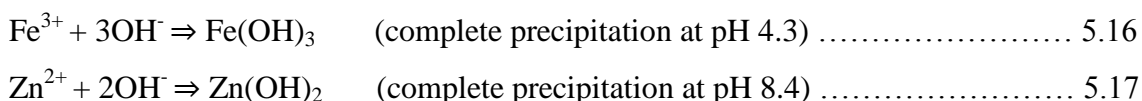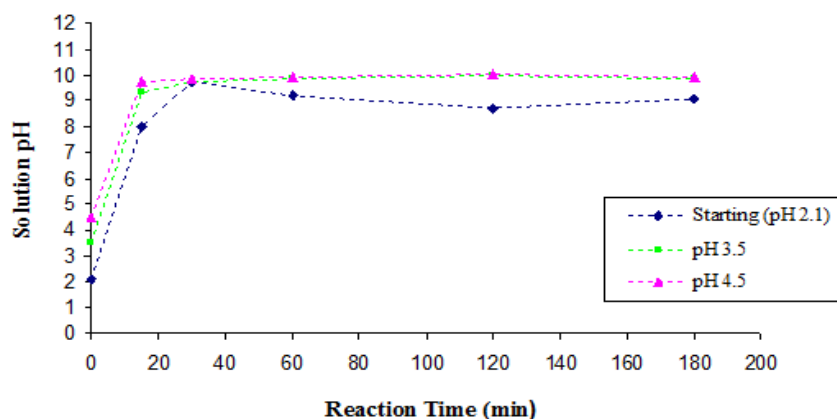


**Figure 5.17: Change in solution pH as adsorption proceeds (200ml single zinc component solution; 24g BOS; particle size +1mm,-1.4mm).**

Figures 5.15-5.17 indicate that pH level increases as contact time increases for each adsorbent dosage. For 8g BOS sample on zinc adsorption, as shown in Figure 5.18; all three initial pH values exhibit a steep increase as contact time increases for the first 15min. After 15min into reaction time, the metal ion concentrations measured were 15.4, 6.7 and 2.1 mg/l for pH 2.1, pH 3.5 and pH 4.5 respectively. As Figure 5.18 shows, for pH 2.1 and 3.5 a slight increase in metal adsorption was attained throughout the reaction period. At pH 3.5 and 4.5, for the first 60min the BOS produced a progressive increase in efficiency of zinc ions adsorption from the AMD solution. This clearly indicates the significance of starting pH on metal removal kinetics from sAMD solution.

Figure 5.19 shows that as solution pH decreases from 4.5 to 2.1 (starting pH), heavy metal removal efficiency also decreases; this is because $H^+$ ions compete with zinc metal cations for the same exchange sites. Result in Figure 5.19, for 16g BOS shows pH 3.5 and 4.5 produced similar trends with an increase in pH for the first 15min, decreasing between 30min to 120min and a slight increase between 120-180min. However for pH 2.1 which was essentially the initial pH sAMD solution, an increase was reached from the beginning until 60min and subsequently a decrease was detected towards the end of the reaction period. Inconsistent behaviour in terms of zinc metal ions adsorption for pH 2.1 and pH 3.5 is observed. For pH 2.1 at 60min and for pH 3.5 at 30min, it is suggested that re-dissolution of zinc occurs from the BOS. Adsorption rate is 100% for all pH values at the end of the experiments.

Results for 24g BOS show that during the first 15min of the process at all pH values almost all of the zinc ions were captured, (See Figure 5.20). An increasing trend of adsorption was followed by all pH values, however higher efficiency is shown by pH 4.5 compared to other starting pH values. The pH increase in treated water reveals that BOS adsorbs $H^+$ ions from sAMD solution to heavy metal ions, and hence the reason at lower pH values the $H^+$ ions are more concentrated and thus are adsorbed first. However at higher pH values the $H^+$ ion concentration becomes lower, and electrostatic repulsion between metal ions and surface charges is less; providing way to more heavy metal ions being adsorbed from solution as indicated by the increase in the amount of solute adsorbed per unit mass of adsorbent at equilibrium. This finding is in agreement with results of other researchers (Feng et al., 2004; Manchisi et al., 2013; Motsi et al., 2010, Alvarez- Ayuso et al., 2003, Sprynskyy et al., 2006).
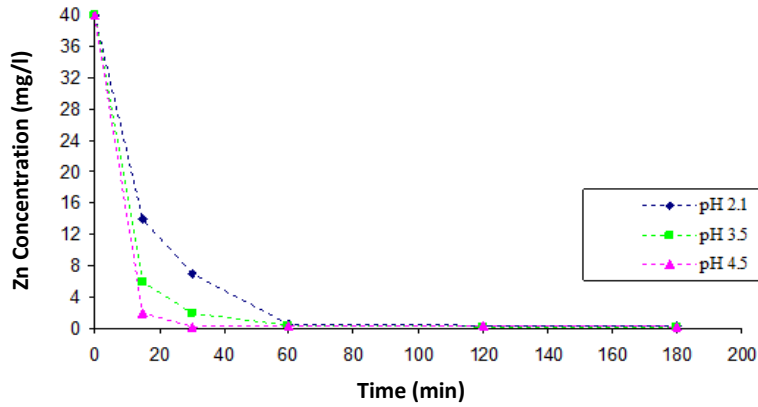
**Figure 5.18: Effect of initial solution pH on the adsorption capacity of BOS (200ml single zinc component solution; 8g BOS; particle size +1mm,-1.4mm).**
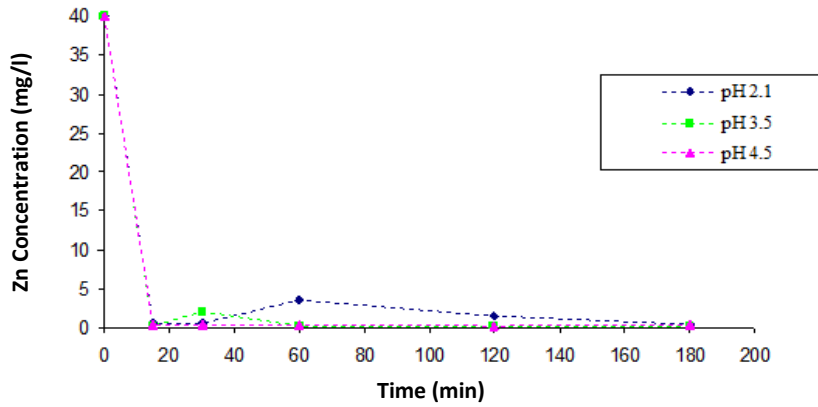


**Figure 5.19: Effect of initial solution pH on the adsorption capacity of BOS (200ml single zinc component solution; 16g BOS; particle size +1mm,-1.4mm).**
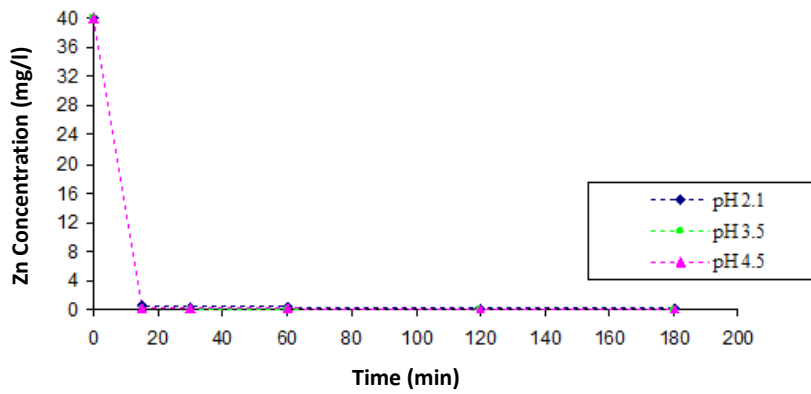


**Figure 5.20: Effect of initial solution pH on the adsorption capacity of BOS (200ml single zinc component solution; 24g BOS; particle size +1mm,-1.4mm).**

## 5.3.2 Encapsulated BOS for sAMD treatment

24g of BOS with a size range of (+180–250μm) was charged into a geotextile membrane as a *'encapsulated product'* and was contacted with 200ml of multi-component synthetic AMD solution at desired concentrations (40 mg/l). Samples were contacted for 180 minutes and agitated using a tumbling mill. These experiments were carried out in duplicate and the concentrations given are average values. The percent standard deviation between two duplicate samples when analysing for iron, copper, manganese and zinc was ±1.1%, 1.4%, 1.2% and 1.3% respectively.

As expected, an increase in pH caused increased metal sorption. As discussed before increasing pH results in an increasingly negative charge conferred on adsorption surfaces, thus favouring adsorption of metal cations and increased pH also favours precipitation of metal oxides/hydroxides.

Adsorption was high and selective towards $Cu^{2+}$ and $Mn^{2+}$ ions in comparison to the other 2 cations. Figure 5.23 shows the amount of $Fe^{3+}$ ions adsorbed by BOS from synthetic AMD was more or less unsteady throughout the sorption for the first 60 min. At 15 min a very high amount of iron leached from BOS into solution due to dissolution of BOS caused by low pH. As contact time increased the solution pH also increased, hence at 60 min controlled precipitation region was established for $Fe^{3+}$, (See Figure 5.21).
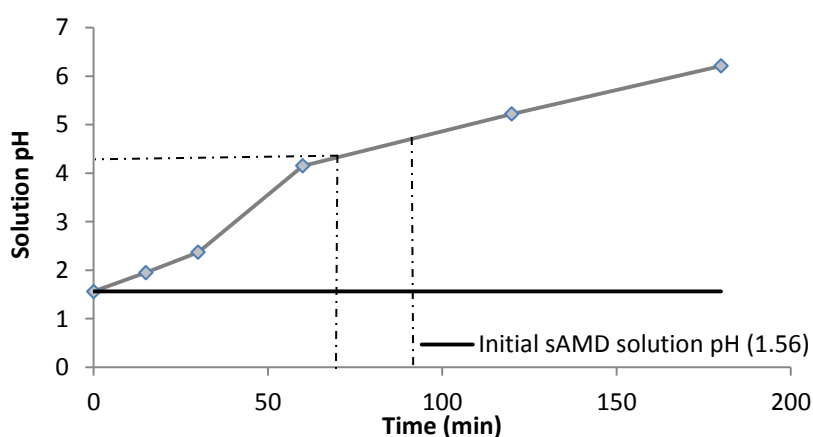


**Figure 5.21: pH change during adsorption by encapsulated BOS for removal of copper, iron, zinc and manganese from synthetic AMD solution.**

The final concentration of $Fe^{3+}$ was found to be 2.74mg/l which is more than the final concentration obtained by free BOS, despite the smaller particle size used in encapsulated method, See Figures 5.23 and 5.24. Results indicate limited mixing results in slower pH change through sorption, thus decreasing the adsorption opportunity between the adsorbent and adsorbate, See Figures 5.21 and 5.22.
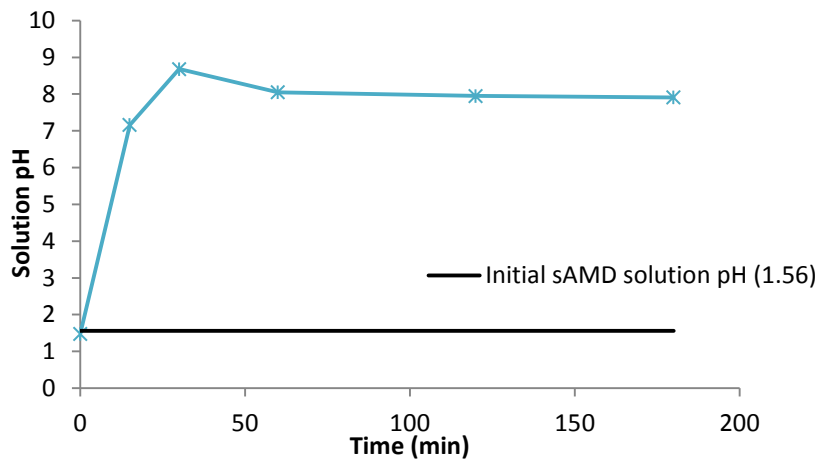


**Figure 5.22: pH change during adsorption by free BOS for removal of copper, iron, zinc and manganese from synthetic AMD solution.**

As shown in Figure 5.23, for $Zn^{2+}$ and $Mn^{2+}$ also leaching effect can be observed at 30 min. For all the ions after 120 min the adsorption levels off as equilibrium is reached. Percent adsorptions of 98.7%, 98%, 93.1% and 95%  for  $Cu^{2+}$, $Mn^{2+}$, $Fe^{3+}$, $Zn^{2+}$ respectively were achieved after three hours of contact. The results reveal that in comparison to $Mn^{2+}$ removal where the maximum removal by +1mm,-1.4mm particle size (free BOS) was 73.2%. Smaller particle size have an impact on the removal of $Mn^{2+}$ as an increase of 25.6% was achieved by decreasing the particle size as this caused the mass transfer resistance to be lower for adsorption (Ahmaruzzaan et al., 2011).
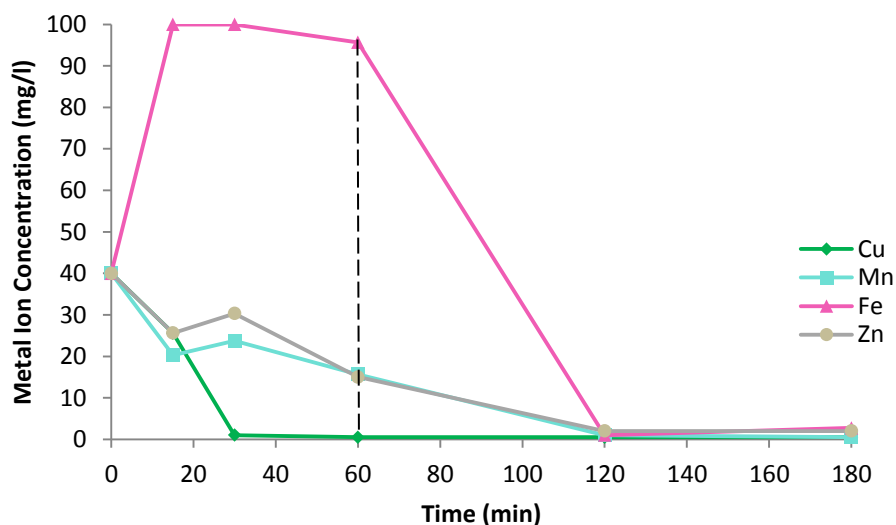
**Figure 5.23: Adsorption capacity of encapsulated BOS for copper, iron, zinc and manganese removal from synthetic AMD solution.**
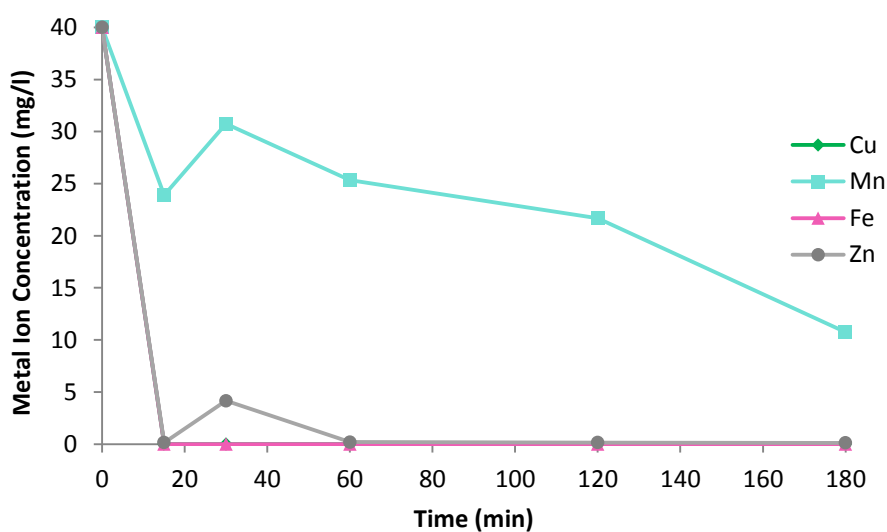


**Figure 5.24: Adsorption capacity of free BOS for copper, iron, zinc and manganese removal from synthetic AMD solution.**

As Figure 5.24 indicates, the adsorption of $Fe^{3+}$ has a different trend to other metals and it is suggested that removal of $Fe^{3+}$ ions occurs at different stages and is mainly due to the precipitation. According to Figure 5.21, the possible mechanism responsible for the removal of $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$ is mainly ion exchange and adsorption; as the final pH value was 6.21 which is far less than the pH obtained in the BOS free tests and below

the minimum pH required for complete precipitation of respective cations (Dimitrova et al., 1996; Dimitrova and Mehandgiev, 1998, 2000; Feng et al., 2004; Kim et al., 2008).

The Wheal Jane Mine water maximum consent limit for copper, iron, zinc and manganese in discharge water are 0.08, 5.0, 2.5 and 1.0 mg/l respectively. From the results obtained, it is evident that encapsulated BOS was able to treat $Mn^{2+}$, $Fe^{3+}$ and $Zn^{2+}$ within the maximum consent limit requirement.

In practice it is recommended that BOS can be used effectively for AMD with pH above 2 (more alkaline solution) such as AMD from coal mines rather than Wheal Jane mine AMD which is more acidic. However BOS treatment system could be more efficient if AMD is flowing freely through BOS with small particle size range, resulting in better and faster contact between the solution and BOS.

### 5.3.3 Comparison of adsorption capacity on sAMD solution

A comparison between adsorption capacities of BOS sludge, GGBS (ground granulated blast furnace slag) and (BOS/GGBS mixture) was performed in order to investigate the impact and the effectiveness of each on the removal of heavy metals from synthetic AMD solution. The mixture, that is 24g of each sample in 200ml synthetic solution was agitated using the tumbling mill rotating at a speed of 110 rotations per minute; the results are shown in Figure 5.26. For the (BOS/GGBS mixture) sample (50 % w/w) of each were mixed together to make up a 24g as a sample on its own.
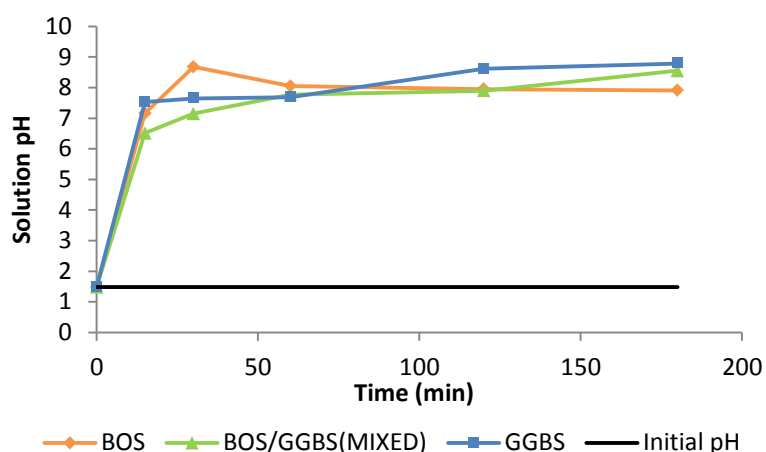


**Figure 5.25: Effect of various samples on pH of the synthetic AMD solution; average room temperature; 24g of each sample; 200ml sAMD solution, initial solution concentration, (40mg/l); initial pH 1.48.**

From the results shown in Figure 5.26, it is evident that at 15min for all samples, the adsorption of $Cu^{2+}$, $Fe^{3+}$ and $Zn^{2+}$ were instantaneous and complete (100%) under the experimental conditions employed. At 15min precipitation is thought to be the mechanism for $Fe^{3+}$ and adsorption and ion exchange for the other three cations according to pH values as shown in 5.25. The magnitude of adsorption of BOS and (BOS/GGBS mixture) followed this order: $Cu^{2+} \geqq Fe^{3+} \geqq Zn^{2+} > Mn^{2+}$ and for GGBS the order follows as: $Cu^{2+} \geqq Fe^{3+} \geqq Zn^{2+} >> Mn^{2+}$.
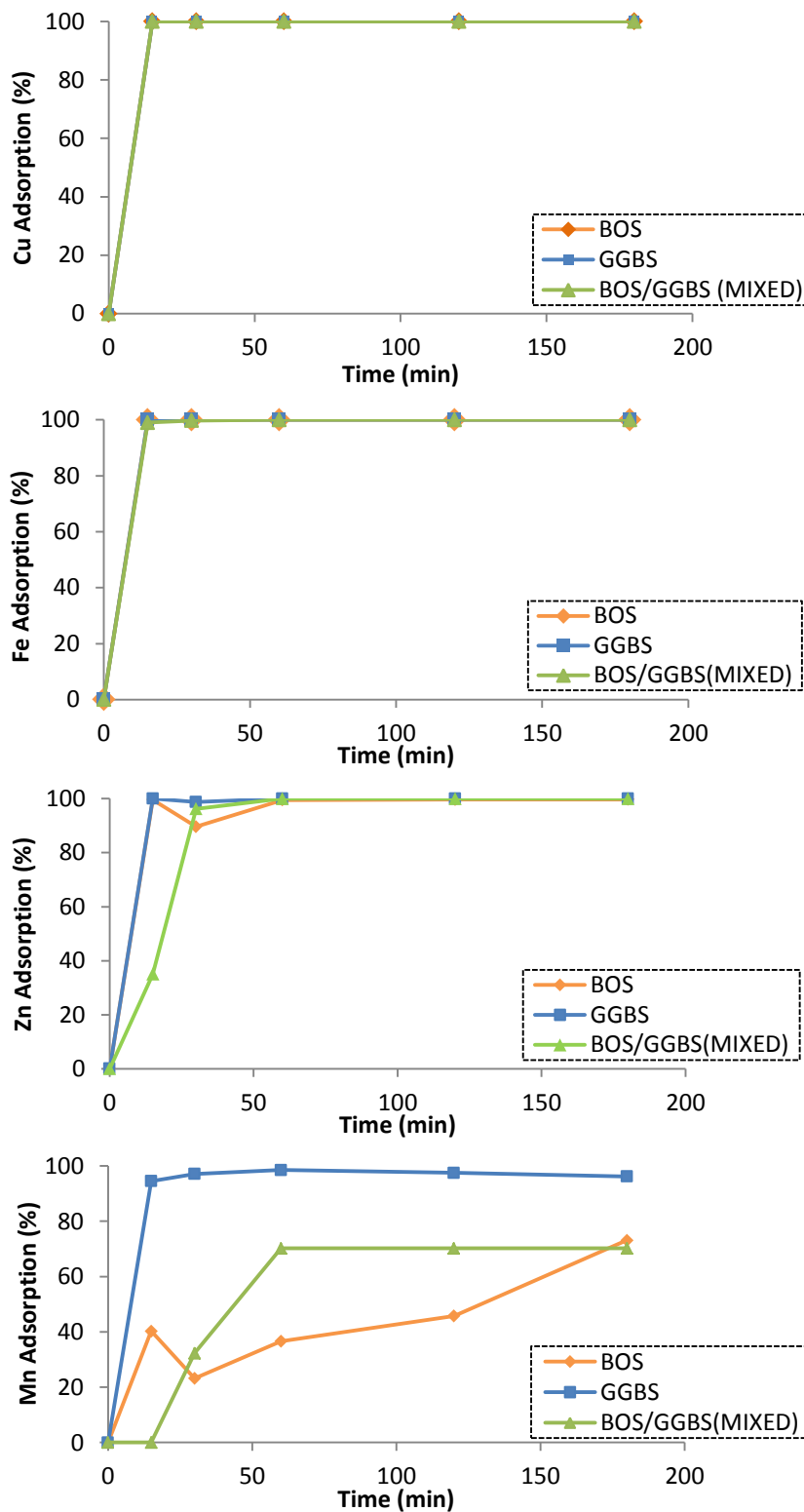
**Figure 5.26: Comparison of the adsorption capacity of BOS, GGBS and (GGBS/BOS mixture) samples for copper, iron, zinc and manganese removal from sAMD solution.**

GGBS sample was more effective in removing $Mn^{2+}$ (96.3%) compared to the other two samples regardless of its higher pH value after three hours of contact which caused the solution pH to reach 8.79. As discussed before the presence of higher CaO (% w/w) and the finest particle size distribution gives GGBS to be in a more favourable position in terms of adsorption of $Mn^{2+}$ compared to other samples. For BOS and (BOS/GGBS mixture) samples, the highest equilibrium pH were 7.91 and 8.55 respectively and $Mn^{2+}$ removal adsorption percent were 73.2% and 70.2% for BOS and (BOS/GGBS mixture) respectively. From experimental data it is suggested that adsorption and chemisorption play major roles in the uptake of heavy metal ions.

## 5.4 Kinetic modelling

Kinetic modelling was carried out to investigate the rate controlling steps in the removal of heavy metals from AMD solution by BOS. To interpret the experimental data, it is important to identify the steps involved during the sorption process. It is generally agreed that there are four consecutive steps which describe the overall sorption process of solute from a solution by a sorbent particle (Furusawa and Smith, 1973). These steps are as follow:

1. Transfer of adsorbate from the solution bulk to the boundary layer recovering the surface of the solid phase (bulk diffusion);
2. Diffusion of adsorbate through the boundary film to the surface of the sorbent particle (film diffusion);
3. Diffusion of adsorbate from the solid phase surface to the sorption sites (intraparticle diffusion);
4. Final uptake of adsorbate at the sorption sites, via chemisorption, ion exchange, complexation or precipitation, which is rapid (chemical reaction control).

In the process of establishing the rate limiting step, the fourth step is assumed to be fast and is therefore considered in this kinetic analysis. Second step is external mass transfer resistance which is dependent on parameters such as agitation. In this study, the

agitation given to the solutions (110 rpm) is assumed to be sufficient to avoid steps 1 and 2 being controlling steps. In a well agitated batch system, the boundary layer surrounding the particle is much reduced, reducing the external mass transfer coefficient (Sag and Aktay, 2000); hence, the third intraparticle diffusion resistance step can also be considered as a rate controlling step in this particular study.

Batch adsorption tests were conducted by mixing 16g of BOS with 200 ml of single component solutions (with fixed concentration of 100mg/l of each metal ion) at $20\pm 2$ºC. For comparison the same adsorption batch tests were also conducted by mixing 16g of BOS with 200 ml of multi-component solution containing a mixture of all 4 metal ions ($Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$), as shown Figure 5.27.

The particle size of BOS used was in the range of +1mm,-1.4mm. In this study Pseudo first order, Pseudo second order, Elovich's rate equations based on chemical adsorption, Weber-Morris and Vermeulen's approximation as intra particle diffusion model were applied to the experimental data.
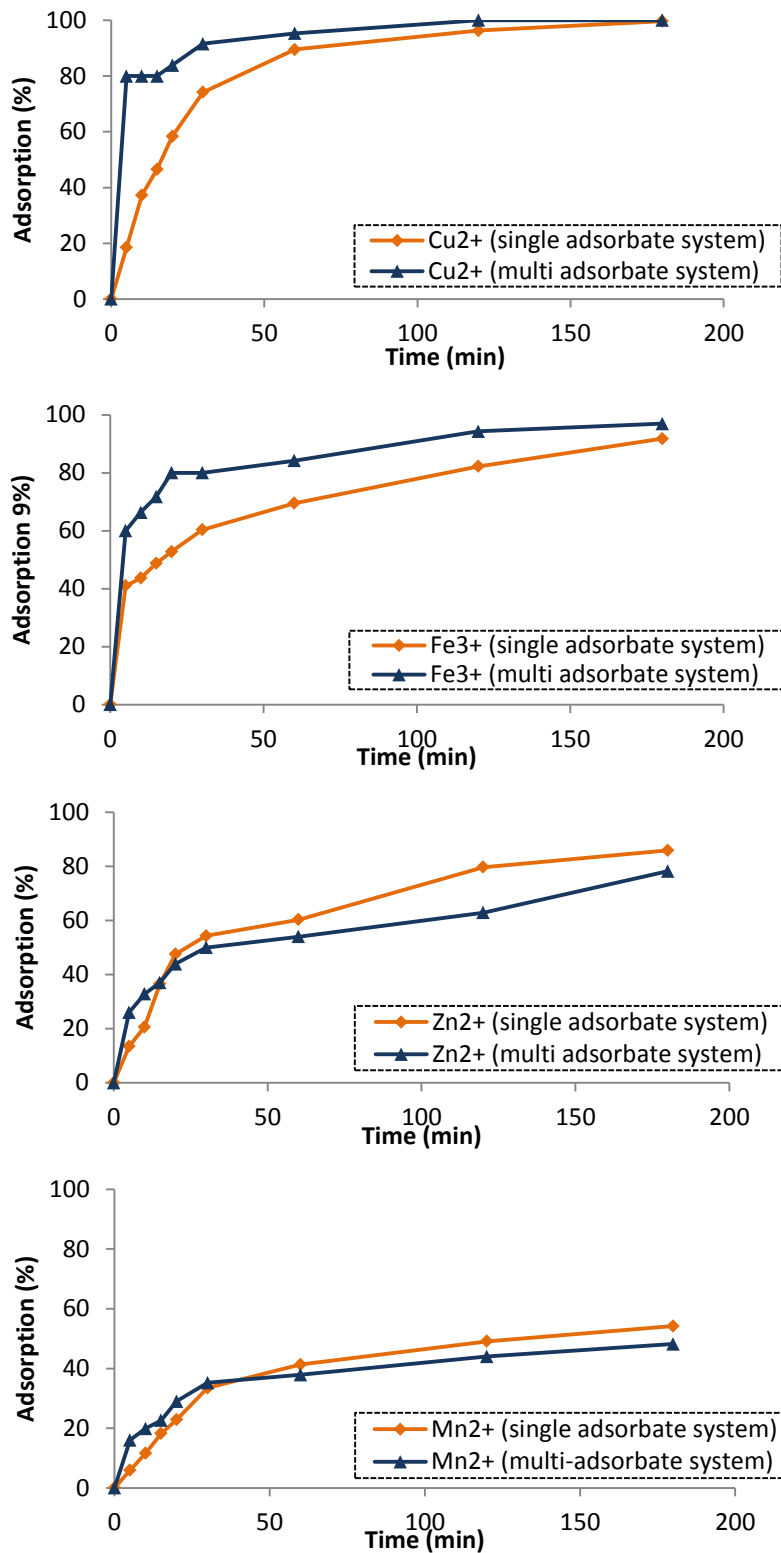
**Figure 5.27: Comparison of adsorption capacities from single component solution and multi-component synthetic acid mine drainage solution (sAMD).**

## 5.4.1 Chemical Reaction Control

The pseudo first and second order kinetic models were used to investigate whether chemical reaction at the adsorption sites of BOS was rate controlling. The experimental data that fit to any of these models indicate that the rate limiting step for process involves chemical reaction, which is chemisorption.

The Lagergren's pseudo first order rate equation is the earliest model known to describe the adsorption rate based on adsorption capacity (Ho and Mckay, 1998).The order rate equation is as follows:

$$dq_t /d_t = k_1(q_e - q_t) \qquad 5.22$$

Equation [5.22] is integrated (t = 0 to t = 0 and $q_t$ = 0 to $q_t$ = $q_t$) and expressed in linear form as:

$$Log\ (q_e - q_t) = Log\ (q_e) - k_1/2.303t \qquad 5.23$$

Where $q_e$ is the amount of metal adsorbed per unit weight of adsorbent at equilibrium (mg/g), $q_t$ is the amount of metal adsorbed at any time and $k_1$ is adsorption constant (mg/g min). If the model applies, a plot of $Log\ (q_e - q_t)$ vs. t should be linear.

The pseudo second order kinetic model was used to investigate whether chemical reaction at the adsorption sites of adsorbent was rate controlling (Ho et al., 2006; Ho and Mckay, 1998; Ho and Mckay, 1999; Qiu et al., 2009). The order rate equation is as follows:

$$dq_t /dt = k_2\,(q_e - q_t)^2 \qquad 5.24$$

The equation that describes the pseudo-second order model is given in the following linear form:

$$t/q_t = t/q_e + 1/k_2q_e^2 \qquad 5.25$$

Where $q_t$ and $q_e$ are the amount of metal adsorbed per unit weight of adsorbent (mg/g) at time t, and at equilibrium respectively. $k_2$ is adsorption rate constant (g mg$^{-1}$min$^{-1}$). The $k_2$ and $q_e$ can be determined from the intercept and slop of linear plots of $t/q_t$ vs. $t$. The initial adsorption rate, h, (mg/g min) is also expressed as:

$$h = k_2 q_e{}^2 \qquad\qquad 5.26$$

The Elovich equation based on adsorption capacity is also used to support second order kinetic assuming that the actual solid surfaces are energetically heterogeneous, but the equation does not propose any definite mechanism. The differential equation (Ho et al., 2006) is given as:

$$dq_t/dt = ae^{-\alpha qt} \qquad\qquad 5.27$$

The integrated (t = 0 to t = 0 and $q_t$ = 0 to $q_t$ = $q_t$) and linearised form is:

$$q_t = [2.3/\alpha]\ log(t+t_o) - [2.3/\alpha]log\ t_o \qquad\qquad 5.28$$

Equation [5.28] was simplified on assumption that aαt >> 1 to give a linear equation [5.29]:

$$q_t = \alpha ln(b_e a) + \alpha ln(t) \qquad\qquad 5.29$$

Where $b_e$ is related to desorption constant (g/mg), $\alpha$ = initial adsorption rate (mg/g min), $t_o$ =1/($\alpha b_e$), $q_t$= amount of metal ions adsorbed per unit weight of adsorbent (mg/g) at any time t (min). A plot of qt vs. ln(t) gives a straight line from which the parameters are obtained.

## 5.4.2 Intra-Particle diffusion control

The rate of adsorption, desorption, and ion exchange in porous materials are generally thought to be controlled by mass transport within the pore network/channels (Erdem et al., 2004). Thus, one of the parameters could be the pore/intraparticle diffusion coefficient. There are a number of models for the estimation of intraparticle diffusion coefficients, in this study only Weber-Morris and Vermeulen's approximations were considered. It is assumed that the BOS particle is spherical containing $X^+$; these are agitated in a solution containing of $Y^+$ ions. It is assumed that the mixing is perfect and thus the composition in the bulk liquid phase is assumed constant throughout. $Y^+$ ions diffuse from the bulk solution into the BOS and are exchanged with the $X^+$ ions. Intraparticle diffusion can be considered to be the rate limiting step under stated assumption (Inglezakis et al., 2001).

The rate expression for intraparticle diffusion is presented by Weber-Morris (Qiu et al., 2009) and is calculated by linearised of equation [5.30]:

$$q_t = K_i\,t^{1/2} + C \qquad\qquad\qquad 5.30$$

Where, C is the intercept and $K_i$ is the intra-particle diffusion rate constant (mg/g min$^{1/2}$). A plot of $q_t$ vs.$t^{1/2}$ should be linear if intraparticle diffusion is the rate determining step of the process.

Vermeulen's approximation is applied in literature mainly in the case of the exchange of isotopes on resins (Motsi et al., 2010); Vermeulen's approximation can be used as:

$$U(t)= [1\text{-}exp\,(\text{-}\pi^2 T)]^{0.5} \qquad\qquad\qquad 5.31$$

$U(t)$ is the fractional attainment of equilibrium in the ion exchanger (BOS) at time t and defined as:

$$U(t)= (C_o - C_{(t)})\,/\,(Co - C_\infty) \qquad\qquad\qquad 5.32$$

$C_o$ is the initial metal concentration, C (t) is the metal concentration a time (t) and $C_\infty$ is the equilibrium metal concentration and $r_o$ is the particle radius (cm). The diffusion coefficient of BOS was calculated by rearranging equation [5.31] and plotting $\ln[1-U(t)^2]$ vs. time, this should give a straight line with slope equal to $\pi^2 D`/r_o^2$.

## 5.4.3 Results and discussion

For single adsorbate system Lagergren's pseudo first order model was applicable up to about 5 minutes at best, and therefore the results are not shown. The results for linear data fit to pseudo second order model are shown in Figure 5.28; the adsorption obeys to the pseudo-second-order with good correlation. The pseudo second order model provided high values of regression coefficient ($R^2 \geq 0.99$) which indicates chemisorption may be the rate limiting step.
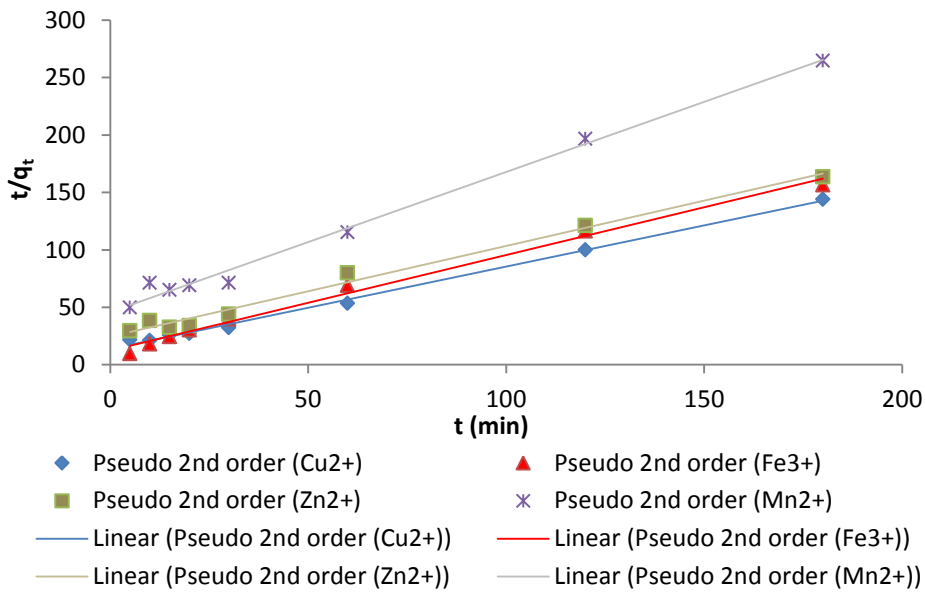


**Figure 5.28: Linear plots of $t/q_t$ vs. t for pseudo second order kinetic model for single adsorbate system, (16g BOS; 200ml solution; particle size: +1mm,-1.4mm; 20$^o$C).**

**Table 5.8: Pseudo second order kinetic parameters for adsorption of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ by BOS (single adsorbate system).**

| Heavy Metals | Initial Solution Conc. ($C_o$) mg/l | Rate constant ($k_2$) g/mg min | Amount adsorbed $qe_{Exp}$ (mg/g) | Amount adsorbed $qe_{Pred}$ (mg/g) | Initial adsorption rate (h) mg/g min | $R^2$ |
|---|---|---|---|---|---|---|
| $Cu^{2+}$ | 100 | 0.037 | 1.25 | 1.39 | 0.071 | 0.99 |
| $Fe^{3+}$ | 100 | 0.056 | 1.15 | 1.2 | 0.081 | 0.99 |
| $Zn^{2+}$ | 100 | 0.025 | 1.1 | 1.27 | 0.04 | 0.99 |
| $Mn^{2+}$ | 100 | 0.032 | 0.68 | 0.82 | 0.022 | 0.99 |

The equilibrium adsorption constant $q_{e[pred]}$ determined using the pseudo second order kinetic model were in agreement with experimentally determined $q_{e[exp]}$. The rate constants are important for the determination of the kinetic feasibility of heavy metal ion uptake from solution by BOS under experimental conditions. The rate constants presented in Table 5.8 can be used to compare the kinetics of the heavy metal ions.
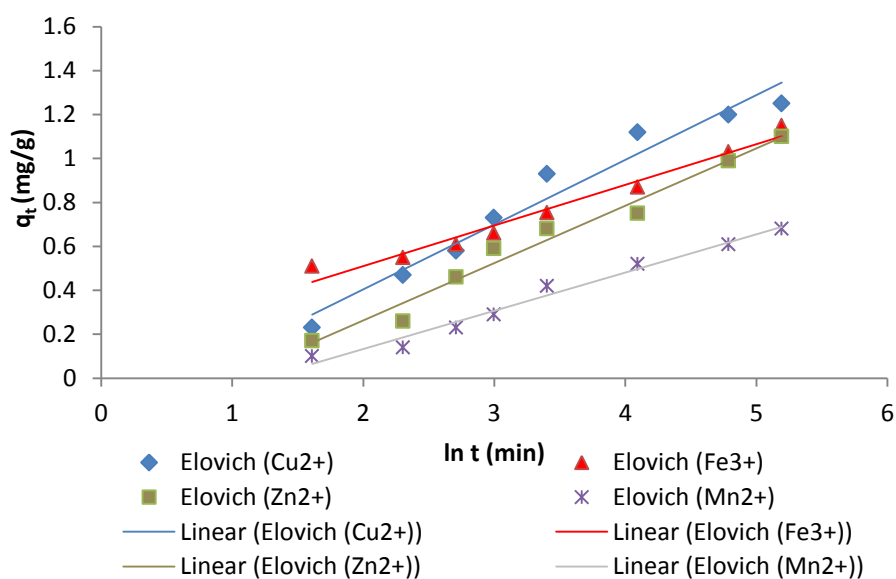


**Figure 5.29: Linear plots of $q_t$ vs. ln(t) for Elovich model for single adsorbate system, (16g BOS; 200ml solution; particle size: +1mm,-1.4mm; $20^o$C).**

Figures 5.29 depicts linear fits of the Elovich model with ($R^2 > 0.95$). As Figure 5.29 shows the fit for the Elovich model was only applicable for $Fe^{3+}$ which this supports the uptake of $Fe^{3+}$ by a second order kinetic model. As shown in Figures 5.30 and 5.31 for the intraparticle models, the straight lines do not pass through the origin which suggests that intraparticle diffusion may be the rate controlling step as shown by the $R^2$ values in Table 5.9 and 5.10. This is indicative of some degree of boundary layer control or other possible complex mechanisms which may control the rate of adsorption, all of which may be arising simultaneously through sorption.

**Table 5.9: Weber-Morris model parameters for adsorption of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ by BOS (single adsorbate system).**

| Heavy Metals | Initial Solution Conc. ($C_o$) mg/l | $K_i$, diffusion Rate constant mg/g min$^{-1/2}$ | C | $R^2$ |
|---|---|---|---|---|
| $Cu^{2+}$ | 100 | 0.085 | 0.267 | 0.83 |
| $Fe^{3+}$ | 100 | 0.058 | 0.394 | 0.91 |
| $Zn^{2+}$ | 100 | 0.079 | 0.122 | 0.91 |
| $Mn^{2+}$ | 100 | 0.053 | 0.037 | 0.92 |

**Table 5.10: Intraparticle diffusion coefficients calculated from Vermeulen's approximation for BOS (single adsorbate system).**

| Heavy Metals | D`; cm$^2$ s$^{-1}$ | $R^2$ |
|---|---|---|
| $Cu^{2+}$ | $1.21 \times 10^{-5}$ | 0.42 |
| $Fe^{3+}$ | $1.65 \times 10^{-5}$ | 0.58 |
| $Zn^{2+}$ | $1.48 \times 10^{-5}$ | 0.51 |
| $Mn^{2+}$ | $1.51 \times 10^{-5}$ | 0.51 |
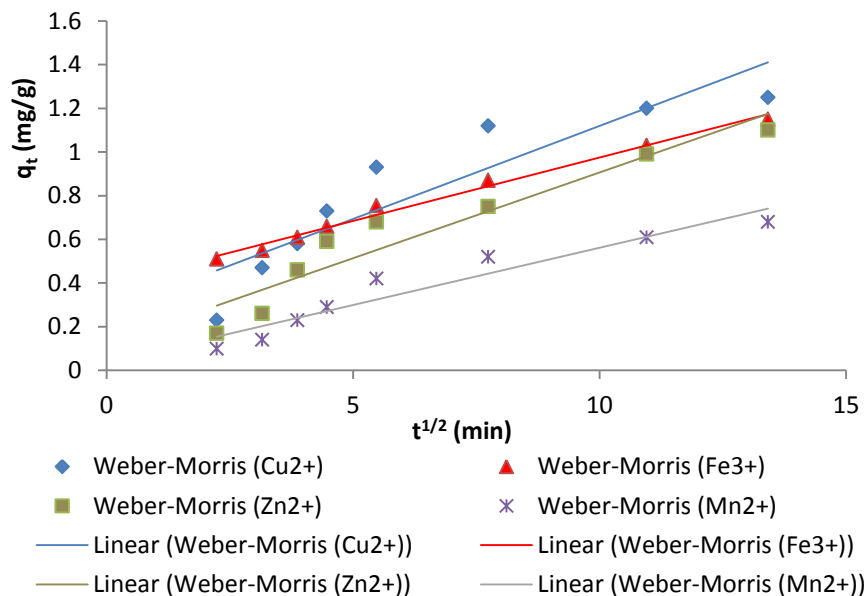
**Figure 5.30: Linear plots of $q_t$ vs. $t^{1/2}$ for Weber-Morris model for single adsorbate system, (16g BOS; 200ml solution; particle size: +1mm,-1.4mm; 20$^o$C).**
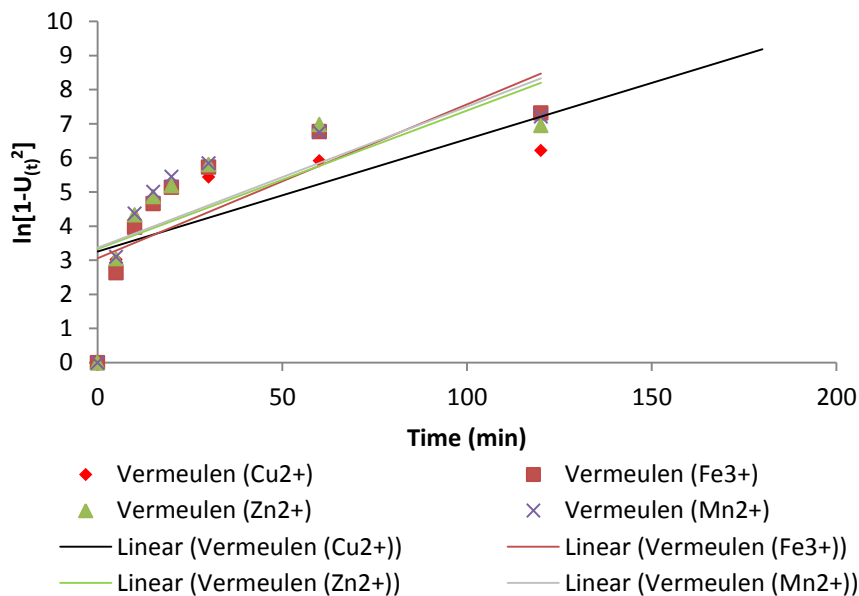


**Figure 5.31: Intraparticle diffusion control: Vermeulen's approximation for single adsorbate system, (16g BOS; 200ml solution; particle size: +1mm,-1.4mm; 20$^o$C).**
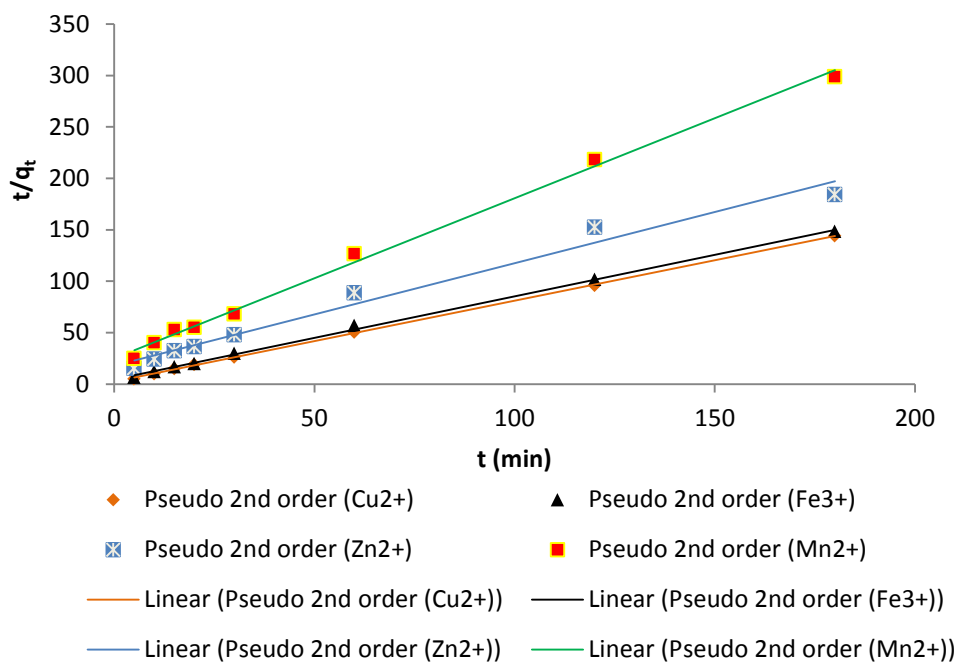
**Figure 5.32: Linear plots of $t/q_t$ vs. t for pseudo second order kinetic model for multi adsorbate system. (16g BOS; 200ml solution; particle size: +1mm,-1.4mm; 20$^o$C).**
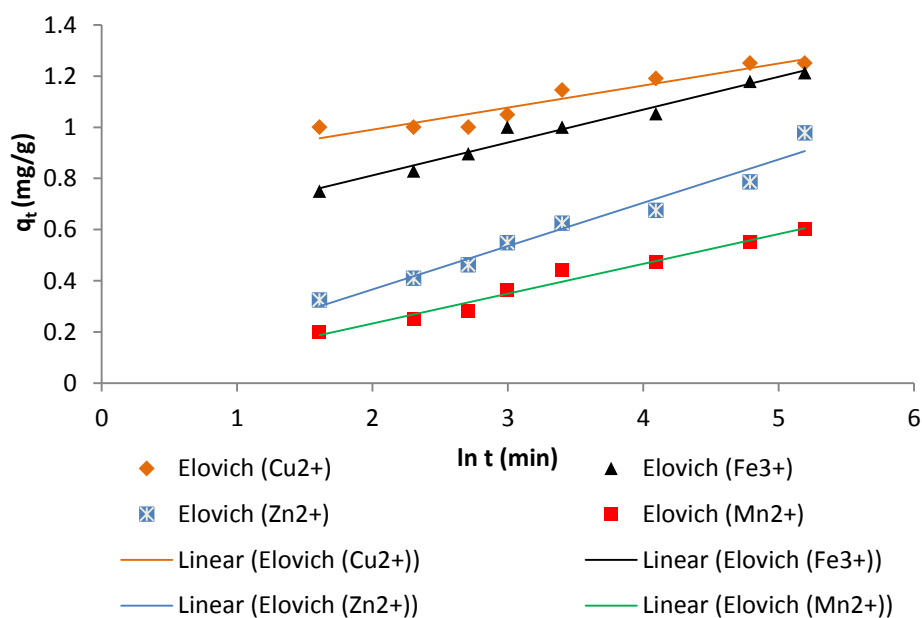


**Figure 5.33: Linear plots of $q_t$ vs. ln(t) for Elovich model for multi adsorbate system. (16g BOS; 200ml solution; particle size: +1mm,-1.4mm; 20$^o$C).**

**Table 5.11: Pseudo second order kinetic parameters for adsorption of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ by BOS (multi adsorbate system).**

| Metal | Initial Solution Conc. ($C_o$) mg/l | Rate constant ($k_2$) g/mg min | Amount adsorbed $qe_{Exp}$ (mg/g) | Amount adsorbed $qe_{Pred}$ (mg/g) | Initial adsorption rate (h) mg/g min | $R^2$ |
|---|---|---|---|---|---|---|
| $Cu^{2+}$ | 100 | 0.245 | 1.25 | 1.27 | 0.395 | 0.99 |
| $Fe^{3+}$ | 100 | 0.138 | 1.25 | 1.24 | 0.212 | 0.99 |
| $Zn^{2+}$ | 100 | 0.055 | 0.98 | 1.0 | 0.055 | 0.98 |
| $Mn^{2+}$ | 100 | 0.096 | 0.6 | 0.64 | 0.039 | 0.99 |

Similarly to the single adsorbate system, kinetic models were applied to test whether metal adsorption was controlled by intraparticle diffusion or chemisorption for the multi adsorbate system. A Pseudo first order model was applicable up to 10 minutes at best, and therefore the results are not shown. Based on pseudo second order kinetic model parameters and good regression coefficient ($R^2 > 0.99$) from fitting experimental data for multi-component system, chemisorption is thought to be the rate limiting step, (See Figure 5.32). As shown in Table 5.11, the rate constants are critical for the determination of the kinetic feasibility of heavy metal ion uptake from solution by BOS under multi-adsorbate condition.

The hydration radii of the cations are: $r_H Zn^{2+} = 4.30Å$, $r_H Fe^{3+} = 4.57Å$, $r_H Cu^{2+} = 4.19Å$ and $r_H Mn^{2+} = 4.38Å$ (Nightingale, 1959). The smallest particles should ideally be adsorbed faster and in larger quantities compared to the larger particles, since the smaller particles can pass through the surface of BOS structure with ease. According to the results shown in Table 5.11, the initial adsorption rates (h) of diffusion are in the sequence: $Cu^{2+} > Zn^{2+} > Mn^{2+}$; this is in agreement with the hydration radii of the cations. According to the hydration radii of $Fe^{3+}$ it is suggested that $Fe^{3+}$ ions should ideally be adsorbed slower than the other 3 cations. However the above results show that $Fe^{3+}$ adsorption is much more complicated and does not obey the hydration radii sequence.
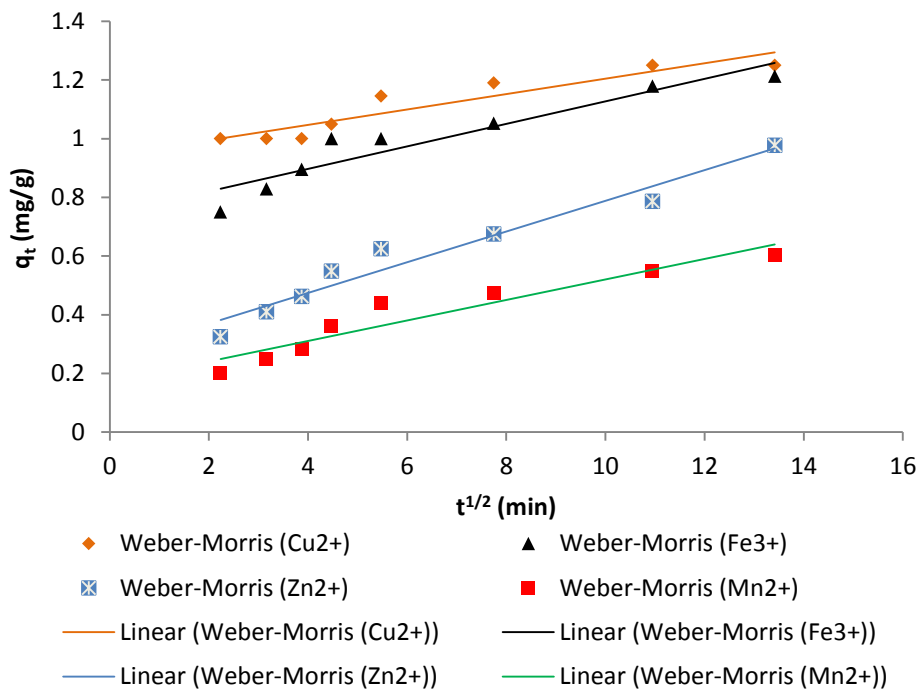
**Figure 5.34: Linear plots of $q_t$ vs. $t^{1/2}$ for Weber-Morris model for multi adsorbate system. (16g BOS; 200ml solution; particle size: +1mm,-1.4mm; 20$^o$C).**
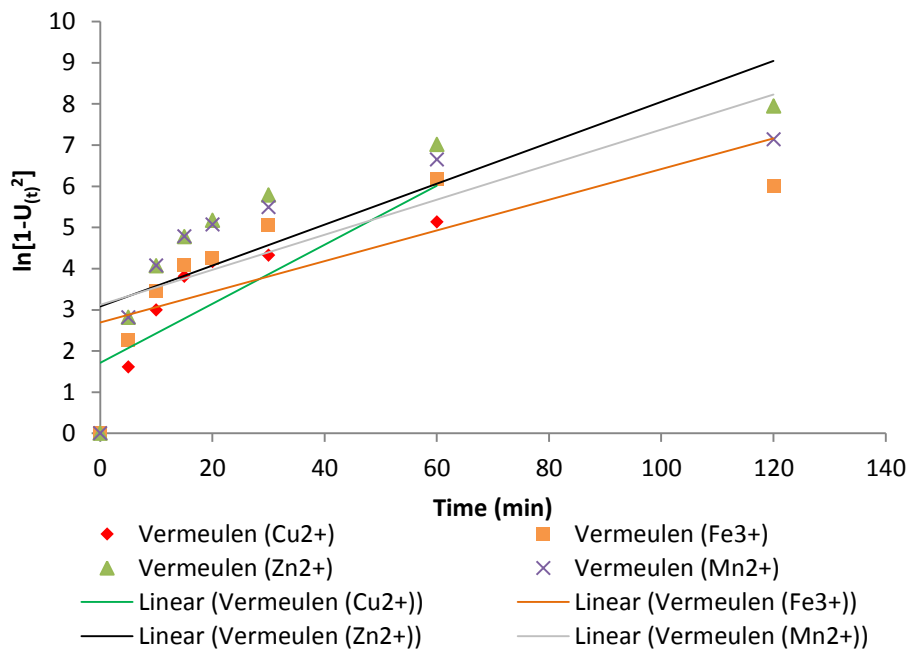


**Figure 5.35: Intraparticle diffusion control: Vermeulen's approximation for multi adsorbate system (16g BOS; 200ml solution; particle size: +1mm,-1.4mm; 20$^o$C).**

**Table 5.12: Elovich model parameters for adsorption of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ by BOS (multi adsorbate system).**

| Heavy Metals | Initial Solution Conc. ($C_o$) mg/l | Desorption constant g/mg | Initial adsorption rate (mg/gmin) | $R^2$ |
|---|---|---|---|---|
| $Cu^{2+}$ | 100 | … | … | 0.91 |
| $Fe^{3+}$ | 100 | 7.78 | 9.63 | 0.97 |
| $Zn^{2+}$ | 100 | 5.92 | 0.2 | 0.96 |
| $Mn^{2+}$ | 100 | 8.59 | 0.12 | 0.97 |

The rate constants presented in Table 5.12 for the Elovich model supports the pseudo second order kinetics of $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ uptake. From data, the intercept values indicate that lines were only passing through origins of respective metal ions with ($R^2>0.95$), Figure 5.33. Figures 5.34 and 5.35 depict linear fits of the intraparticle diffusion models, the straight lines do not pass through the origin to suggest intraparticle diffusion may be rate controlling step, as shown by the poor $R^2$ values in Table 5.13 and 5.14.

**Table 5.13: Weber-Morris model parameters for adsorption of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ by BOS (multi adsorbate system).**

| Heavy Metals | Initial Solution Conc. ($C_o$) mg/l | $K_i$ , diffusion Rate constant mg/g min$^{-1/2}$ | C | $R^2$ |
|---|---|---|---|---|
| $Cu^{2+}$ | 100 | 0.0263 | 0.9418 | 0.89 |
| $Fe^{3+}$ | 100 | 0.0383 | 0.7441 | 0.89 |
| $Zn^{2+}$ | 100 | 0.0523 | 0.2657 | 0.94 |
| $Mn^{2+}$ | 100 | 0.0397 | 0.1223 | 0.85 |

**Table 5.14: Intraparticle diffusion coefficients calculated from Vermeulen's approximation for BOS (multi adsorbate system).**

| Heavy Metals | D`;cm$^2$ s$^{-1}$ | $R^2$ |
|---|---|---|
| $Cu^{2+}$ | $2.61 \times 10^{-5}$ | 0.66 |
| $Fe^{3+}$ | $1.36 \times 10^{-5}$ | 0.53 |
| $Zn^{2+}$ | $1.81 \times 10^{-5}$ | 0.64 |
| $Mn^{2+}$ | $1.56 \times 10^{-5}$ | 0.56 |

## 5.5 Conclusion

The adsorption of metal ions from aqueous solutions by the amphoteric surfaces of metal oxide/silicate materials is due to a number of different mechanisms such as ligand exchange, surface precipitation, co-precipitation and bulk precipitation (Apak et al., 2002; Zhou and Haynes, 2010). The adsorption processes onto pure oxide surfaces are complex (McBride et al., 2000; Bradl et al., 2004) and the poly-mineral composition of adsorbents further complicates the sorption. The materials used in this study have similar compositions and they were all shown to have significant capacity to adsorb metal cations.

In this study the adsorption of the heavy metal ions from solution onto BOS sludge was investigated. Analysis of pH trends indicated that ion exchange between the heavy metals in solution and the exchangeable cations in the BOS was taking place. Thus, ion exchange was one of the processes responsible for the removal of heavy metals from solution by BOS.

The pH is strongly affected by the sorbent rather than synthetic AMD composition and predominantly with a higher BOS dosage. There are two competing processes affecting sorption process, release of alkalinity from BOS and the removal of acidity from AMD components at higher sorbent dosage the acidity from solution is overwhelmed and pH is bound to increase while with lower BOS dosage the alkalinity from the sorbent is overwhelmed by the acidity from AMD solution and the pH remains a little lower.

High acidic AMD can affect adsorbed metals through a number of ways. Low pH favours desorption and/or dissolution of metal cations since both their sorption and precipitation are favoured at high pH. In very acidic conditions strong competition between $H^+$ ions and metal cations for adsorption sites causing displacement of cations into solution. Acidic conditions also favours dissolution of $Fe^{3+}$ oxides on adsorption surfaces and thus the release of precipitated metal ions.

Adsorption kinetics describes the heavy metal ions uptake rate which in turn controls the residence time and hence the size of the adsorption unit. Kinetic studies indicated that the rate of adsorption of the heavy metals by BOS was rapid for the first 15 min and then gradually levelled off as equilibrium was approached. The adsorption kinetics were fitted satisfactorily to the pseudo second order kinetic model, which is based on assumption that chemisorption is the rate limiting/controlling step.

There were a number of operational conditions which were found to affect the adsorptive properties of BOS and influence the rate of metal uptake; these include initial solution pH, initial solution metal concentration, particle size, BOS mass loading and presence of competing cations. However the effect of agitation which is an important parameter in adsorption process will be investigated in reactor study of this research work to assess the efficiency and rates of adsorption by BOS.

Results reveal that the efficiency and adsorption rates were favoured with decrease in particle size, decrease in initial metal concentration, increase in mass loading and increase in initial pH. The removal of heavy metals from synthetic solution was due to a combination of mechanisms and these include chemisorption, adsorption, ion exchange, precipitation and accompanied by other complex processes.

The effect of competing cations was investigated and it was observed that the adsorption of $Cu^{2+}$ was unaffected by the presence of competing ions. The adsorption of $Fe^{3+}$ was affected (but not significantly) by the presence of competing ions and increased in multi-component solution compared to the amount adsorbed from single component solution.

The other two heavy metals ($Mn^{2+}$ and $Zn^{2+}$) were affected by the presence of competing cations. This can be due to the competitive adsorptive effect among heavy metal ions for the same available or free adsorption sites and many other factors that may influence the heavy metal uptake such as differences in BOS's pore sizes relative to that of metal ionic radii, differences in element electronegativities, high affinity of

BOS towards specific metal ions and probably a general limitation in the BOS's physical properties.

Studies in multicomponent systems that reflect actual industrial effluent composition are limited and need to be conducted in order to understand kinetics in relation to adsorption of metal ions. Further, there are very few reported studies that have employed kinetic models to study mechanism of metal adsorption with slags. In many instances, studies on the proposed mechanisms of metal adsorption with iron/steelmaking slags are limited, inconsistent and not yet clearly understood.

Results from equilibrium studies showed that BOS was capable of removing heavy metals from synthetic AMD solution. Equilibrium studies were used to determine the selectivity series of BOS for the adsorption of $Cu^{2+}$, $Fe^{3+}$, $Mn^{2+}$ and $Zn^{2+}$ from solution. The experimental data obtained from batch studies were fitted satisfactorily to Langmuir isotherm model.

According to the Langmuir isotherm, the series was found to be: $Cu^{2+}>Fe^{3+}>Zn^{2+}>Mn^{2+}$ and this was in agreement with the order of adsorption from batch experiments. As stated before, metal selectivity can depend on the nature of the surfaces and reactive groups present, level of adsorption, pH and ionic strength of the equilibrium solution as well as properties of the metal cations including ability to form covalent bonds (softness), electronegativity, charge-to-radius ratio and pKa values (Sposito et al., 1989; McBride et al., 2000; Bradl et al., 2004). Thus, the order can differ under different operational parameters and conditions (such as, initial solution pH and concentration, agitation speed, pre-treatment methods) used in each study, See Table 5.15.

**Table 5.15: Comparison of inorganic adsorbents in relation to uptake of heavy metal cations in aqueous solution from literature.**

| Researcher | Adsorbent type | Experimental selectivity series |
|---|---|---|
| This study | Waste gas sludge (BOS) | $Cu^{2+} \geqq Fe^{3+} > Zn^{2+} > Mn^{2+}$ |
| This study | Blast furnace flue dust | $Cu^{2+} >> Fe^{3+} > Zn^{2+} > Mn^{2+}$ |
| This study | Ground granulated blast furnace slag | $Cu^{2+} \geqq Fe^{3+} \geqq Zn^{2+} >> Mn^{2+}.$ |
| Manchisi et al., 2013 | Granulated blast furnace slag | $Fe^{2+} > Cu^{2+} > Cd^{2+} > Co^{2+} > Mn^{2+}$ |
| Chen et al., 2011 | Electric arc furnace slag | $Cr^{3+} > Pb^{2+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ |
| Ochola and Young, 2005 | Steel slag | $Fe^{3+} > Cu^{2+} > Pb^{2+} > Zn^{2+} > Al^{3+}$ |
| Mohan and Chander , 2001 | Lignite | $Fe^{2+} > Zn^{2+} > Mn^{2+}$ |
| Rios et al., 2008 | Natural clinker | $Fe^{2+} > As^{3+} > Pb^{2+} > Zn^{2+} > Cu^{2+} > Ni^{2+} > Cr^{3+}$ |
| Zhou and Haynes, 2010 | Fly ash | $Cr^{3+} = Pb^{2+} = Cu^{2+} = Cd^{2+} > Zn^{2+}$ |
| Zhou and Haynes, 2010 | Bottom ash | $Pb^{2+} = Cr^{3+} = Cu^{2+} > Zn^{2+} > Cd^{2+}$ |
| Zhou and Haynes, 2010 | Air-cooled blast furnace slag | $Cd^{2+} = Pb^{2+} = Cu^{2+} = Cr^{3+} >> Zn^{2+}$ |
| Zhou and Haynes, 2010 | Red mud | $Pb^{2+} > Cr^{3+} > Cu^{2+} > Cd^{2+} > Zn^{2+}$ |
| Zhou and Haynes, 2010 | Water treatment sludge | $Pb^{2+} > Cr^{3+} > Cu^{2+} > Zn^{2+} > Cd^{2+}$ |
| Erdem et al., 2004 | Natural zeolite | $Co^{2+} > Cu^{2+} > Zn^{2+} > Mn^{2+}$ |
| Motsi et al., 2010 | Synthetic zeolite | $Zn^{2+} = Mn^{2+} > Fe^{3+} > Cu^{2+}$ |
| Motsi et al., 2010 | Natural zeolite | $Fe^{3+} > Zn^{2+} > Cu^{2+} > Mn^{2+}$ |

Iron and steel by-products and more particularly BF (blast furnace) slag have been used previously as functional adsorbents. Although more studies need to be conducted to understand the adsorption process in detail, it is believed that such materials may be sustainable alternative adsorbents to activated carbons and ion exchange resins (Ahmaruzzaman et al., 2011; Bailey et al., 1999; Barakat et al., 2011; Kurniawan et al., 2006).

The results show that BOS sludge can be used effectively for the removal of heavy metal ions from acidic solutions. This material known as waste from steelmaking process can be used as a substitute for the more expensive adsorbents like activated carbon or other AMD treatment methods due to its availability, large quantities and low cost. However there are still issues with the potential disposal of the sludge after use and release of metals from stockpiled material before using for AMD treatment.

# CHAPTER 6

# TREATMENT OF WHEAL JANE AMD WITH BOS SLUDGE AND OTHER ADSORBENTS

## 6.1 Introduction

BOS sludge was used to treat Wheal Jane Mine (Cornwall, UK) AMD in this research. Batch kinetic studies were performed to assess the potential of BOS sludge as a low cost adsorbent for real AMD treatment. Different parameters were used to investigate the capacity and efficiency of BOS samples, this entailed use of batch experiments under different methods to study the performance of BOS sludge in removing copper, iron, zinc and manganese. This chapter presents the results and discussion on the use of BOS sludge in treating actual AMD from Wheal Jane Mine.

## 6.2 Batch Experiments

Batch adsorption tests/studies provide information on adsorption equilibrium characteristics and adsorption kinetics, which are important in determining the effectiveness of the adsorbent in removing solute from solution. The potential of BOS sludge as an adsorbent for the treatment of Wheal Jane acid mine drainage was determined using batch experiments. Different masses of samples were mixed with 200 ml solution of Wheal Jane AMD for 180 minutes and agitated over tumbling mill at 110 rpm. The initial concentrations of copper, iron, zinc and manganese in AMD from Wheal Jane mine collected were approximately 1.1, 74, 23 and 4 mg/l respectively and these were measured using the AAS. The pH of Wheal Jane water was in a range of about 2.7- 2.9 ± 0.1. A comparison was also carried out for the removal of each metal ion in AMD water by ground granulated blast furnace slag (GGBS), granulated blast furnace slag and blast furnace flue dust samples.

## 6.2.1 BOS sludge for Wheal Jane AMD treatment

Wheal Jane AMD treatment was carried out using 24g of BOS sludge in a constant volume (200 ml) of AMD solution. The agitation time was predetermined for 180 minutes. Figure 6.1 shows the neutralising behaviour of BOS when contacted with Wheal Jane mine AMD as a function of pH. The kinetics of neutralisation reaction is instantaneous, with the final pH 9.9; increasing from 2.9 which was the initial Wheal Jane AMD solution pH. The initial rates of adsorption were rapid because of high mass transfer based on high concentration gradient of adsorbates that drives diffusion flux across layers into BOS pores which possess large surface areas, as shown in Figure 6.2.
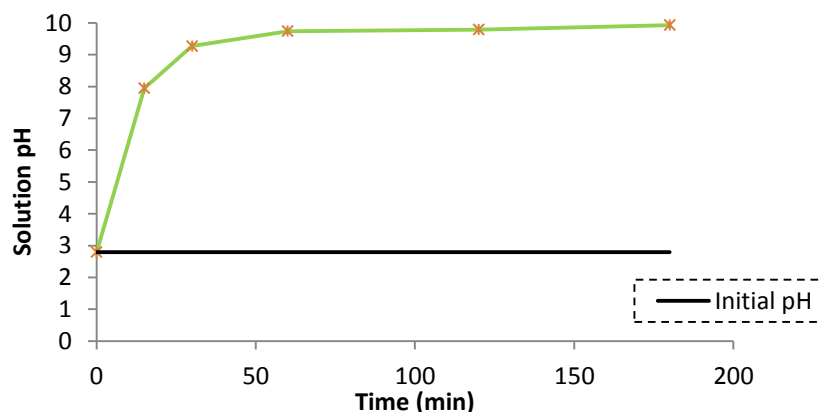


**Figure 6.1: Solution pH trend on the adsorption of selected heavy metals from Wheal Jane AMD. (200ml solution; 24g sample; particle size: +1mm,-1.4mm; initial pH~ 2.9; average room temperature (20$^o$C).**

The high pH obtained is also due to the dissolution of the BOS sludge during the agitation; exposing high number active adsorption sites. More copper and iron were adsorbed from solution in comparison to the other metals (Mn, Zn). Interestingly the order of metal ions adsorbed by BOS from Wheal Jane was more or less similar to the results of synthetic AMD treatment (chapter 5). The order of adsorption from Wheal Jane AMD was found to be: copper≧iron>zinc>manganese.
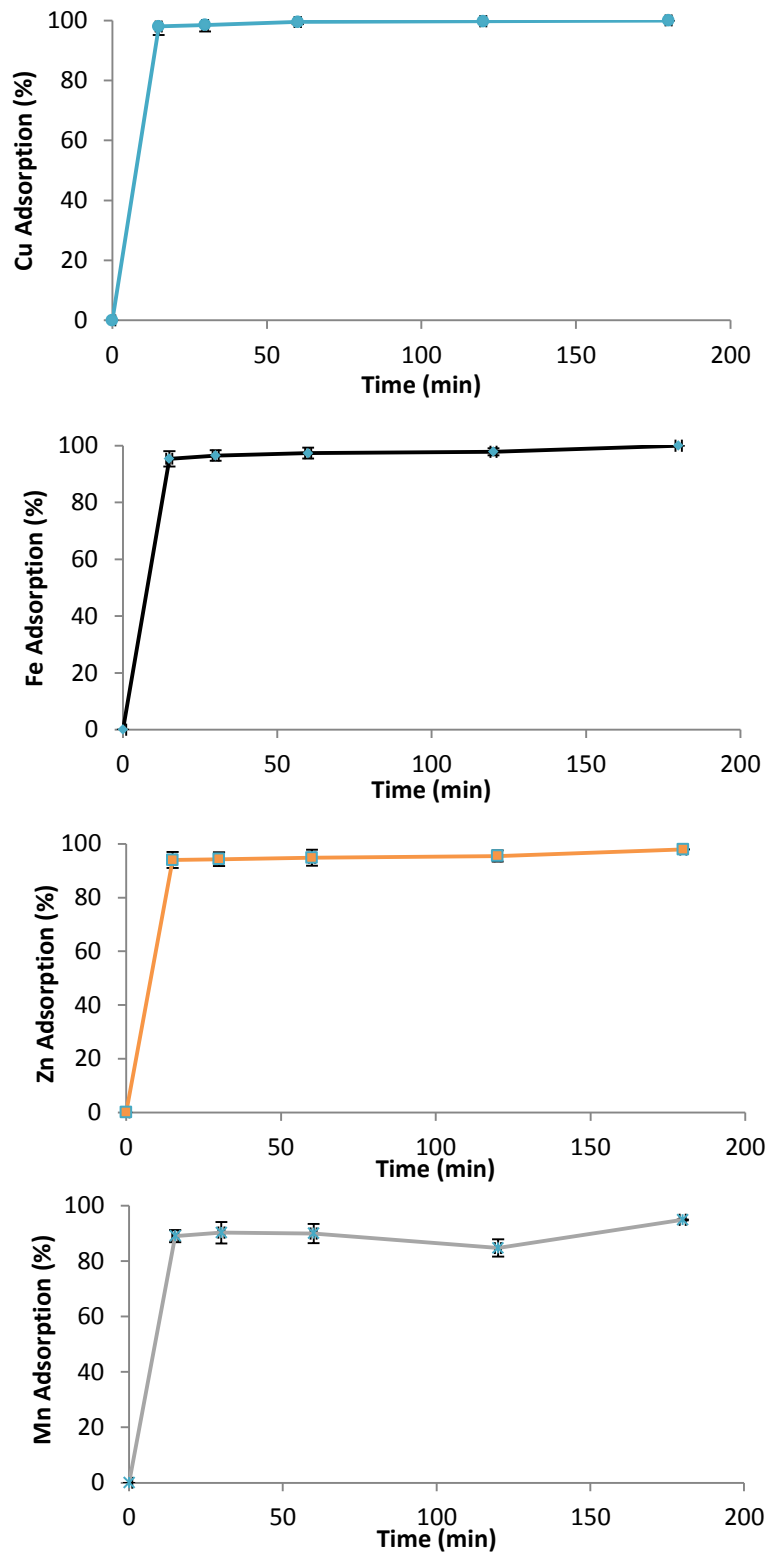
**Figure 6.2: The adsorption of heavy metals from Wheal Jane AMD solution using BOS.**

Increasing the pH of AMD water to the desired value causes metal precipitation in the form of hydroxides. Therefore, the way that AMD is treated highly depends on the type and concentrations of the metal cations in water. The series shows that more manganese ions were removed from Wheal Jane AMD compared to the synthetic AMD adsorption and that is not only because of the concentration differences which may influence the adsorption rates but also due to other parameters.

The adsorption of all metal ions displayed a similar trend to one another, as shown in Figure 6.2. For all the ions, adsorption is steep for the first 15 min, after which for all respective metals the adsorption levels off as equilibrium is attained. Percent adsorption of 100%, 100%, 97.9%, and 94.8% for copper, iron, zinc and manganese respectively were achieved after 3 hours of contact with BOS sludge.

The final concentrations of selected heavy metals in the Wheal Jane AMD were 0, 0, 0.5 and 0.21 mg/l of copper, iron, zinc and manganese respectively. These final concentrations fall within Wheal Jane maximum consent limit and thus it is recommended that BOS sludge can effectively be used to treat real AMD.

### 6.2.1.1 Effect of BOS dosage on metal recovery from Wheal Jane AMD

Similarly to the synthetic AMD treatment results, a series of kinetic experiments at different adsorbent masses, that is, $8 - 16 - 24$ g, were performed using the Wheal Jane solution. Typical plots of the amount of metal adsorbed versus time are shown in Figure 6.5 and 6.6.

In terms of the percentage of heavy metals adsorbed from solution, it is once again evident that an increase in BOS mass resulted in an increase in the adsorption of the heavy metals just for iron, zinc and manganese, See Table 6.1. Results show the amount of metal adsorbed ($q_e$) at equilibrium is lower as the mass of the samples increased. This is because as adsorbent mass increases more adsorption sites are available per unit mass of adsorbent added. Hence the amount of metal adsorbed from AMD water per unit mass of samples at equilibrium is moderately lower. For comparison, the same batch

experiments using the Wheal Jane AMD were also conducted using ground granulated blast furnace slag (GGBS) samples, an alternative sorbent for AMD, as shown in Table 6.2
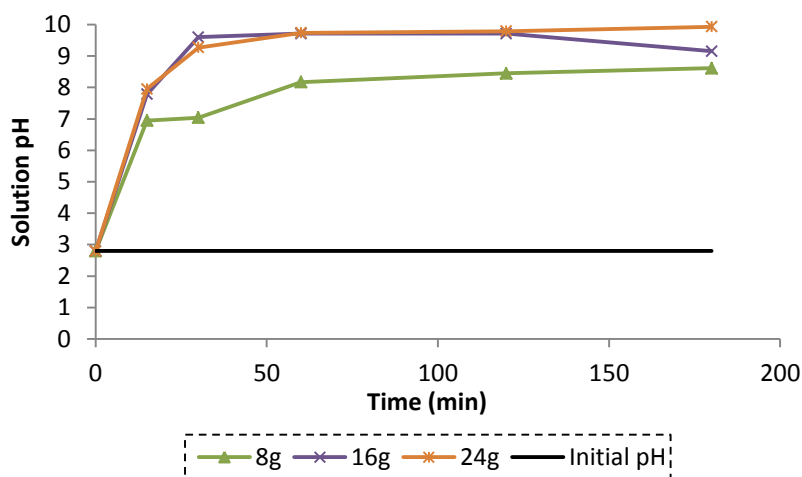


**Figure 6.3: Effect of BOS mass vs. solution pH trend on the adsorption of heavy metals from Wheal Jane AMD (200ml solution); particle size: +1mm,-1.4mm; initial pH~ 2.8.**

Higher adsorbent dosage promoted a better efficiency in the removal of heavy metal ions. As the final heavy metal concentration for both samples at 24g dosage show; BOS was able to treat copper, iron and zinc within EQS limit whereas GGBS sample was able to treat all four metal ions within the Environmental Quality Standard (EQS) values, which are 1.0, 0.5, 0.028 and 0.03 mg/l for $Fe^{3+}$, $Zn^{2+}$, $Cu^{2+}$ and $Mn^{2+}$ respectively (Bone, 2003).

The Wheal Jane mine water maximum consent limit for iron, copper, manganese and zinc in discharge water are 5.0, 0.08, 1.0 and 2.5mg/l respectively (Bone, 2003; United Kingdom). Results from Table 6.1 and 6.2 prove that BOS and GGBS as adsorbents are capable of treating real AMD as the final concentrations of four heavy metals ($C_e$) meet the maximum Wheal Jane consent limit requirement.
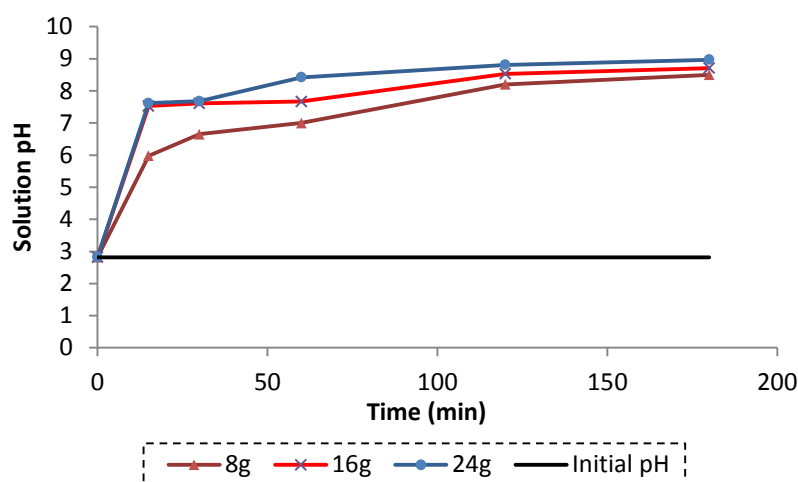
**Figure 6.4: Effect of GGBS mass vs. solution pH trend on the adsorption of heavy metals from Wheal Jane AMD (200ml solution); particle size: (dp<180 μm); initial pH~2.8.**

Figure 6.5 shows that the rate of metal removal is initially instant and progressive, that is within the first 15min. The kinetics of the neutralisation reaction is rapid as the pH increased through the sorption period. This effective removal can also be a result of the interactions of heavy metals with the adsorption sites on the surface of BOS, which can easily be accessed by the diffusing heavy metals. However the effect of precipitation of metal hydroxides must not be ruled out.

In general, all metals showed a very steep concentration decrease during the first 15min reaching plateau values with a very low residual concentration for the rest of the time intervals. After the initial period slower adsorption may be due to slower diffusion or the build-up of passive layers. The adsorption rates by GGBS was more or less equal to that obtained from BOS sample, however the adsorption rates of $Mn^{2+}$ by GGBS at lower dosages were much slower compared to BOS samples. This can be due to the presence of other metal cations and anions in Wheal Jane AMD which could affect and influence the heavy metal uptake capacity.
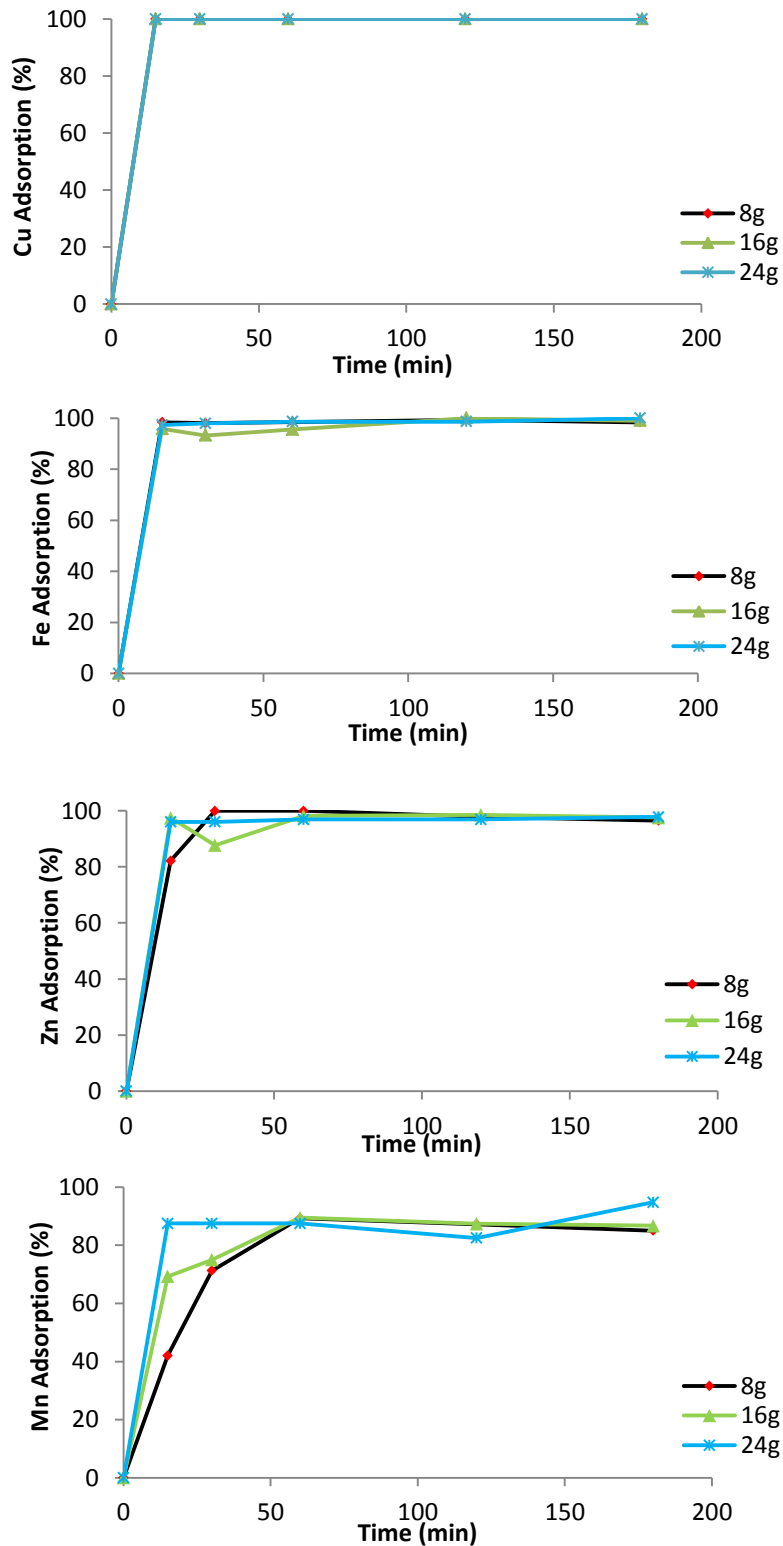
**Figure 6.5: The effect of mass of BOS on the adsorption of copper, iron, zinc and manganese from Wheal Jane solution (particle size: +1mm,-1.4 mm; initial: pH~ 2.8).**
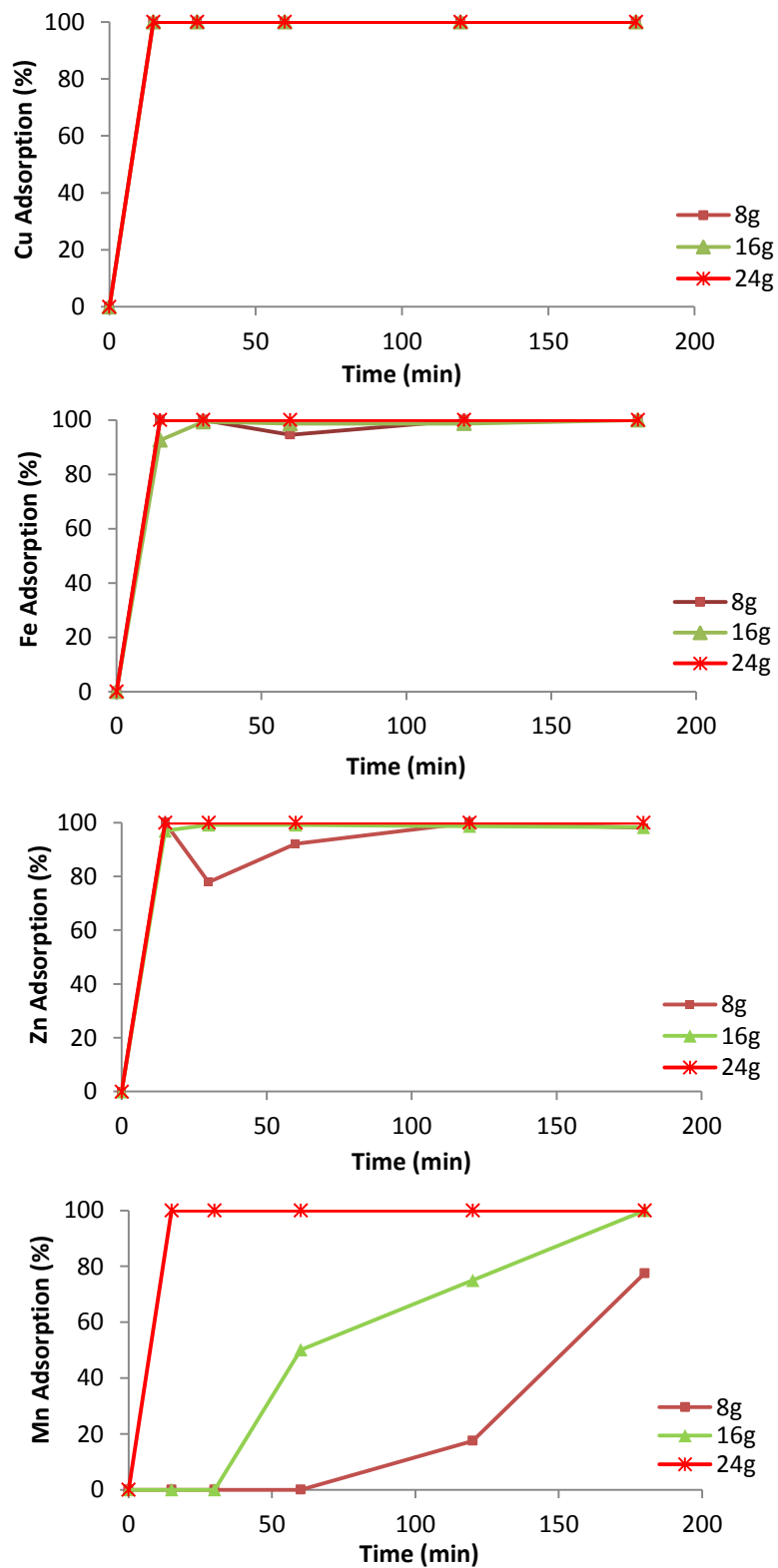
**Figure 6.6: The effect of mass of GGBS on the adsorption of copper, iron, zinc and manganese from Wheal Jane solution (particle size: dp<180μm; initial: pH~ 2.8).**

**Table 6.1: Effect of BOS mass on the removal of heavy metals from Wheal Jane AMD solution at pH ~ 2.8; 20°C; total contact time 180min; particle size: (+1mm,-1.4mm).**

| Heavy metal ions | Adsorbent Mass (g) | Percentage Adsorption (%) | Amount Adsorbed, qe (mg/g) | Final Concentration (mg/l) | Wheal Jane maximum consent limit (mg/l) | EQS limit (mg/l) |
|---|---|---|---|---|---|---|
| Copper | 8 | 100.00 | 0.0275 | 0 | 0.08 | 0.028 |
| | 16 | 100.00 | 0.0138 | 0 | | |
| | 24 | 100.00 | 0.0092 | 0 | | |
| Iron | 8 | 98.38 | 1.820 | 1.2 | 5.0 | 1.0 |
| | 16 | 99.04 | 0.916 | 0.71 | | |
| | 24 | 100.00 | 0.617 | 0 | | |
| Zinc | 8 | 96.52 | 0.555 | 0.8 | 2.5 | 0.5 |
| | 16 | 97.61 | 0.281 | 0.55 | | |
| | 24 | 97.87 | 0.188 | 0.49 | | |
| Manganese | 8 | 85.0 | 0.085 | 0.6 | 1.0 | 0.03 |
| | 16 | 86.75 | 0.043 | 0.53 | | |
| | 24 | 94.75 | 0.032 | 0.21 | | |

**Table 6.2: Effect of GGBS mass on the removal of heavy metals from Wheal Jane AMD solution at pH ~ 2.8; 20ºC; total contact time 180min; particle size: (dp<180μm).**

| Heavy metal ions | Adsorbent Mass (g) | Percentage Adsorption (%) | Amount Adsorbed, qe (mg/g) | Final Concentration (mg/l) | Wheal Jane maximum consent limit (mg/l) | EQS limit (mg/l) |
|---|---|---|---|---|---|---|
| **Copper** | 8 | 100.00 | 0.0275 | 0 | 0.08 | 0.028 |
| | 16 | 100.00 | 0.0138 | 0 | | |
| | 24 | 100.00 | 0.0092 | 0 | | |
| **Iron** | 8 | 100.00 | 1.850 | 0 | 5.0 | 1.0 |
| | 16 | 100.00 | 0.925 | 0 | | |
| | 24 | 100.00 | 0.617 | 0 | | |
| **Zinc** | 8 | 98.00 | 0.564 | 0.46 | 2.5 | 0.5 |
| | 16 | 98.26 | 0.283 | 0.4 | | |
| | 24 | 100.00 | 0.192 | 0 | | |
| **Manganese** | 8 | 77.50 | 0.078 | 0.9 | 1.0 | 0.03 |
| | 16 | 100.00 | 0.050 | 0 | | |
| | 24 | 100.00 | 0.030 | 0 | | |

In comparison to synthetic AMD treatment leaching effect does not appear throughout the sorption process. This can be due to the composition and concentration of real AMD solution, as in real acid mine drainage various species (cations and anions) of elements and metals are also present besides the four metals studied in this research. The sorption becomes complicated because of the ratios of heavy metals to one another resulting in solute-solute competitions and the solute-surface interactions. This indicates that besides chemisorption, ion exchange and precipitation some other complex mechanisms are predominantly involved.

### 6.2.1.2 Use of thermally pre-treated BOS Sludge in treating real AMD

From the kinetic studies carried out earlier in this study it was established that BOS sludge had extensive adsorption capacity in treating Wheal Jane AMD solution. A furnace was used for heating 24g BOS sample at 200$^{\circ}$C in an air atmosphere. BOS sample was contacted in 200ml Wheal Jane AMD solution and was agitated using the tumbling mill; the results are presented in Table 6.3. This experiment was carried out in duplicate and the percent standard deviation between two duplicate samples when analysing for copper, iron, zinc and manganese was $\pm 1.1\%$, 1.3%, 1.4% and 1.4% respectively.
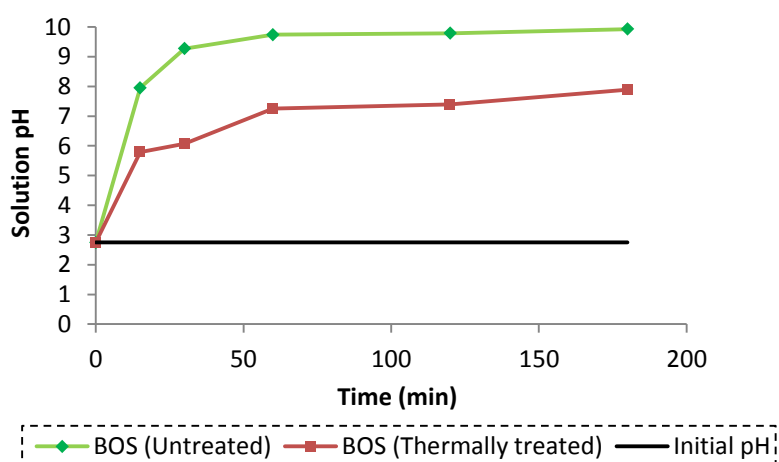


**Figure 6.7: Comparison between thermally pre-treated BOS and untreated BOS in treating Wheal Jane AMD after 180 minutes.**

**Table 6.3: Comparison between thermally pre-treated BOS and untreated BOS in treating Wheal Jane AMD after 180 minutes.**

| Heavy metals | % Adsorption | Final concentration (mg/l) | Wheal Jane maximum consent limit (mg/l) | Adsorption capacity adsorbed (mg/g) |
|---|---|---|---|---|
| **Copper** | | | | |
| *BOS (untreated)* | 100 | 0 | **0.08** | 0.0092 |
| *BOS (pre-treated)* | 73.7 | 0.289 | | 0.0068 |
| **Iron** | | | | |
| *BOS (untreated)* | 100 | 0 | **5.0** | 0.617 |
| *BOS (pre-treated)* | 96.6 | 2.50 | | 0.596 |
| **Zinc** | | | | |
| *BOS (untreated)* | 97.9 | 0.49 | **2.5** | 0.188 |
| *BOS (pre-treated)* | 92.6 | 1.698 | | 0.178 |
| **Manganese** | | | | |
| *BOS (untreated)* | 94.8 | 0.21 | **1.0** | 0.032 |
| *BOS (pre-treated)* | 85 | 0.60 | | 0.028 |

Figure 6.8 shows how heat/thermal pre-treatment of the BOS affects its efficiency in heavy metal ion adsorption. For BOS exposed under thermal condition at $200^{o}C$ for 60 min; the adsorption rate increased with time, but to a limit. The rate of adsorption of all heavy metal ions were reduced when thermally pre-treated BOS was used, copper and manganese adsorption rates were reduced significantly.
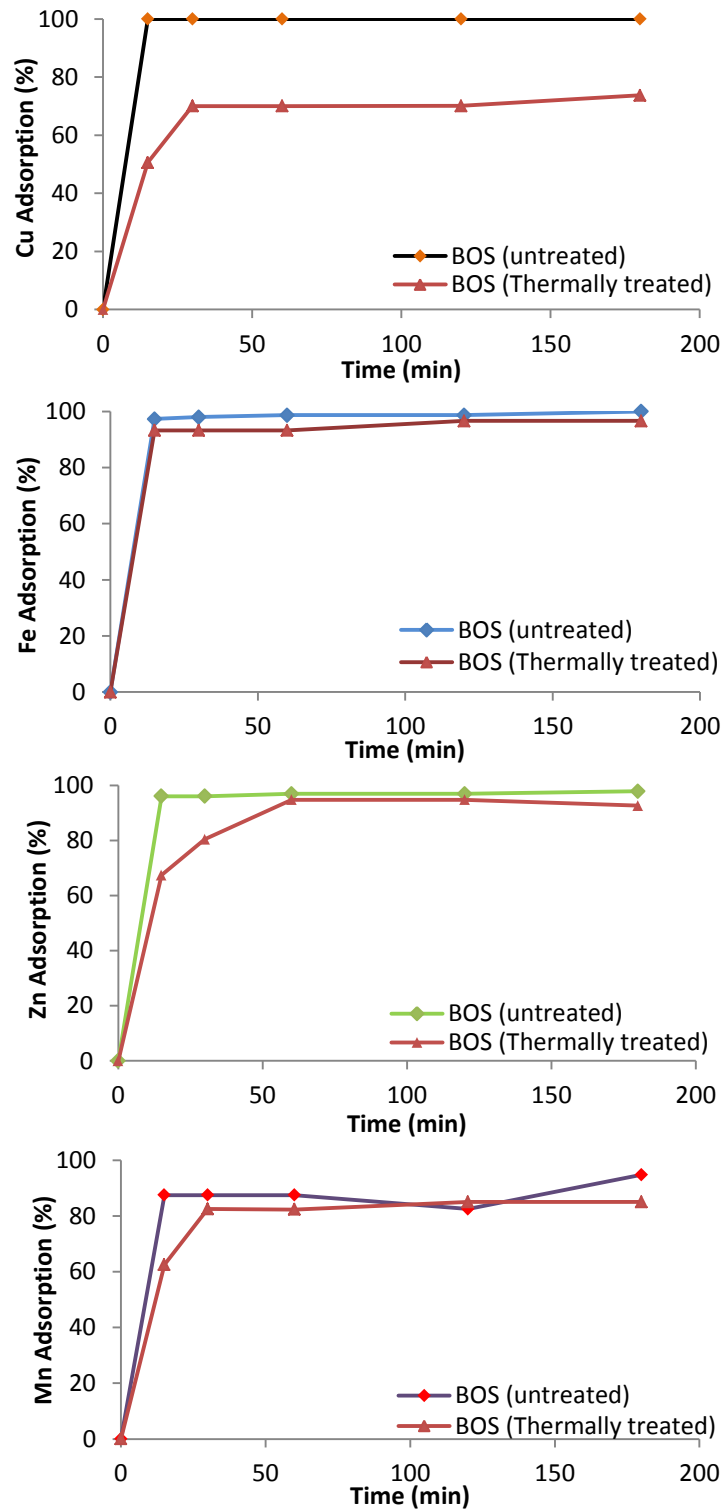
**Figure 6.8: Effect of thermally pre-treating BOS on its capacity to remove heavy metals from Wheal Jane mine AMD; particle size: +1mm,-1.4 mm; maximum contact time: 180 minutes.**

The physical properties of untreated BOS comply with a greater uptake of this sample rather than those of thermally pre-treated sample. Surface area measurements for thermal pre-treated BOS were determined by Nitrogen adsorption fitted to the BET equation (Brunauer 1943). The samples that were exposed to thermal condition had reduction in surface area (12.92 $m^2g^{-1}$) resulting in a lower total pore area (porosity 66.29%); this is because of thermal runaway, while the BOS structure collapses the porosity of BOS also decreases and hence the adsorption capacity is reduced. This is also observed in the difference in pH obtained through the sorption as untreated sample depicts higher pH, which in turn promotes higher metal removal levels, See Figure 6.7. Moreover, after thermally treating BOS its colour changed slightly; this may be an indication of a change in structure and/or composition of the BOS.

The Wheal Jane mine-water maximum consent limits for iron, copper, manganese and zinc in discharge water are 5.0, 0.08, 1.0 and 2.5 mg/l respectively (Bone, 2003; United Utilities, 2007). Table 6.3 shows that copper was not reduced to concentration levels less than the maximum consent limit by pre-treated BOS sample. The concentration of iron, zinc and manganese were lower than their respective consent limits, but the final concentration can be reduced if untreated BOS is used. The difference in the amount removed from solution by the two samples was substantial to justify the use of untreated BOS samples, since pre-treatment increases the cost of AMD treatment in practice. Therefore, untreated BOS can be used to treat AMD for the rest of this study.

### 6.2.1.3 Effect of initial solution pH on metal recovery

Wheal Jane AMD solution containing a mixture of heavy metal ions was contacted with 24g of BOS sample. The solution pH was varied from the initial pH (2.8) to 3.5 and 4.5 to investigate the influence of initial pH in relation to removal of heavy metals from real AMD solution using BOS sludge.

One of the methods of acid mine water treatment is chemical precipitation, which is related to increase of AMD pH (Plasari and Muhr, 2007). The pH required to precipitate most metals from AMD water ranges from pH 6 to 9 (except $Fe^{+3}$, which precipitates at pH >3.5) (Skousen et al., 2000). Increasing the pH of AMD water can lead to metal precipitation in the form of hydroxides and the interaction among the metals in AMD water can largely influence the reaction rate and oxidation state of the metals during contact with adsorbents or solvents.

For instance, manganese will be simultaneously co-precipitated with Fe precipitation from water at pH 8, only if the concentration of iron in the water is much greater than the manganese content (Sheremata and Kuyucak, 1996). This finding that in the presence of a large excess of Fe the Mn is precipitated at pH 8 may be confirmed in this study, as at pH 8 (89.1%) of manganese was recovered, as shown in Figure 6.9.

In oxygen-poor AMD iron is mainly as $Fe^{2+}$, which should be precipitated at pH 8 according to literature (Xinchao et al., 2005). In this study at pH 8 (95.4%) was recovered from solution. The reason for the iron precipitation across the studied range may also be progressive oxidation of $Fe^{2+}$ to $Fe^{3+}$ which iron precipitates in the form of $Fe(OH)_3$, which starts at pH>3.5. More iron is recovered when solution pH increased to 4.5 (98.5%) compared to pH 2.8 (95.4%), See Figure 6.11. According to literature zinc is precipitated in the range pH 5.5 to 7 in acid mine drainage (Sheremata and Kuyucak, 1996); pH 9.9 removed 94% of zinc from solution with initial pH of 2.8, as shown in Figure 6.9.
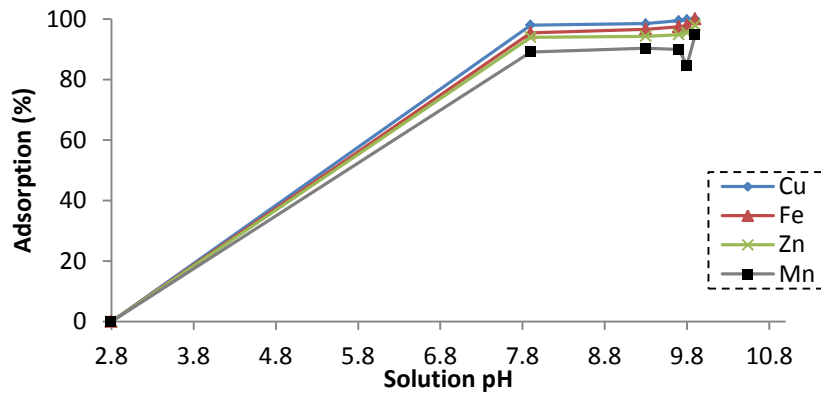
**Figure 6.9: Effect of initial pH (2.8) on the adsorption capacity of BOS. (24g BOS; 200ml Wheal Jane AMD solution (contact time: 3 hours; particle size: +1mm,-1.4mm).**
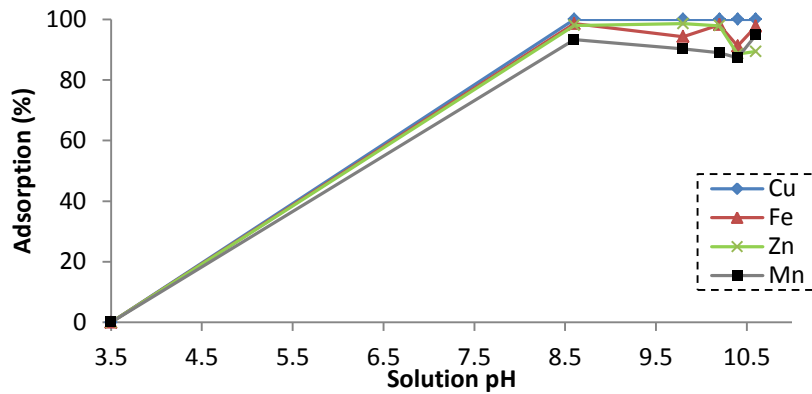


**Figure 6.10: Effect of initial pH (3.5) on the adsorption capacity of BOS. (24g BOS; 200ml Wheal Jane AMD solution (contact time: 3 hours; particle size: +1mm,-1.4mm).**
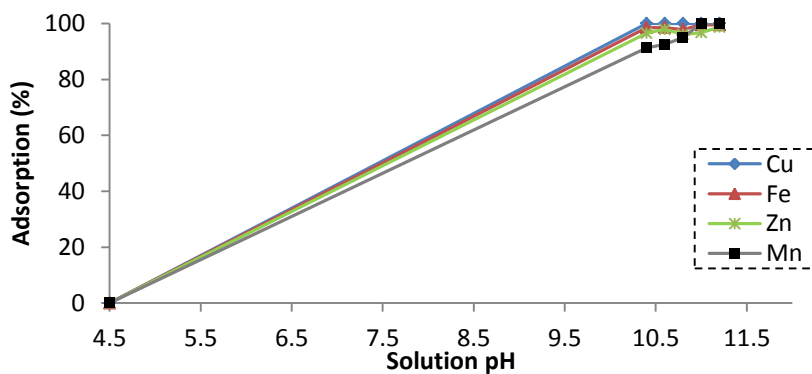


**Figure 6.11: Effect of initial pH (4.5) on the adsorption capacity of BOS. (24g BOS; 200ml Wheal Jane AMD solution (contact time: 3 hours; particle size: +1mm,-1.4mm).**

Figure 6.12 indicates that the rate of adsorption of heavy metals by BOS was extremely rapid for the first 15 minutes and then gradually reached equilibrium. An increase in the initial solution pH from 2.8 to 4.5 on copper adsorption was unaffected, whilst for iron, zinc and manganese the efficiency of BOS for adsorption is dependent on the initial solution pH. It is evident again that high pH promotes adsorption possibly by precipitation and/or ion exchange processes.

**Table 6.4: Effect of initial pH on the adsorption capacity of BOS. 24g BOS; 200ml Wheal Jane AMD solution (contact time: 3 hours; particle size: +1mm,-1.4mm).**

| Heavy metals | Final Concentration (mg/l) | Wheal Jane maximum consent limit (mg/l) |
|---|---|---|
| **Iron** | | |
| *pH 2.8 (Initial)* | 1.2 | **5.0** |
| *pH 4.5* | 0.4 | |
| **Manganese** | | |
| *pH 2.8 (Initial)* | 0.6 | **1.0** |
| *pH 4.5* | 0 | |
| **Zinc** | | |
| *pH 2.8 (Initial)* | 1.0 | **2.5** |
| *pH 4.5* | 0.3 | |
| **Copper** | | |
| *pH 2.8 (Initial)* | 0 | **0.08** |
| *pH 4.5* | 0 | |

Jenke and Diebold (1983) reported removal of metals from AMD by adding sulphide and subsequent oxidation and selective titration. Cu and Zn have precipitated in the form of sulphides and Fe, Al, Mn and Mg were recovered in the form of hydroxides. Up to 85 % of metals were recovered in different pH regimes.

In a study conducted at Slovakia, tests on Fe, Cu, Mn and Zn precipitation was investigated by raw AMD. The initial concentrations of copper, iron, zinc and

manganese in AMD were 0.46, 256.8, 7.1 and 23.9 mg/l respectively and the initial AMD pH was 3.06 close to that of Wheal Jane mine AMD. 500ml of real AMD similar to Wheal Jane mine (non-coal mines) was neutralised by NaOH (0.5 mol/L) as a precipitating reagent. Results reported that AMD neutralisation with NaOH to the pH of 8.2 was achieved which removed 92.3 % of copper, 93.3% of zinc, 96.6 % of iron and 15.9 % of manganese (Balintova and Petrilakova, 2011).

The Wheal Jane mine water maximum consent limit for iron, copper, manganese and zinc in discharge water are 5.0, 0.08, 1.0 and 2.5mg/l respectively (Bone, 2003; United Kingdom). Results show that BOS as an alternative sorbent in contact with different initial solution pH is capable of treating real AMD as the final concentrations of four heavy metals ($C_e$) meet the maximum consent limit requirement, as shown in Table 6.4.

The final concentrations obtained from pH 4.5 fall within the Environmental Quality Standard (EQS) values, which are 1.0, 0.5, 0.028 and 0.03 mg/l $Fe^{3+}$, $Zn^{2+}$, $Cu^{2+}$ and $Mn^{2+}$ respectively (Bone, 2003). Therefore it is recommended that BOS can be used to treat real AMD solutions.
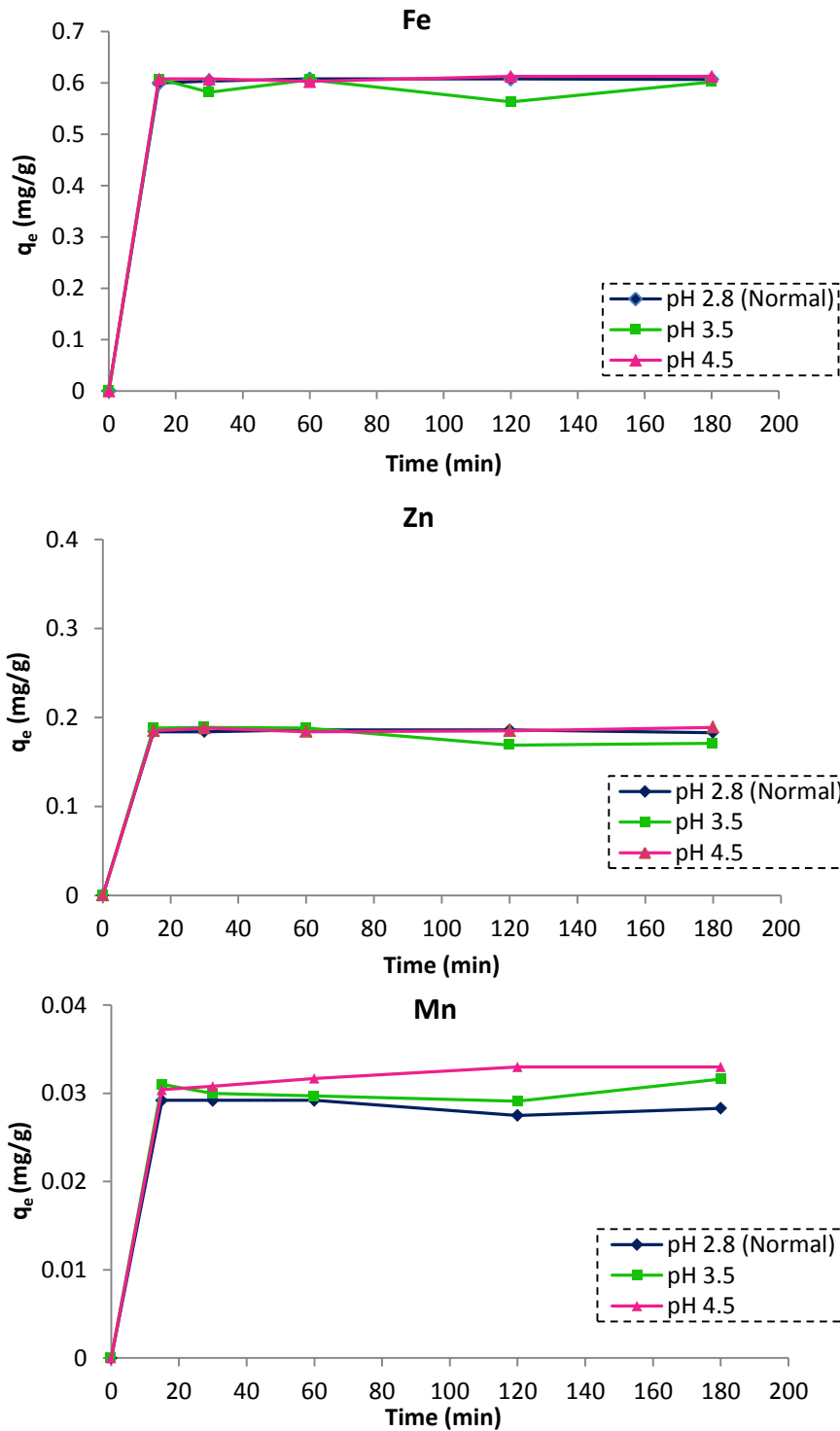
**Figure 6.12: Comparison of uptake ($q_e$) of heavy metal ions at different starting pH (24g of BOS samples; 200ml solution agitated over tumbling mill at 110rpm (contact time: 3 hours; particle size: +1mm,-1.4mm).**

### 6.2.1.4 Desorption/ Regeneration

A good adsorbent must have a high adsorption capacity, but also needs to exhibit good regeneration for multiple usages (Richardson et al., 2002). Desorption of heavy metal ions from an adsorbent or the regeneration of an adsorbent is of great practical importance. This is one of the characteristics which is considered in choosing an adsorbent for any practical application (Richardson et al., 2002). In this study a waste by-product is being used as an adsorbent with the main aim of maximum utilisation, hence regeneration of this material is not process priority.

In this study 200 ml of Wheal Jane solution was contacted with 24g of BOS sludge for 180 minutes (untreated run). The loaded solid samples were filtered and then separately contacted with NaCl or sulphuric acid for 20 minutes. Two different desorption reagents were used in this study: $H_2SO_4$ at a concentration of 2 % (wt) and pH $\approx$ 0.98 $\pm$ 0.1 and NaCl at a concentration of 20 g/l and pH $\approx$ 5.77. Desorption experiments were carried out at 19 $\pm$2ºC. The mixture was filtered and solution analysed using the AAS.

Two adsorption − desorption cycles were performed for all 4 heavy metal ions. The effect of regeneration on adsorption capacity is presented in Table 6.5. For manganese and zinc, adsorption capacity of BOS sludge regenerated using NaCl showed a promising result; despite the high concentration of sulphuric acid it was in favour of iron uptake in comparison to manganese and zinc. Desorption takes place because of the displacement of the heavy metal ions from adsorption sites on the BOS sludge structure by either $H^+$ ions, in the case of acid or Na+ ions from NaCl solution. This process is mainly driven by the concentration driving force, which favours $H^+$ and $Na^+$ ion adsorption because of the high solution concentrations used.

**Table 6.5: The percentage recovery of heavy metals from BOS sludge by regeneration.**

| Heavy metals | % Recovered over cycle 1 | % Recovered over cycle 2 | % adsorption Untreated BOS |
|---|---|---|---|
| **Copper** | | | |
| NaCl | 66.31 | 44.75 | **100.00** |
| $H_2SO_4$ | 42.10 | 11.22 | |
| **Iron** | | | |
| NaCl | 92.45 | 90.12 | **100.00** |
| $H_2SO_4$ | 97.39 | 93.71 | |
| **Zinc** | | | |
| NaCl | 93.22 | 89.96 | **97.87** |
| $H_2SO_4$ | 87.35 | 80.48 | |
| **Manganese** | | | |
| NaCl | 72.40 | 54.82 | **94.75** |
| $H_2SO_4$ | 64.25 | 52.13 | |

According to Table 6.5 it is evident that neither of regenerating agents performed as anticipated. The desorption series follow this order: iron>zinc>manganese>copper and adsorption series follow this trend: Copper=iron>zinc>manganese. There is an observable drop in the adsorption capacity of BOS sludge that has been regenerated using sulphuric acid, as shown in Table 6.5. The adsorption capacity of regenerated BOS sludge dropped, since there was a decrease in adsorption capacity from cycle 1 to 2; this is because of acid resulting in neutralisation of much of alkalinity present in BOS.

This drop in capacity may also be due to the possible destruction and distortion of the BOS sludge structure by acid dissolution. Zhou and Haynes (2010) also found that sorption capacity of blast furnace and steel slags on removal of heavy metals such as of $Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$, $Zn^{2+}$ and $Cr^{3+}$ from aqueous solution also decreased appreciably,

hence it was evident that acid is not a suitable reagent for regeneration of blast furnace or steel slags.

Some other reagents, such as the metal complexing agent EDTA might however be appropriate (Santona et al. 2006). The effectiveness of different regenerating solutions such as $NaNO_3$, HCl, $CaCl_2$ at different concentrations could also be investigated if regeneration is considered to be an option. The adsorption capacity of BOS sludge regenerated using NaCl was also reduced. Therefore, regenerated BOS sludge cannot effectively meet the maximum Wheal Jane consent limit thus insuring that regenerated BOS sludge can handle only relatively dilute AMD solutions or preferably downstream to another treatment process.

## 6.2.1.5 BOS Sludge as pellets for AMD treatment

The potential of BOS sludge as an adsorbent for the treatment of Wheal Jane acid mine drainage solution was determined by using a pelletising method. BOS sludge samples were mixed with water and Bentonite (binder) and made into mini-pellets (diameter of +1-1.5cm). Mini-pellets (24 g) were contacted with 200 ml of real AMD; the mixture was agitated for 180 minutes and the samples were collected at regular intervals and analysed using AAS. Figure 6.13 illustrates the effect of BOS pellets on the adsorption of heavy metal ions.
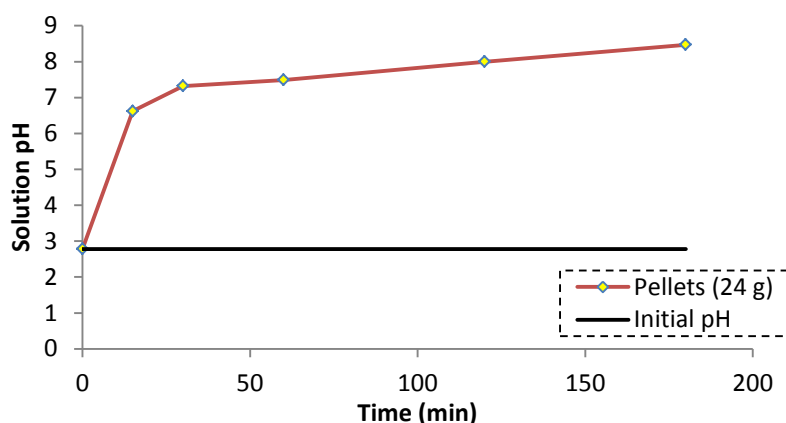


**Figure 6.13: Effect of BOS pellets vs. solution pH on the adsorption of heavy metals from Wheal Jane AMD.**

For adsorption the first stage of this fast adsorption can potentially correspond to ion exchange of calcium oxide ($Ca^{2+}$) of BOS and the acidic composition of AMD solution (neutralisation behaviour). The results indicate that the heavy metal uptake capacity increased considerably as contact time increases (that is tending toward equilibrium). All copper and iron were adsorbed from solution within the first 15 min of the reaction in comparison to manganese, as shown in Figure 6.14. The zinc adsorption rate was slower compared to copper and iron for the first 15 min and manganese uptake starts after 15min with an observable drop in concentration .After 120 min the adsorption levels off as equilibrium is reached and the final percent adsorptions of all metals were 100%.
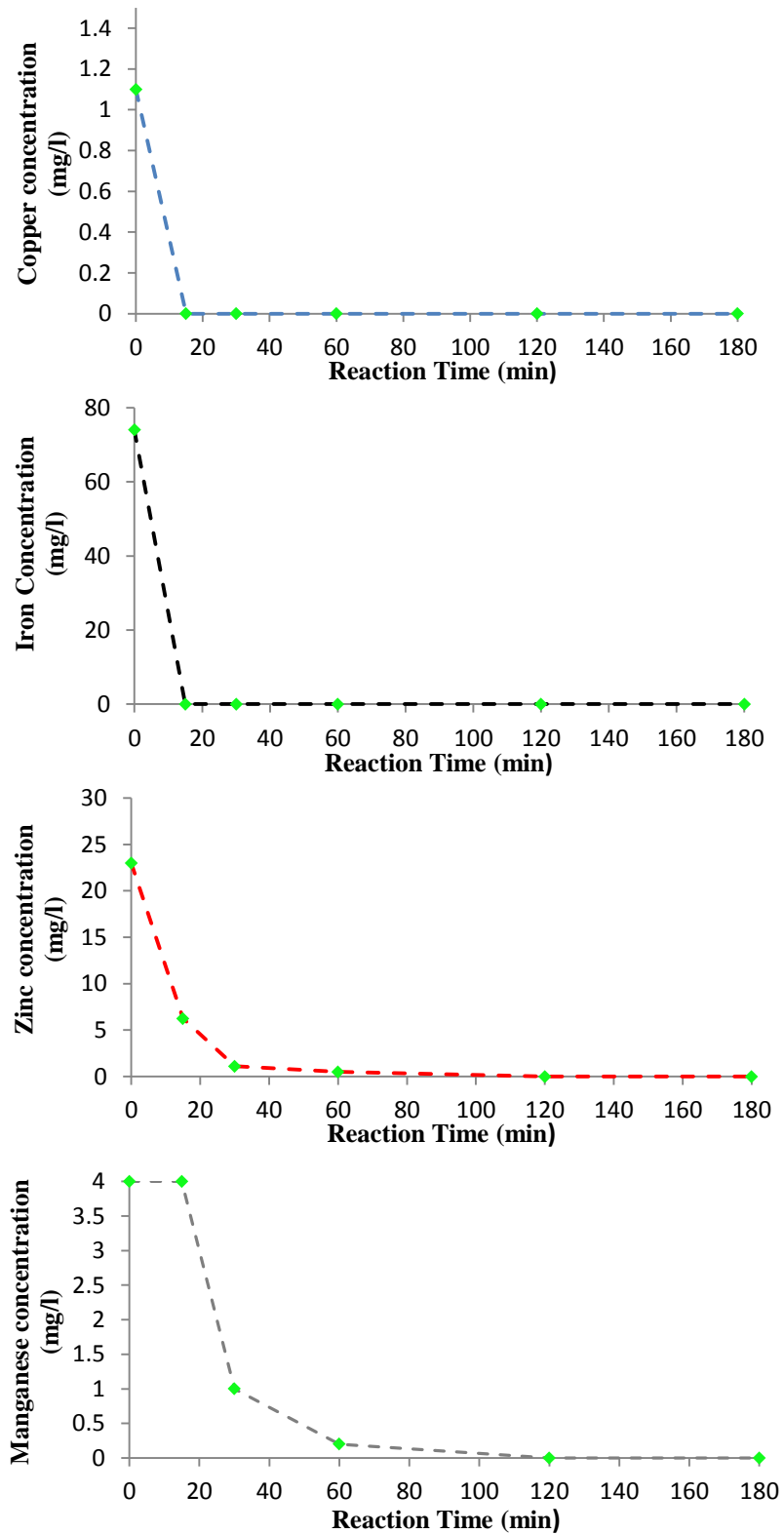
**Figure 6.14: Effect of BOS pellets capacity on removal of heavy metals from Wheal Jane mine AMD solution.**

The Wheal Jane mine water maximum consent limit for iron, copper, manganese and zinc in discharge water are 5.0, 0.08, 1.0 and 2.5mg/l respectively (Bone, 2003; United Kingdom). Hence the results demonstrate that BOS pellets are capable of treating Wheal Jane AMD as the final concentrations of four heavy metals meet the maximum consent limit requirement.

The final concentrations obtained from pelletising method also fall within the Environmental Quality Standard (EQS) values, which are 1.0, 0.5, 0.028 and 0.03 mg/l $Fe^{3+}$, $Zn^{2+}$, $Cu^{2+}$ and $Mn^{2+}$ respectively (Bone, 2003). Therefore it is recommended that using a binder which provides further physical strength, and extra adsorption ability to BOS in acidic conditions, BOS sludge can effectively be used to treat Wheal Jane AMD.

## 6.3 Conclusion

Kinetic studies indicated that the rate of adsorption of the heavy metals by BOS sludge was rapid for the first 15 minutes and then gradually decreased. About 100%, 100%, 97% and 94% of copper, iron, zinc and manganese respectively were adsorbed from Wheal Jane AMD solution. Removal of the heavy metal ions was not only due to ion exchange or adsorption but also due to co-precipitation.

There were a number of operational conditions which were found to influence and increase the rate of metal uptake by BOS; these include an increase in adsorbent dosage; an increase in initial solution pH and for thermal treatment of BOS prior to adsorption, the results showed that thermally treated BOS sludge did not enhance the capacity and efficiency of BOS sludge in treating AMD water.

The adsorption capacity of regenerated BOS sludge reduced, since there was a drop in the adsorption rates through regeneration cycles. Thus, regenerated BOS sludge cannot effectively meet the maximum Wheal Jane consent limit thus insuring that regenerated BOS sludge can handle only relatively dilute AMD solutions.

BOS sludge as mini-pellets were also used to treat AMD in batch mode, the adsorption capacity of BOS pellets was found to be greater than the normal contact of BOS with AMD with 100% adsorption rates for all respective cations. Although the results show that BOS sludge can be used effectively for the removal of heavy metal ions from real acidic solutions and replace other sorbents such as natural zeolite, activated carbon or steel slag. However using BOS sludge for real AMD treatment is fledgling science and further research and studies are needed in this area if this concept is to be fully utilised on an industrial scale.

Table 6.6 shows the performance of BOS sludge in treating Wheal Jane mine AMD compared to previous work carried out in this area at the University of Birmingham. The results from this study were an improvement on other research work carried out at the University of Birmingham for the treatment of Wheal Jane mine AMD.

**Table 6.6: Research carried out at the University of Birmingham for the treatment of Wheal Jane mine AMD and the results obtained.**

| Heavy metals | BOS sludge [a] (This study) | GGBS [b] (This study) | Blast furnace flue dust [c] (This study) | BOS pellets[d] (This study) | GBS [e] (This study) | Blast furnace slag [f] | Calcium Alginate Beads [g] | Column Flotation[h] | Natural Zeolite [i] | Synthetic Zeolite [J] |
|---|---|---|---|---|---|---|---|---|---|---|
| Copper (%) | 100.00 | 100.00 | --- | 100 | 100.00 | --- | 42.00 | 99.00 | 85.6 | 95.90 |
| Iron (%) | 100.00 | 100.00 | 100.00 | 100 | 98.90 | 97.00 | 90.00 | 76.00 | 99.8 | 99.40 |
| Zinc (%) | 97.90 | 100.00 | 98.13 | 100 | 99.60 | 67.00 | 32.00 | 89.00 | 68.7 | 100.00 |
| Manganese (%) | 94.80 | 100.00 | --- | 100 | 95.90 | 22.00 | 32.00 | --- | 39.6 | 100.00 |

a.  This study; Experimental conditions: Batch mode, BOS sludge used as 24g sample, particle size: +1mm,–1.4 mm, Wheal Jane pH ~ 2.7- 2.9, 200 ml AMD solution, contact time 180 minutes, agitation rate 110 rpm.
b.  This study; Experimental conditions: Batch mode, GGBS used as 24g sample, particle size: dp<180μm, Wheal Jane pH ~ 2.7- 2.9, 200 ml AMD solution, contact time 180 minutes, agitation rate 110 rpm.
c.  This study; Experimental conditions: Batch mode, Blast furnace flue dust used as 16g sample, particle size: dp<600μm,, Wheal Jane pH ~ 2.7- 2.9, 200 ml AMD solution, contact time 180 minutes, agitation rate 110 rpm.
d.  This study; Experimental conditions: Batch mode, BOS pellets binded with Bentonite used as 24g sample, particle size: +1mm,–1.4 mm, Wheal Jane pH ~ 2.7- 2.9, 200 ml AMD solution, contact time 180 minutes, agitation rate 110 rpm.
e.  This study; Experimental conditions: Batch mode, Granulated Blast furnace slag used as 16g sample, particle size: +1mm,–1.4 mm, Wheal Jane pH~ 2.7- 2.8, 200 ml AMD solution, contact time 180 minutes, agitation rate 110 rpm.
f.  Darkwah, L., 2005. Experimental conditions: 0.5 g blast furnace slag in 50 ml solution in a batch reactor. Agitation rate 200 rpm.
g.  Nantumbwe, B.B., 2007. Experimental conditions: Column height 100 cm; flow rate 50 ml/min; contact time ≈ 500 minutes.
h.  Lynch, B., 2003. Experimental conditions: Protocol CA540 dosage 15ml/l, pH 9.0, froth depth 16 cm, air flow 600 cm3/min.
i.  Motsi et al., 2010. Experimental conditions: Batch mode, Natural zeolite used as 20g sample, particle size: 1-3mm, 100 ml AMD solution, contact time 360 minutes, agitation rate 110 rpm.
j.  Motsi et al., 2010. Experimental conditions: Batch mode, Synthetic zeolite used as 3.7g sample, particle size: ≤ 20 μm, 100 ml AMD solution, contact time 360 minutes, agitation rate 110 rpm.

# CHAPTER 7

# REACTOR STUDIES FOR SYNTHETIC AMD TREATMENT

## 7.1 Introduction

Semi-continuous operations can be performed in practice to provide preliminary data required in design procedures and treatment of real AMD. A semi pilot scale reactor was designed and built to scale up for AMD treatment, this reactor was operated as a fixed bed and mixed vessel. A number of parameters were tested in order to investigate their affect in this study. These consist of the effect of adsorbent dosage (g/ml), adsorbent particle size, initial metal concentration and different mixing regimes. This chapter presents the results and discussion on efficiency of BOS in removal of $Fe^{3+}$, $Cu^{2+}$, $Zn^{2+}$ and $Mn^{2+}$ from synthetic AMD solution in a semi-pilot scale reactor tank.

## 7.2 Treatment of synthetic acid mine drainage (sAMD)

### 7.2.1 Preliminary test of BOS

From the results obtained earlier in this thesis, removal rates and capacities from batch experiments depict high potential of BOS as an adsorbent. Nonetheless the capacity of BOS for the treatment of synthetic acid mine drainage was determined in a reactor tank by contacting 40L of multi-component synthetic AMD solution (mixture of all four metal ions) with 2kg of BOS sample. The mixtures were agitated with flow rate of 181 ml/min using a mechanical agitator at a speed of 45rpm. The samples were withdrawn during each experiment at predetermined time intervals and filtered and the filtrate was analysed for heavy metal ions using the AAS.

From previous batch experiments earlier carried out in this study, it is indicated that the adsorption of heavy metal ions from solution onto BOS was due to a number of

different mechanisms such as ion exchange, chemisorption and precipitation. The rate of adsorption was again dependent upon pH as discussed in previous chapters; BOS has neutralising potential with a high porosity level. Hence when the exchangeable cations present in BOS are equilibrated with acidic solution; the solution pH increases as reaction proceeds, See Figure 7.1.
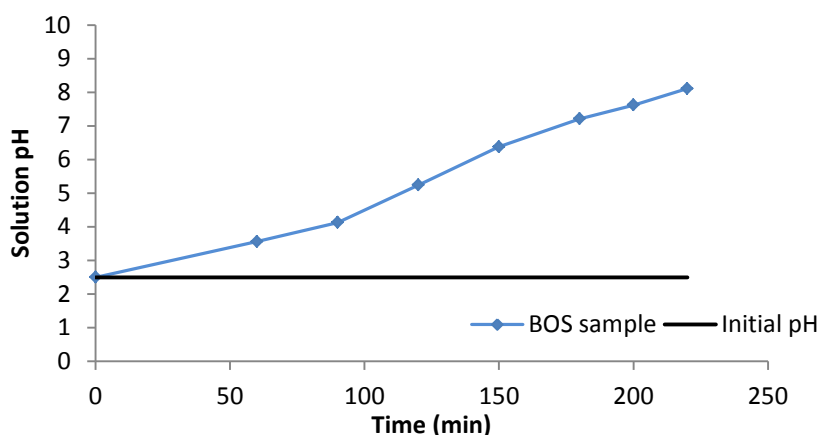


**Figure 7.1: pH change during adsorption by BOS from 40L of sAMD solution containing 5 mg/l of $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$.**

More $Cu^{2+}$ and $Zn^{2+}$ ions were adsorbed from solution in comparison to the other cations ($Mn^{2+}$, $Fe^{3+}$). The order of adsorption from this sorption experiment was found to be $Cu^{2+}>Zn^{2+}>Fe^{3+}>Mn^{2+}$. Percent adsorptions of 100%, 91%, 86.9 and 80.8% for $Cu^{2+}$, $Zn^{2+}$, $Fe^{3+}$ and $Mn^{2+}$ respectively were achieved after 220 minutes of contact with BOS sample, as shown in Figure 7.2.
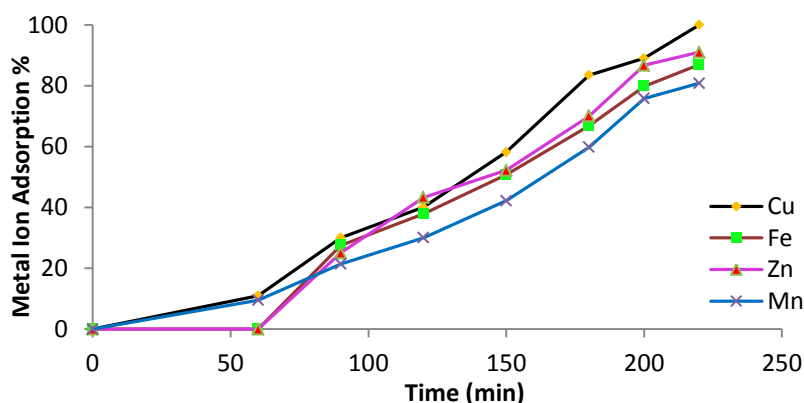


**Figure 7.2: The adsorption of heavy metal ions adsorbed from 40L of sAMD solution containing 5 mg/l of $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$.**

172

The order of adsorption from batch experiments carried out earlier in this study ($Cu^{2+}>Fe^{3+}>Zn^{2+}>Mn^{2+}$) is similar to the order obtained from this reactor study. However the difference in the orders of adsorption by BOS for the removal of heavy metal ions can be due to different operational conditions. Other factors that influence the difference in adsorption rate of heavy metal ions can be related to metal ionic radii, difference in electronegativities and high affinity of BOS for specific metals and generally limitation in the BOS's adsorptive properties. The results in Figure 7.3 show that at 90 min, the adsorption sites are widely available and the cations interact readily with the active sites on BOS and hence the adsorption rates increase.

The final heavy metal concentrations were 0, 0.7, 0.5 and 0.9 mg/l of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ respectively. The Wheal Jane mine water maximum consent limits for iron, copper, manganese and zinc in discharge water are 5.0, 0.08, 1.0 and 2.5 mg/l respectively (Bone, 2003). The concentrations of copper, iron, zinc and manganese were reduced adequately to meet the consent limit requirement.
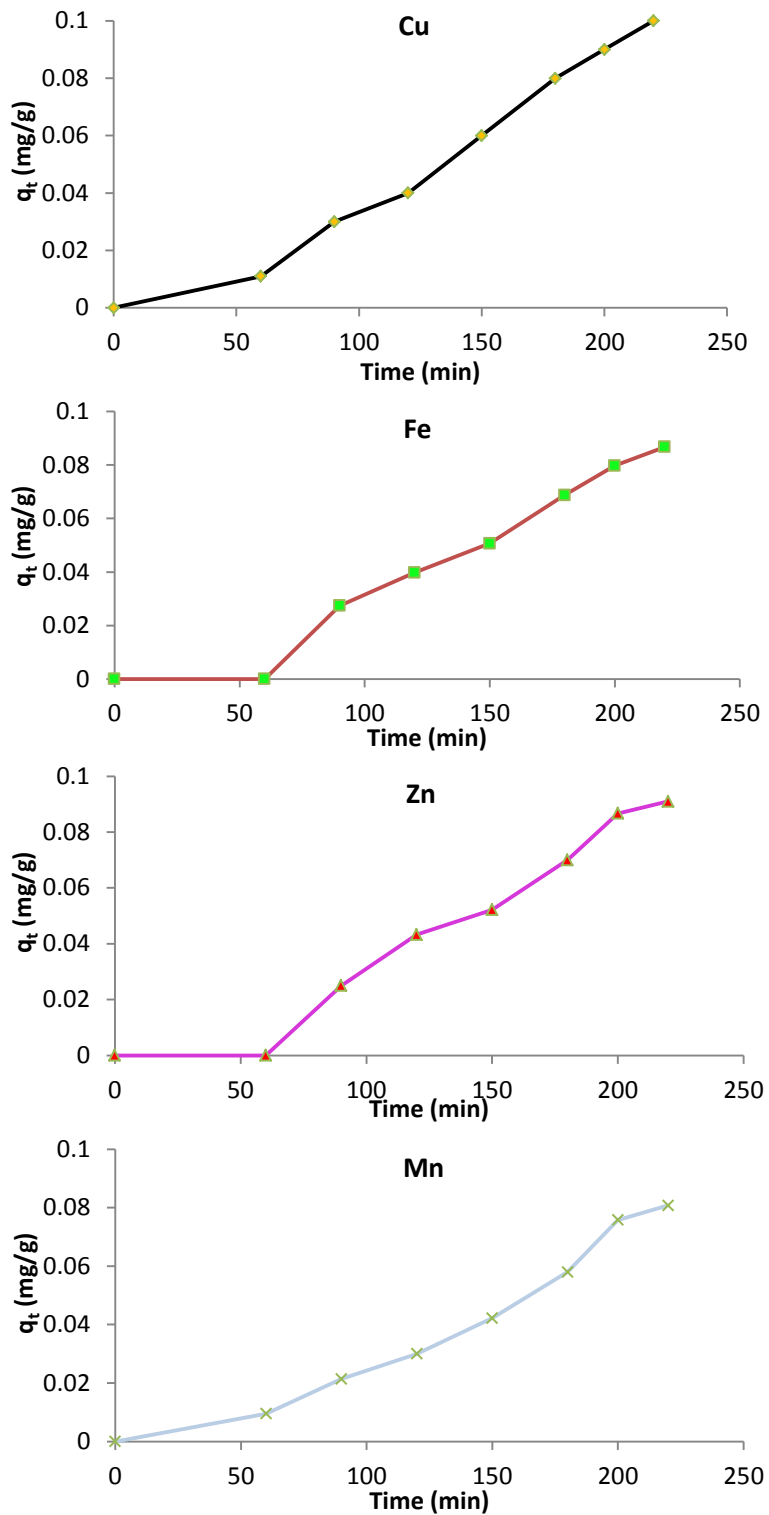
**Figure 7.3: The amount of heavy metal ions adsorbed from 40L of sAMD solution containing 5 mg/l of $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$.**

## 7.2.2 Effect of agitation on metal recovery

Agitation affects reaction rate by increasing the amount of collisions between the adsorbent and adsorbate with one another, thus speeding up the reaction rate. Agitation is an important parameter in adsorption as it helps in overcoming the external mass transfer resistance (Sensel and Myers, 1992). Solid-liquid mass transfer is critical in many industrial processes; agitated vessels are often used because they are very effective in suspending solids particles, ensuring that all the surface areas available are utilised and hence leading to an increased reaction rate. Agitation of AMD solution and BOS was carried out using a mechanical agitator at two different blade speeds (20 and 45 rpm). The result of the effect of agitation was compared to non-mixing (standing mode) and shown in Figures 7.4 and 7.5.
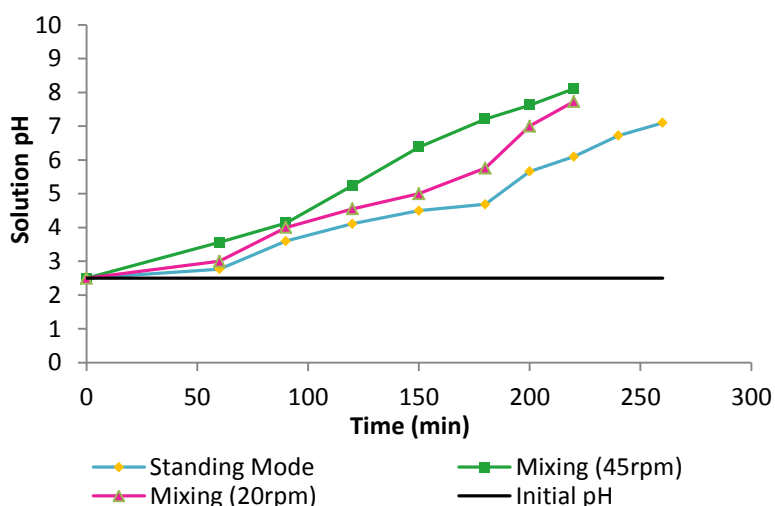


**Figure 7.4: Comparison of change in solution pH in three different modes (2kg BOS sample; particle size: +1mm,-1.4mm; Initial solution pH: 2.5; flow rate: 181 ml/min up flow).**

As Figure 7.4 shows that the pH level increases as agitation is induced. This is attributed to the increased sorbent area and the availability of more sorption sites. This leads to an increase of the amounts of adsorbed metals by BOS. For standing test different behaviour of BOS for the sorption of $Fe^{3+}$, $Mn^{2+}$ and $Zn^{2+}$ was observed.
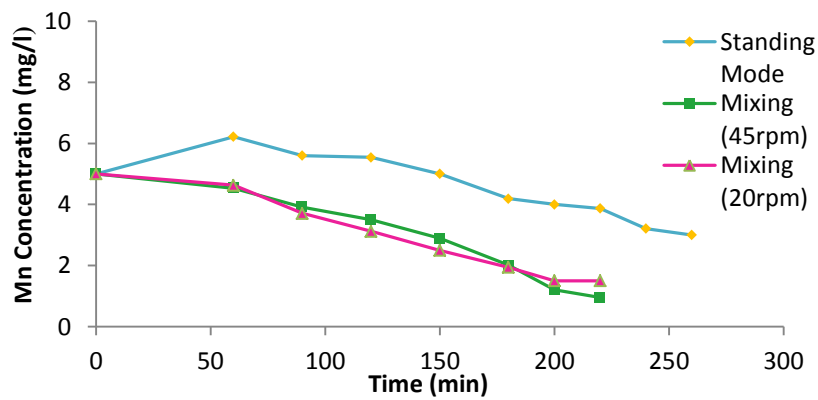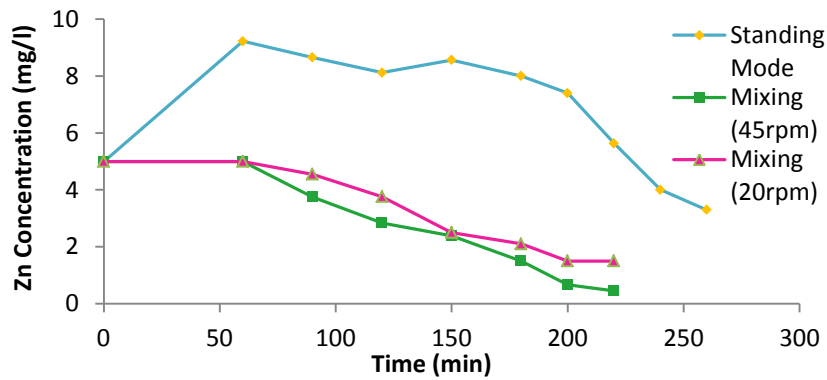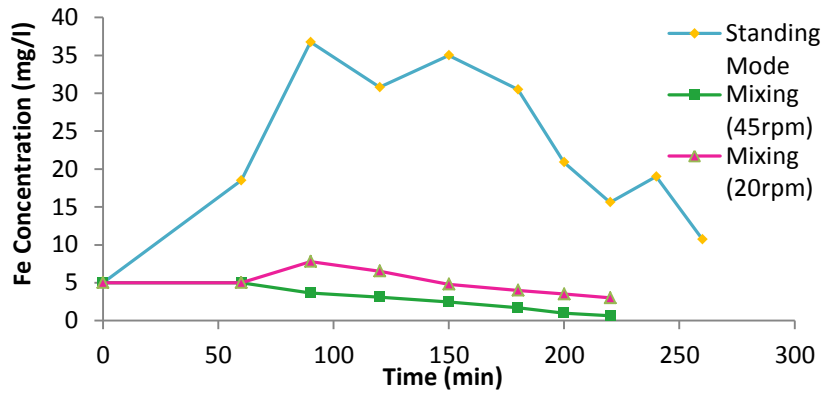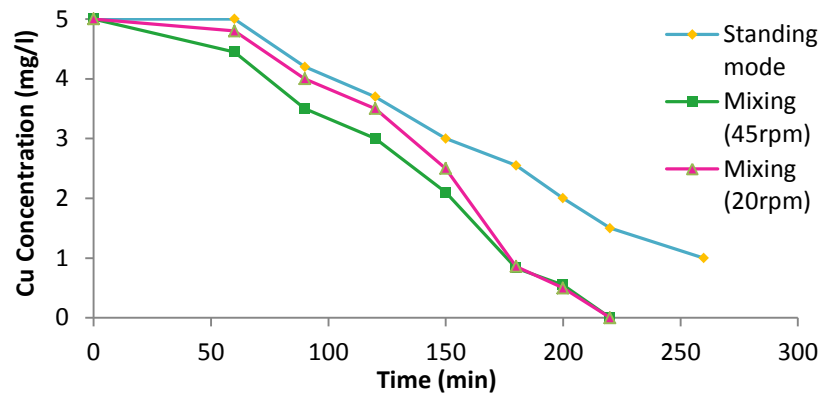
**Figure 7.5: Comparison of adsorption capacity from sAMD multi-component mixture solution.**

Figure 7.5 shows that the metal removal efficiency and adsorption rate increased as the speed of agitation increased for all heavy metal ions. The difference in the amount of heavy metal ions removed from solution at the different speeds (20 and 45rpm) reduces with time. For the standing mode more $Zn^{2+}$, $Cu^{2+}$ and $Mn^{2+}$ ions were adsorbed from solution in comparison to $Fe^{3+}$ cations, however as Figure 7.5 shows for the standing mode at 60min for $Mn^{2+}$, $Zn^{2+}$ and $Fe^{3+}$ leaching of these respective metal ions into solution were observed. The amount of $Fe^{3+}$ ions adsorbed by BOS followed an unsteady rate through the sorption, at 90 min a large amount of iron leached out from BOS into solution and thereafter most $Fe^{3+}$ cations were still remained in the solution as there was no indication of recovery. For $Zn^{2+}$ and $Mn^{2+}$ as contact time increases, the uptake rate begins to increase since these metal ions would have had sufficient time to diffuse from solution through the surface and layers of the BOS bed.

Since there is no agitation for standing mode operation, desorption seems to take place, this is evident for $Fe^{3+}$ and $Zn^{2+}$. This can be as result of desorption of these metal ions from the layers of BOS. Since the system is not agitated the solid-liquid contact is not effective hence most BOS particles may not be totally in contact with flowing AMD, resulting in poor adsorption rates and hence the slowing down of the uptake rate.

Mixing and apparent reaction rate are related for the reaction to occur; the reactants need to be homogenised at the molecular scale so that molecules can collide. If the mixing is fast, the intrinsic chemical kinetics governs the rate of production of new species (Boon-long et al., 1978). Furthermore agitation of the mixture not only results in a decrease in film transfer resistance but also results in the abrasion of BOS, producing freshly broken and highly reactive sites on large surface areas; thus increasing the chances of faster collisions. The mixing in plant practice of BOS as a sorbent for AMD treatment is an important factor to take into consideration predominately in designing and modelling of CSTR reactors.

The final concentrations of $Fe^{3+}$ were 0.66 and 3 mg/l for 45 and 20rpm respectively. Based on the sorption results of $Mn^{2+}$ and $Zn^{2+}$, it is suggested that the uptake of these two particular cations and $Fe^{3+}$ were highly affected by agitation. The agitation effect

suggests that leaching of heavy metals from BOS into solution can be prevented during sorption. Regardless of agitation being often costly in adsorption processes and practices, the difference in the amount removed from solution by mixing was significant to justify the use of fast mixing (45rpm) of BOS samples in the treatment of synthetic AMD in this study.

### 7.2.3 Effect of particle size of BOS on metal recovery

The rate of chemical reactions in terms of adsorption that involve solids depends on the particle size of the solid and also the intraparticle diffusion resistance. Smaller reactant particles provide a greater surface area which increases the chances for particles collisions thus sorption rates increase. Two particle size ranges were used: +0.18mm,-0.5 mm and +1mm,- 1.4mm. The use of very fine particles was avoided in the reactor tank as it can cause operational difficulty in particular at the filtering stage.

The results as shown in Figure 7.6 indicate that decreasing the particle size of BOS results in higher heavy metal removal rates and efficiencies, but as contact time increases, (that is, tending toward equilibrium) there is a slight decrease in the degree of the effect of particle size on adsorption in particular for $Cu^{2+}$ adsorption. Figure 7.6 also indicates that $Mn^{2+}$ was the most affected cation; reduction in particle size caused an increase of 15.2% in adsorption rate of $Mn^{2+}$. As Figure 7.6 for $Zn^{2+}$ and $Fe^{3+}$ depicts smaller particle size range requires shorter residence time predominantly in the beginning of sorption which ultimately leads to a shorter distance of diffusion between the adsorbent and the adsorbate through sorption.
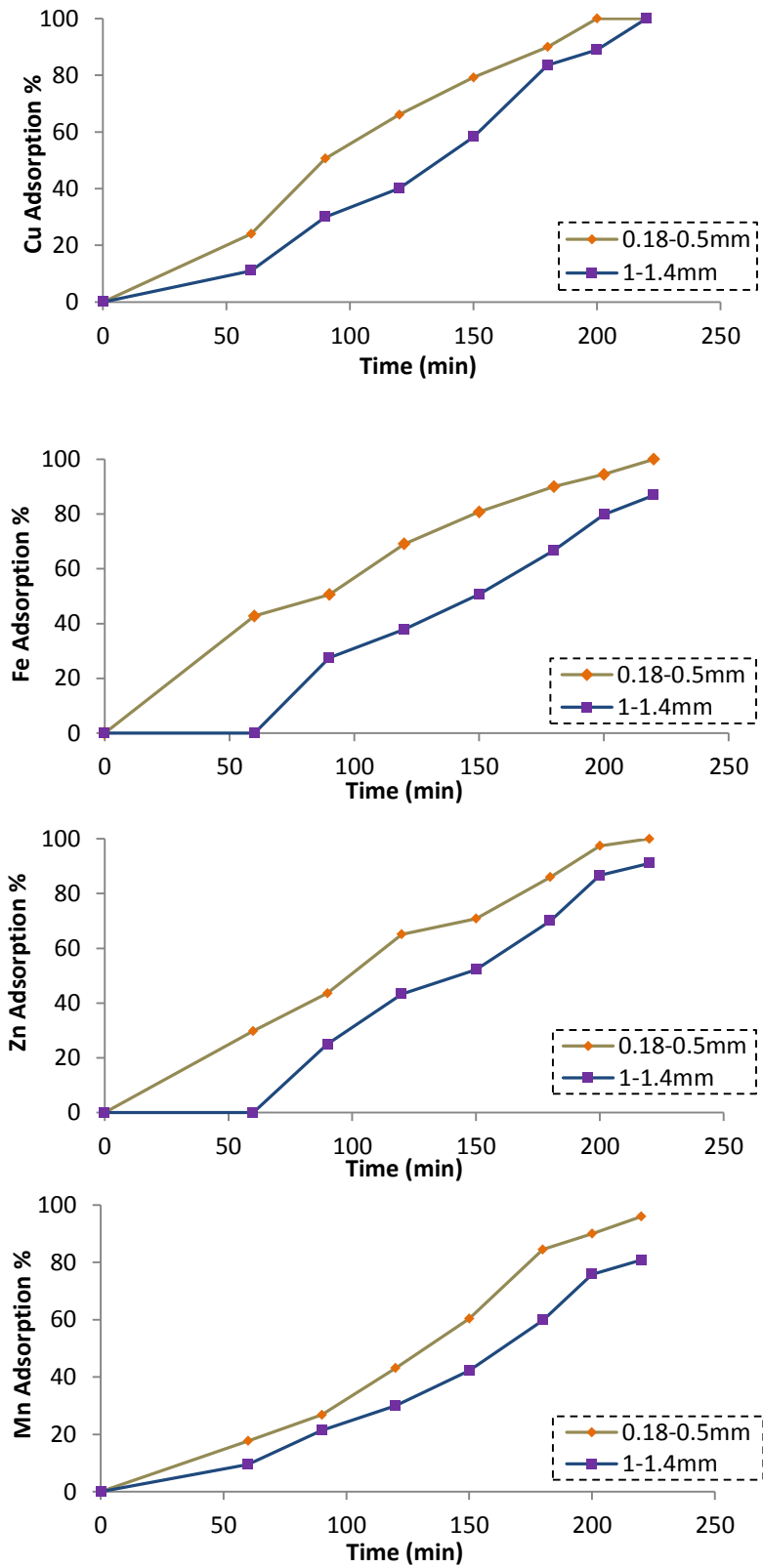
**Figure 7.6: The Effect of particle size on the adsorption of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$.**

### 7.2.4 Effect of adsorbent dosage on metal recovery

Experiments at two different adsorbent masses of BOS sample (2 and 6kg) were performed in the reactor tank using fixed initial multi-component mixture solution ($C_o$;20mg/l) for the respective cations ($Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$) at the same experimental condition. Typical plots of the amount of metal adsorbed by BOS versus time are presented in Figure 7.7. As reported previously, the adsorption rates of most heavy metal ions were favoured by higher adsorbent dosage and thus the efficiency of BOS for metal adsorption was dependent on the uptake capacity.

In this study, this effect is also assessed and results show that all metal ions adsorption rates were affected by an increase in adsorbent dosage. It is evident that an increase in adsorbent mass resulted in an increase in the adsorption of the heavy metals. An increase in adsorption rate is because as adsorbent mass increases more adsorption sites are available per unit mass of adsorbent added. Thus the amount of metal adsorbed per unit mass of BOS at equilibrium is lower, as presented in Table 7.1.

**Table 7.1: Effect of BOS mass on the removal of heavy metals from synthetic sAMD solution at pH 2.1 ± 0.1(particle size: +1mm,-1.4mm; 40L sAMD solution of fixed concentration of 20 mg/l of $Fe^{3+}$, $Cu^{2+}$, $Mn^{2+}$ and $Zn^{2+}$.**

| Heavy metal ions | Adsorbent mass (kg) | Percentage Adsorbed (%) | Amount Adsorbed qe (mg/g) |
|---|---|---|---|
| Copper | 2 | 80.6 | 0.32 |
| | 6 | 100 | 0.13 |
| Iron | 2 | 64.00 | 0.26 |
| | 6 | 100 | 0.13 |
| Zinc | 2 | 70.00 | 0.28 |
| | 6 | 100 | 0.13 |
| Manganese | 2 | 50.3 | 0.2 |
| | 6 | 91.51 | 0.12 |
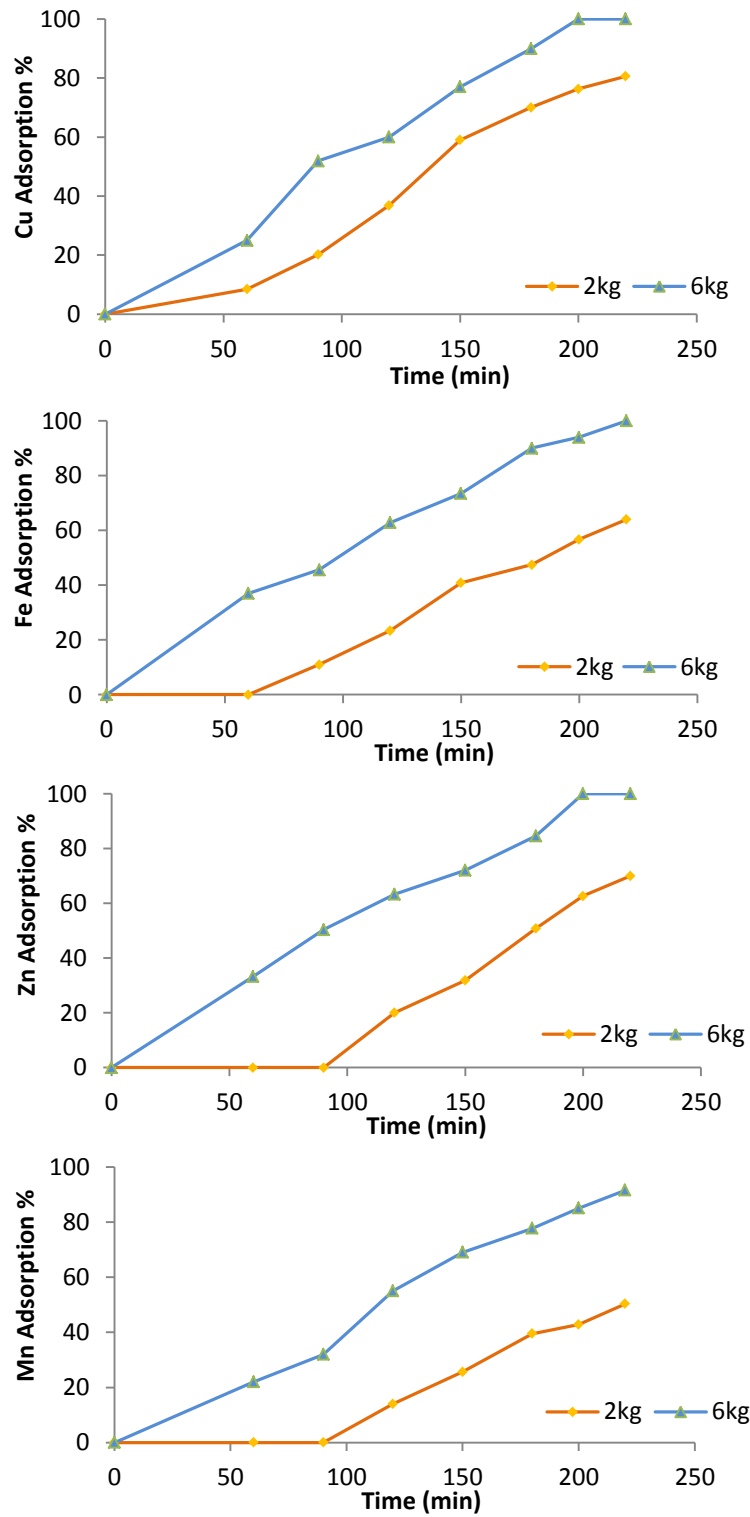
**Figure 7.7: Effect of BOS mass on the removal of heavy metals from synthetic sAMD solution.**

## 7.2.5 Proposed design of a passive AMD treatment reactor vessel

BOS and blast furnace flue dust samples were mixed and contacted with 40L of synthetic AMD solution with fixed initial concentration of heavy metals (20mg/l of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$); these mixtures were not agitated, they were left standing in the tank and AMD solution was pumped in an upward flow through BOS bed. Upward flow was preferred because it insured that there is total coverage of the BOS by the solution and it also prevented the formation of channels during the operation. BOS and blast furnace flue dust samples were used without screening process (as received) in these tests.

The results of the standing tests are presented and compared to the mixing test which also employed raw BOS and blast furnace mixture as its feed, See Table 7.2. The purpose of this experiment was to establish whether BOS or blast furnace flue dust/BOS mixtures could be utilised in the pilot passive treatment plant at Wheal Jane mine and substitute or optimise some of the treatment systems.

Both BOS sludge and blast furnace flue dust mixture samples were able to remove significant amounts of heavy metals, as shown in Table 7.2 and presents the percentage metals adsorbed from solution and the final concentrations after different contact times. It is generally not economical to have longer contact times hence; 50 hours would be a long residence time for any economical system. From the results obtained from the mixing test for BOS and blast furnace flue dust mixture, removal rates and capacities from agitated experiment were higher than those obtained from standing test; hence the proposed design is based on experiment carried out with agitation.

.

**Table 7.2: Comparison between removal rates of heavy metals from synthetic AMD using BOS and blast furnace flue dust (6kg samples; 40L of sAMD solution of fixed concentration of 20 mg/l of $Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ ; Initial solution pH: 2.1 ± 0.1, room temperature.**

| Heavy metals | 50 hours contact (Standing test; 13.3 ml/min) (6 kg BOS sludge sample) | | 50 hours contact (Standing test; 13.3 ml/min) (3kg BOS sludge and 3kg BF flue dust mixture sample) | | 5 hours contact (Mixing test; 133ml/min) (3 kg BOS sludge and 3 kg BF flue dust mixture sample) | | Wheal Jane maximum consent limit (mg/l) |
|---|---|---|---|---|---|---|---|
| | Final Concentration (mg/l) | % Adsorption | Final Concentration (mg/l) | % Adsorption | Final Concentration (mg/l) | % Adsorption | |
| **Copper** | 0 | 100 | 0 | 100 | 0 | 100 | **0.08** |
| **Iron** | 3.7 | 81.4 | 6.9 | 65.6 | 2.8 | 86 | **5.0** |
| **Zinc** | 2.6 | 87 | 3.6 | 82 | 2.1 | 89.5 | **2.5** |
| **Manganese** | 3.4 | 83.1 | 2.4 | 88.2 | 2 | 90 | **1.0** |
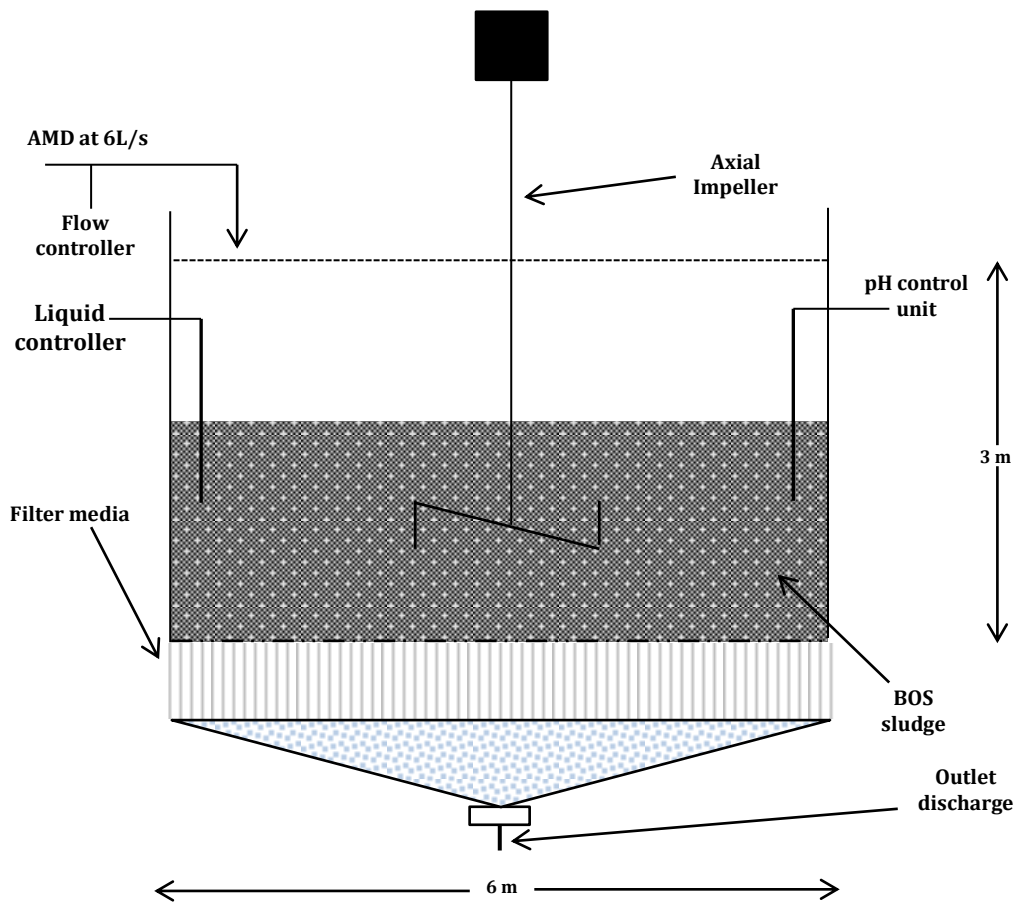
**Figure 7.8: Sketch of the proposed reactor for the passive treatment of Wheal Jane AMD.**

The proposed reactor implements certain elements from the vertical flow reactors used in the passive treatment of AMD. The sizing calculations for this proposed reactor are shown in Appendix B. The sketch of the reactor is presented in Figure 7.8. The reactor vessel will be a 6 m square tank with a working depth of 3 m, and working capacity of 108 $m^3$. The reactors will be constructed from concrete, for longevity and resistance to acidic nature of AMD and the residence time for reactor tank will be 5 hours.

The AMD solution is pumped at a flow rate of 6 litres per second; this is comparable with flow rates that were used at the Wheal Jane pilot passive treatment plant (Whitehead et al., 2005). The solution then cascades down through the bed of BOS (15% w/v adsorbent/sorbate ratio) where the AMD and BOS are agitated. The water eventually drains out of the vessel through a drain pipe. The solution from the vessel

can be drained into a settling pond. The pond is designed to allow adequate residence time for the precipitation of trace heavy metals in the solution to settle at the bottom of the pond and the clear solution is decanted from the surface of the pond to a chosen watercourse.

**Table 7.3: Removal efficiencies of heavy metals from Wheal Jane mine passive treatment plant (Whitehead et al., 2005).**

| System | Copper (%) | Manganese (%) | Zinc (%) | Iron (%) |
|--------|-----------|---------------|----------|----------|
| **LF** | 42 | 45 | 47 | 95 |
| **ALD** | 95 | 60 | 73 | 99 |
| **LD** | 73 | 54 | 66 | 97 |
| **Proposed**[*] | 100 | 90 | 89 | 86 |

[*]These results are from mixing test using 6kg of BOS/BF flue dust mixture as shown in Table 7.2.

This system could give better removal efficiencies compared to those obtained from mixing, but for comparison purposes the removal efficiencies from mixing test (6 kg of BOS/BF flue dust mixture) are shown in Table 7.3 alongside those obtained from passive treatment systems used at Wheal Jane mine.
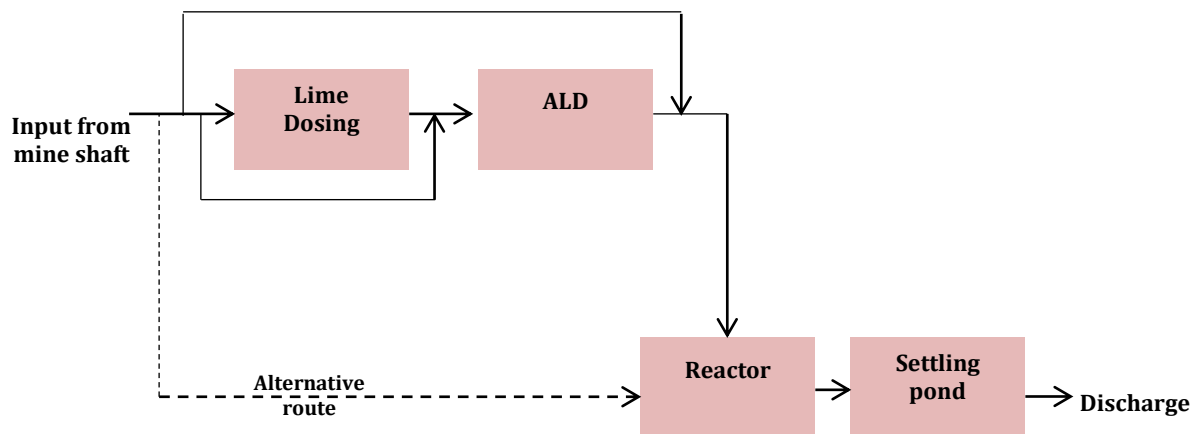


**Figure 7.9: Proposed flow diagram for the passive treatment of AMD from Wheal Jane mine.**

From Table 7.3 it can be observed that the removal efficiencies expected from the proposed design should be comparable to those obtained from other passive treatment technologies such as the Lime free system (LF), Anoxic limestone drain system (ALD) and Lime dosed system (LD). Thus, this proposed technology could be integrated into the AMD treatment flow diagram.

In the case of Wheal Jane pilot passive treatment process flow diagram (Figure 2.7), the proposed reactor could be placed after the Lime dosing and ALD stages depending upon inlet concentrations, thus eliminating the aerobic cells, anaerobic cells and rock filters; the proposed flow diagram is shown in Figure 7.9.

## 7.3 Conclusion

The results of kinetic studies revealed that operational conditions such as rate of agitation, residence time, adsorbent particle size and adsorbent dosage are able to affect the adsorption capacity and efficiency of BOS. The agitation in practice of BOS as a sorbent for AMD treatment is an important factor to take into account, predominately in designing and modelling of reactors. Despite agitation being expensive, the difference in the amount removed from solution by mixing was significant enough to justify the use of mixing in the treatment of synthetic AMD in this study.

The results of kinetic study revealed that operational conditions such as rate of agitation, residence time, adsorbent particle size and adsorbent dosage were able to influence the adsorption capacity and efficiency of BOS. The speed of agitation enhanced the rate of removal significantly at the beginning of the process, thus it was observed that an increase in agitation speed resulted in an increase in the initial rate of adsorption and the total amount adsorbed after equilibrium was higher for the agitation speeds. The increase in agitation resulted in an increase in adsorption rates of BOS for removal of $Cu^{2+}$, $Mn^{2+}$, $Zn^{2+}$ and $Fe^{3+}$ by 20%, 40%, 57% and 86% respectively. Thus the efficiency of BOS for metal adsorption is highly dependent on agitation.

Fixed bed (standing mode) and mixing tests were also performed and the results were found to be comparable with removal capacities from other treatment processes that were used at the Wheal Jane passive treatment plant. From these results a reactor vessel was designed which is expected to give comparable removal rates with the Lime dosed system (LD), Anoxic limestone drain system (ALD), or the Lime free system (LF) systems used at Wheal Jane mine. From an economic perspective the use of BOS in its slurry form could possibly offset the cost of agitation as a particle size reduction stage could be eliminated; hence an optimised pilot plant could provide various data and economic appraisal for the treatment purpose.

Longer contact times (low flow rates) between BOS and sAMD solution also proved to be efficient and prevented any leaching of heavy metals from BOS through sorption. If the system is optimised the removal rates after 50 hours could become comparable with mixing test. A cost effective way to this would be to allow the solution to cascade down the BOS bed by gravitational forces.

One of the conclusions drawn from this study through synthetic AMD treatment was that BOS sludge was capable of treating relatively concentrated heavy metals from continuously flowing solutions. The work carried out and presented in this chapter has shown that BOS or its mixture with other steelmaking wastes as sorbents have also extensive potential for use in treating acidic water based upon water chemistry and flow rates. Overall, it is recommended that BOS sludge can be used in passive treatment. It is a relatively cheap source of alkalinity that increases pH quickly compared to limestone. It also does not require as much land area as conventional limestone-based passive treatment systems.

# CHAPTER 8

# CONCLUSIONS AND RECOMMENDATIONS

## 8.1 Conclusions

The potential and functionality of waste gas sludge (BOS) as a low cost adsorbent for the removal of copper, iron, zinc and manganese from synthetic metal solutions and real AMD from Wheal Jane mine was assessed and investigated in this study. A number of experiments were performed in order to determine the capacity and potential of BOS; these included characterisation of BOS, equilibrium experiments, kinetic experiments and reactor studies. A summary of the conclusions of the experimental results will be presented in this chapter.

### 8.1.1 Characterisation of BOS sludge

SEM micrographs revealed that the BOS samples used in this study have a heterogeneous and porous structure. The SEM/EDS techniques were performed to determine the elemental composition of BOS. It was proved by use of this method that the main exchangeable cations in the structure of BOS were $Ca^{2+}$ and $Mg^{2+}$.

From EDS analysis of the BOS surface, it was concluded that the zinc particles are evenly distributed and dispersed in BOS and appeared as frankelite ($FeZn_2O_4$) and can be described as a mirror image of iron particles. Calcium ions were also visibly present as clusters in SEM micrographs of the BOS.

Magnetic separation was conducted in order to separate zinc from the metallic iron content present in the BOS sludge. Results revealed that zinc particles were attracted more towards paramagnetic fraction and the zinc particles were dispersed, distributed and bonded within other magnetic elements in the BOS sample, thus the process

becomes complex for any physical separation method to be successful in removing Zn from the BOS to allow its direct recycling to a furnace in the process.

Froth flotation has also been investigated in this study, chemical analysis of the froth phase indicated low iron content but no significant change in zinc level. This indicated that the Ca/Si particles are being floated but, the Zn and Fe are closely associated and not liberated.

A range of size distribution ($+38\mu m \leq dp \leq 180\mu m$) were used for size classification, from the results it was concluded that the values of iron are similar at each size range and zinc values also remain constant throughout. This confirmed that the zinc metal is dispersed within the ferrous elements in the BOS samples and evenly distributed across all size ranges of BOS.

XRF analysis revealed that BOS sample used in this research is enriched with calcium and iron. Due to iron and appreciable amount of CaO, BOS sludge can be a good raw material for recycling to iron and steel units however, this is much dependent upon zinc removal from the BOS prior to considering feasible recycling options.

The true density of BOS (particle size ranging from 1 – 1.4 mm) was determined to be $4.27 g/cm^3$, using a helium gas pcynometer. The other particle characteristics determined were porosity (%) and BET surface area ($m^2 g^{-1}$), these were 74.25 and 16.95 respectively and the moisture content of BOS sludge was approximately 19.2%.

## 8.1.2 Treatment of synthetic AMD with BOS and other adsorbents

Batch experiments were performed for the treatment of synthetic AMD. There were a number of parameters which were found to affect the rate of metal uptake by BOS. These include initial metal concentration, presence of competing cations, adsorbent dosage (grams/litre), adsorbent particle size, initial solution pH and other different operational conditions.

An increase in initial solution concentration resulted in an increase in the amount of heavy metals adsorbed, q, and a decrease in the efficiency of BOS for the removal of heavy metals from solution. Hence the BOS became an inefficient sorbent at higher concentrations, the reason being at low concentrations the ratio of surface active sites to total metal ions in the solution was high and thus more metal ions could interact with BOS particles and thus being removed from the solution. However at higher concentrations the BOS could easily become saturated and hence a decrease in the amount adsorbed was exhibited. This decrease in efficiency was observed by a general reduction in the percentage adsorption (which represents the efficiency of the process).

Results from equilibrium studies showed that BOS was capable of removing heavy metals from synthetic AMD solution. Equilibrium studies were used to determine the selectivity series of BOS for the adsorption of copper, iron, zinc and manganese from solution. The experimental data obtained from batch studies were fitted satisfactorily to Langmuir isotherm model with correlation coefficients $R^2$ ranging from 0.9-0.99 and according to the Langmuir isotherm, the series was found to be $Cu^{2+}>Fe^{3+}>Zn^{2+}>Mn^{2+}$.

The effect of competing cations was also investigated in this study and it was observed that the adsorption of $Zn^{2+}$ and $Mn^{2+}$ reduced in multi-component solutions. Adsorption of $Cu^{2+}$ was not affected by the presence of competing ions. This may be because one of the mechanisms responsible for the removal of $Cu^{2+}$ cations from solution is thought to be precipitation. The adsorption of $Fe^{3+}$ was increased in multi-component solution compared to single component solution. This indicates that different adsorption mechanisms were involved in the adsorption of each cation from solutions.

There were two competing processes affecting sorption process, release of alkalinity from BOS and the removal of acidity from AMD components at higher sorbent dosage the acidity from solution is overwhelmed and pH is bound to increase while with lower BOS dosage the alkalinity from the sorbent is overwhelmed by the acidity from AMD solution and the pH remained a little lower. High acidic AMD affected adsorbed metals through a number of mechanisms which are not well understood.

Low pH favoured desorption and/or dissolution of metal cations since both their sorption and precipitation were favoured at high pH. In very acidic conditions strong competition between $H^+$ ions and metal cations for adsorption sites in BOS caused displacement of cations into solution. Acidic conditions also favoured dissolution of $Fe^{3+}$ oxides on adsorption surfaces and thus the release of precipitated metal ions.

The results also showed that for BOS and GGBS samples, an increase in adsorbent mass resulted in an increase in the adsorption of the heavy metals. An increase in adsorption rate was because as adsorbent mass increased more adsorption sites were available per unit mass of adsorbent added. About 100%, 100%, 99% and 73% of copper, iron, zinc and manganese respectively were adsorbed from multi component solution by BOS and about 100% of copper, iron, zinc and 96% of manganese by GGBS sample.

The results also indicated that decreasing the particle size of BOS resulted in a higher heavy metal removal rate and efficiencies for $Zn^{2+}$ and $Mn^{2+}$ removal with an increase of 3.8% and 3.3% for $Zn^{2+}$ and $Mn^{2+}$ respectively (99.7% of $Zn^{2+}$ and 73.2% of $Mn^{2+}$) and this was due to an increase in BOS surface area. The initial rates of all metal ions were rapid because of high mass transfer rates based on high concentration gradient of adsorbates across micropores in BOS. However as contact time increased there was a decrease in the degree of the effect of particle size on adsorption rates and particle size distribution became less significant to removal levels because free adsorption sites and concentration gradient decreased.

Batch Kinetic studies indicated that the rate of adsorption of the heavy metals by BOS was rapid for the first 15 min and then gradually levelled off as equilibrium was approached. This rapid removal of heavy metals from synthetic solutions is an advantage in waste water treatment processes. The adsorption kinetics was fitted satisfactorily to the pseudo second order kinetic model with correlation coefficients $R^2 \geq 0.99$. The rate limiting step for the removal of heavy metals from solution by BOS was found to be chemisorption. However a combination of other mechanisms including adsorption, ion exchange and precipitation must not be ruled out.

## 8.1.3 Treatment of Wheal Jane AMD with BOS and other adsorbents

BOS was used to treat Wheal Jane Mine (Cornwall, UK) AMD in this research. Batch mode kinetic studies were performed to assess the potential of BOS as a low cost sorbent for real AMD treatment. Results showed high pH obtained due to the dissolution of the BOS (neutralising potential) during the agitation of AMD solution and BOS. This exposed a high number of active adsorption sites, resulting in effective adsorption rates.

Adsorption was rapid for the first 15 minutes, after which for all metal ions adsorption rates levelled off as equilibrium was attained. About 100%, 100%, 97.9%, and 94.8% of copper, iron, zinc and manganese respectively were adsorbed from Wheal Jane solution (adsorbent/sorbate ratio;12%w/v). This effective removal was a result of the interactions of heavy metals with the adsorption sites on the surface of BOS, which can easily be accessed by the diffusing heavy metals.

The removal of heavy metals from Wheal Jane solution was not only due to adsorption and ion exchange but also due to metal precipitation. This was indicated by the equilibrium pH which was greater than the minimum pH necessary for precipitation to occur. This rapid removal of the heavy metals from real AMD solution is significant and an advantage in waste water treatment purposes.

Interestingly the order of metal ions adsorbed by BOS from Wheal Jane was more or less similar to the results obtained from synthetic AMD treatment. The order of adsorption from Wheal Jane AMD was found to be: copper≧iron>zinc>manganese. About 100% of copper, iron, zinc and manganese were also adsorbed from Wheal Jane solution by GGBS sample as an alternative sorbent.

Results revealed that the efficiency and adsorption rates were favoured with an increase in BOS mass. An increase in the initial solution pH from 2.8 to 4.5 on adsorption of copper was unaffected, whilst for iron, zinc and manganese the efficiency of BOS for

adsorption was dependent on the initial solution pH. It was evident that high pH promotes adsorption possibly by precipitation and ion exchange processes.

Batch experiments using thermally treated BOS showed that thermal pre-treatment of BOS was not as effective as untreated BOS. The treatment of Wheal Jane AMD by thermally pre-treated BOS gave a final concentration of copper higher than the acceptable legal concentration; the concentrations of iron, zinc and manganese were below the maximum consent limit.

Regeneration of BOS was tested using 2% (wt.) sulphuric acid and NaCl (20 g/l). Results showed that neither of regenerating agent performed as anticipated. The desorption series followed this order: iron>zinc>manganese>copper. There was an observable drop in the adsorption capacity of BOS that had been regenerated using sulphuric acid. This may be due to the destructive nature of sulphuric acid on the BOS matrix.

The adsorption capacity of regenerated BOS sludge gave undesirable results; this was also because of acid resulting in neutralisation of much of alkalinity left in BOS. The adsorption capacity of BOS regenerated using NaCl was also negatively affected. Therefore, regenerated BOS sludge cannot effectively meet the maximum Wheal Jane consent limit thus insuring that regenerated BOS sludge could handle only relatively dilute AMD solutions or preferably downstream to another treatment process.

BOS sludge as pellets were also used to treat AMD in batch mode, the adsorption capacity of BOS pellets was found to be greater than the normal contact of BOS with AMD with 100% adsorption rates for all respective cations. The only major disadvantage of pelletising method in real practice of treating real AMD may be the cost of the process.

The final concentrations obtained from pelletsing method fall within the Environmental Quality Standard (EQS) values, which are 1.0, 0.5, 0.028 and 0.03 mg/l $Fe^{3+}$, $Zn^{2+}$, $Cu^{2+}$ and $Mn^{2+}$ respectively (Bone, 2003). Therefore it is recommended that BOS can be used to treat real AMD solutions.

The results from this study were comparable with those from other research work carried out at the University of Birmingham for the treatment of Wheal Jane mine AMD, See Table 6.7. In conclusion the results obtained in this study, when compared to the metal removal efficiencies achieved by the active treatment plant at Wheal Jane, proved that BOS has great potential as a low cost material for AMD treatment.

## 8.1.4 Reactor studies for synthetic AMD treatment

The results of kinetic studies from semi-continuous experiments revealed that operational conditions such as rate of agitation, residence time, adsorbent particle size and adsorbent dosage were able to influence the adsorption capacity and efficiency of BOS. The speed of agitation enhanced the rate of removal significantly at the beginning of the process, thus it was observed that an increase in agitation speed resulted in an increase in the initial rate of adsorption and the total amount adsorbed after equilibrium was higher for the agitation speeds. Effect of agitation resulted in an increase in higher adsorption rates of BOS for removal of $Cu^{2+}$, $Mn^{2+}$, $Zn^{2+}$ and $Fe^{3+}$ by 20%, 40%, 57% and 86% respectively. Thus the efficiency of BOS for metal adsorption is highly dependent on agitation.

The results also indicated that decreasing the particle size of BOS resulted in a higher heavy metal removal rate and efficiencies for $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$ removal with an increase of 13.1% and 9% for $Zn^{2+}$ and 15.2% $Mn^{2+}$ respectively. Correspondingly to batch experiment studies, this was due to an increase in BOS surface area. The initial rates of $Fe^{3+}$ and $Zn^{2+}$ were rapid because of high mass transfer rates based on high concentration gradient of adsorbates and BOS. However as contact time increased there was a decrease in the degree of the effect of particle size on adsorption rates.

An increase in the mass dosage from 2 to 6kg resulted in an increase in the equilibrium adsorption capacity, qe of BOS for $Mn^{2+}$, $Zn^{2+}$, $Fe^{3+}$ and $Cu^{2+}$ by an increase of 41%, 30%, 36% and 19% respectively. Therefore the efficiency of BOS for metal adsorption is also dependent upon sorbent mass.

The results obtained were found to be comparable with removal capacities from other treatment processes that were used at the Wheal Jane passive treatment plant. From these results a reactor vessel was designed which is expected to give comparable removal rates with the Lime dosed system (LD), Anoxic limestone drain system (ALD), or the Lime free system (LF) systems used at Wheal Jane passive treatment plant. One of the conclusions drawn from this study was that BOS sludge and its mixture with other steel wastes was capable of treating relatively concentrated solutions of heavy metals based upon solution chemistry and flow rates.

## 8.2 Recommendations

This thesis has employed and analysed a material which has previously not been studied and examined by academics as an adsorbent for acid mine drainage treatment. The importance of utilising this material for AMD treatment has been highlighted through this research. Therefore this project has established a fundamental and elementary dataset for further investigations. The research carried out and presented in this thesis has shown that waste gas sludge (BOS) can be considered as a commercial product for AMD treatment purposes.

BOS as a sorbent has extensive potential for use in treating synthetic and real AMD solutions. However, further research and studies are certainly required in this area if this technology is to be fully utilised on an industrial scale economically. There are several areas of research that could be pursued and practiced in the future, these are presented below.

In this study equilibrium studies were carried out using single component solutions, and these were modelled using the Langmuir and Freundlich isotherms. In practice, AMD contains a mixture of different cations, thus to obtain more accurate results and a clear picture of the maximum adsorption capacity of BOS when treating AMD; equilibrium studies ought to be performed using solutions containing a mixture of cations such as lead, cobalt, cadmium, aluminium, arsenic and many others. The competitive Langmuir model could potentially be used to model such a system.

Another potential area of research is to understand about the leachability of heavy metals from BOS in acidic environments. Steel slags consist of different types of heavy metals in various concentrations, including Sb, Cu, Mn, Fe, Mo, Ni, Ag, Tl, Sn, V, and Zn. As observed in some experiments carried out in this study there was some concern that some of these heavy metals (for example iron), could have the chance of leaching from BOS matrix when it is used waste water treatment. There are many parameters in relation to weathering and leaching tests that must be assessed and monitored such as

speciation of metal in the BOS which is dependent upon processing history or age of the BOS.

There are a number of methods that can be used for this purpose such as by contacting BOS samples in distilled water or to investigate the release of heavy metals from BOS under different acidic solutions with variable initial solution pH. The possibility that toxic and heavy metals that may become mobile in the waste water treatment when BOS is used could be a potential area of further study.

In this research, AMD from Wheal Jane mine was used as a case study. Due to complex composition of AMD, Acid mine drainage has a number of variables (pH, metal concentrations, elevated sulphate levels, suspended toxic solids) which vary from source to source. For example specific metal conductivity in AMD could influence the uptake rate of other heavy metal ions. Thus laboratory experiments using BOS sludge need to be conducted with different real AMD solutions in order to understand the mechanisms furthermore. Additional work and the objectives need to be established based upon many parameters and essential steps and some are as follow:

➢ Developing a spread sheet based model to identify the most cost-effective methodology of using BOS sludge for optimal removal levels;

➢ Collecting accurate data on oxidising conditions from different real AMD streams (e.g., $Fe^{2+}/Fe^{3+}$ ratios and other chemical compositions);

➢ Constructing a cost and quality performance in order to achieve an optimised process design (unit size, capital cost, operating cost based on volume and flow rates);

➢ An economic evaluation required to compare different processing scenarios before a recommendation can be made as to which process route is preferred.

Acid mine drainage not only contains metal cations but also anions such as $NO_3^{2-}$, $SO_4^{2}$, $HPO_4^{2-}$ and $Cl^-$. Adsorption and uptake rate of certain cations is strongly affected and influenced by the presence of complexing reagents such as the above mentioned anions (Helfferich, 1962; Inglezakis et al., 2003). This research only focused on the removal of

four heavy metals and did not take into account the effect of these anions on the capacity and effectiveness of BOS. Further, detailed investigations could be performed to determine whether BOS is capable to reduce the concentration of these anions from solution and how the anions influence the heavy metal uptake capacity of BOS.

Thermally pre-treated BOS was used in this study for Wheal Jane AMD water; other pre-treatment methods were not investigated. This could also be a potential area of further study, which could result in an increase in the capacity and efficiency of BOS in treating AMD. There are a number of pre-treatment methods that can be used such as chemical treatments using NaCl, $NaNO_3$ or use of cationic surfactants.

Another potential area of research is the determination of a suitable regenerating solution if regeneration is required. It is critical to optimise this process, since the efficiency of BOS for subsequent adsorption stages is affected by the effectiveness of the regeneration process. The effectiveness of regenerating solutions such as NaCl, EDTA, $CaCl_2$ and HCl at different concentrations could be investigated.

One of the conclusions drawn from semi-continuous tests in this study was that BOS and its mixture with blast furnace flue dust as raw was capable of treating relatively synthetic solutions of heavy metals under a cost effective manner. However the use of reactor in this study encountered some obstacles such as failure of pump, leakages of pipelines and other limitations. Therefore a design of an optimised reactor could be another possible area of further research under which various mixing mode, size distribution and other parameters could be examined.

Overall it is recommended that BOS can be used as an alternative in passive treatment due to its availability, low maintenance, safety and more importantly it is a relatively cheap source of alkalinity which increases pH rapidly compared to limestone. It also does not require as much land area as conventional limestone-based passive treatment systems.

The two major restrictions regarding BOS sludge use are that the BOS must remain submerged during treatment. The BOS will harden into a concrete-like substance, thus

reducing surface area and porosity of the BOS available for reaction which this could lead to other operational challenges. Another issue is the disposal of used BOS (Spent sorbent) which was not dealt with in this study and this could be a potential area of further study which could ultimately result in increase of environmental aspects associated for AMD treatment.

Before this technology is implemented on an industrial scale, the construction of an optimised pilot plant using BOS sludge to treat synthetic and real AMD would be a good plan forward. Further research and investigations could be carried out to determine different operating conditions and different flow regimes that simulate real plant operation and to assess the longevity of the treatment. From the pilot plant, the required data for industrial application can be obtained and also an economic appraisal based upon process parameters can be determined more precisely.

# REFERENCES

1. Ahmaruzzaman, M. 2011. Industrial Wastes as Low-Cost Potential Adsorbents for the Treatment of Wastewater Laden with Heavy Metals. *Advances in Colloid and Interface Science,* 166 [1-2], 36-59.

2. Akcil, A., and Koldas, S. 2006.Acid Mine Drainage (AMD): causes, treatment and case studies. *Journal of Cleaner Production*, 14, 1139-1145.

3. Alvarez-Ayuso, E., Garcia-Sanchez, A., Querol, X., 2003. Purification of metal electroplating waste waters using zeolites. *Water Research*, 37, 4855-4862.

4. Amarasinghe, B.M.W. and Williams, R.A., 2007. Tea waste as a low cost adsorbent for the removal of Cu and Pb from wastewater. *Chemical Engineering Journal*, Volume 132, 299-309.

5. American Iron and Steel Institute, 2013. The Basic Oxygen Steelmaking (BOS) Process. [Available at:

   http://www.steel.org/en/Making%20Steel/How%20Its%20Made/Processes/Processes%20Info/The%20Basic%20Oxygen%20Steelmaking%20Process.aspx: last accessed: 23/2/2013].

6. Apak, R., 2002. Adsorption of heavy metal ions on soil surfaces and similar substances. In: Hubbard, A. T., (Ed.), Encyclopedia of Surface and Colloid Science. Marcel Dekker, New York, pp. 385-417.

7. Aube, B. 1999. The Science of Treating Acid Mine Drainage and Smelter Effluents. pp. 1-20. [Available at:
   http://www.infomine.com/library/publications/docs/Aube.pdf : last accessed: 20/07/2010].

8. Aubé, B., and Zinck, J.M., 1999. Comparison of AMD Treatment Processes and their Impact on Sludge Characteristics. Proceedings for Sudbury '99, Mining and the Environment II. [Available at:

   http://pdf.library.laurentian.ca/medb/conf/Sudbury99/AcidicDrainage/AD28.PDF:
   last accessed:12/10/2011].

9. Azapagic, A., 2004. Developing a framework for sustainable development indicators for the mining and minerals industry. *Journal of Cleaner Production*, 12[6], 639-662.

10. Babel, S., and Kurniawan, T. A., 2003. Low-cost adsorbents for heavy metals uptake from contaminated water: a review. *Journal of Hazardous Materials,* B97, 219-243.

11. Bailey, S. E., Olin, T. J., Bricka, R. M., Adrian, O. A., 1999. A review of potentially low-cost sorbents for heavy metals. *Water Research*, 33[11], 2469-2479.

12. Balintova, M., and Petrilakova, A. 2007. Study of pH influence on the selective precipitation of heavy metals from acid mine drainage. *Chemical Engineering Transactions*, 25, 345-350.

13. Bamforth, S.M., Manning, D.A.C., Singleton, I., Younger, P.L., Johnson, K.L. 2006. Manganese removal from mine waters-investigating the occurrence and importance of manganese carbonates. *Applied Geochemistry*, 21, 1274-1287.

14. Barakat, M. A. 2011. New trends in removing heavy metals from industrial wastewater. *Arabian Journal of Chemistry,* 4, 361-377.

15. Boon-Long, S., Laguerie, C., Coudere, J.P. 1978. Mass Transfer from suspended solids to a liquid in Agitated Vessels. *Chem. Eng. Sci*, 33, 813.

16. Bone, B., 2003. Remediation scheme to mitigate the impacts of abandoned mines. Environmental Agency for England and Wales,
[Available at: http://www.cluin.org/romania/presentations/natoccms_uk_cases.pdf:
last accessed:19/12/2012].

17. Bradl, H. B. 2004. Adsorption of metal ions on soils and soils constituents. *Journal of Colloid and Interface Science*, 277[1], 1-18.

18. Branca, T.A., and Colla, V., 2012. Possible uses of steelmaking slag in agriculture: An overview, [Available at:

http://cdn.intechopen.com/pdfs/32571/InTechPossible_uses_of_steelmaking_slag_in_agriculture_an_overview.pdf: last accessed: 14/11/2010].

19. Brown, M., Barley, B., Wood, H., 2002. Mine water treatment: Technology, application and policy. London: IWA Publishing, p. 448.

20. Brunauer, S., 1943. The adsorption of gases and vapours. Oxford University Press.

21. Chartrand, M.M.G., and Bunce, N.J. 2003. Electrochemical remediation of acid mine drainage, *J. Appl. Electrochem*, 33, 259-264.

22. Chaurand, P., Rose, J., Briois, V., Olivi, L., Hazemann, J., Proux, O., Domas, J., and Bottero, J. 2006. Environmental impacts of steel slag reused in road construction: a crystallographic and molecular (XANES) approach. *Journal of Hazardous Materials,* 139[3], 537-542.

23. Chen, HK., Lin CI., Liu SH., 1992. Carbothermic reduction of sludges of blast furnace and basic oxygen furnace. *Scand J Metallurgy*, 21[5], 218-22.

24. Chen, X., Hou, W.H., Song, G.L., Wang, Q.H. 2011. Adsorption of Cu, Cd, Zn and Pb ions from aqueous solutions by electric arc furnace slag and the effects of pH and grain size. *Chem. Biochem. Eng*, 25[1], 105-114.

25. Cho, TR., Song, CB., Goto, SK. 1997. Recovery of zinc from blast furnace dust sludge. *Nonmunjip- Ch' ungnam Taehakkyo. Sanop Kisul Yon'guso*,12[2], 29-34.

26. Connors, K., 1990. Chemical Kinetics: The study of reaction rates in solution. VCH Publishers, USA.

27. Costello, C., 2003. Acid Mine Drainage: Innovative treatment technologies. U.S. Environmental Protection Agency.

28. Coulton, R., Bullen, C., Dolan, J., Hallett, C., Wright, J., Marsden, C., 2003. Wheal Jane mine water active treatment plant–design, construction and operation. *Land Contamination and Reclamation*, 11[2], 245-252.

29. Coulton, R., Bullen, C., Hallet, C., 2003. The design and optimization of active mine water treatment plants. *Land Contamination and Reclamation*, 11, 273-279.

30. Darkwah, L., 2005. Remediation of acid mine drainage. The University of Birmingham, Thesis.

31. Das, B., Prakash, S., Biswal SK., Reddy PSR., Mohapatra BK., Tripathy HK., 2002. Utilisation of solid waste materials generated at steel plants by physical beneficiation technique; report submitted to Ministry of Steel. India.

32. Das, B., Prakash, S., Reddy, P.R.S., Misra, V.N., 2006. An overview of utilization of slag and sludge from steel industries. *Resources, Conservation and Recycling*, 50 [1], 40-57.

33. Deorkar, N.Y., Tavlarides, L.L., 1998. An adsorption process for metal recovery from acid mine waste: the Berkeley Pit Problem. *Environ. Prog*, 17, 120-125.

34. Dimitrova, S.V. 1996. Metal sorption on Blast-furnace slag. *Water Research*, 30, 228–232.

35. Dimitrova, SV., Mehandgie, D.r., 1996. Lead removal from aqueous solutions by granulated blast furnace slag. *Construct Build Mater*, 1[3], 191-193.

36. Dimitrova, S. V. and Mehanjiev, D. R., 1998. Lead Removal from Aqueous Solutions by Granulated Blast Furnace Slag. *Water Research,* 32[11], 3289-3292.

37. Dimitrova, S.V., and Mehandgiev, D.R., 2000. Interaction of Blast-furnace slag with heavy metal ions in water solutions. *Water Research*. 34, 1957-1961.

38. Diz, H.R., Novak, J.T., 1998. Fluidized bed for the removing iron and acidity from acid mine drainage. *J. Environ. Eng*, 124, 701-708.

39. Doya, I. and Duchesne, J. 2003. Neutralisation of acid mine drainage with alkaline industrial residues: laboratory investigation using batch-leaching tests. *Appl. Geochem*, 18, 1197-1213.

40. Dushina, A. and Aleskovski, V. 1976. Ion Exchange as First Stage of the Solid Substance Transformation into Electrolytic Solutions. *Journal of Applied Chemistry,* 49, 41-49.

41. Earle, J. and Callaghan, T., 1998. Coal mine drainage prediction and pollution prevention in Pennsylvania. Department of Environmental Protection, Chapter 4, 4.1- 4.10.

42. Ellis, JD., 1999. Agglomeration or rejection-two cycling alternatives. In: Learn strategies for coping with steel mill wastes and profiting from by-products, p.5.

43. Environmental Agency, 2007. Wheal Jane mine-water treatment plant Baldhu, Cornwall.

44. Environment Agency, 2008. Abandoned mines and the water environment; coal authority. [Available at: http://cdn.environment-agency.gov.uk/scho0508bnzs-e-e.pdf: last accessed: 23/01/2013].

45. Environmental Leadership, 1998. Steel Industry Technology Roadmap, chapter four.[Available at:http://www1.eere.energy.gov/manufacturing/resources/steel/pdfs/roadmap_chap4.pdf:last accessed:18/7/2012].

46. Erdem, E., Karapinar, N., Donat, R., 2004. The removal of heavy metal cations by natural zeolite. *Journal of Colloid and Interface Science*, 280, 309-314.

47. Fallman, A. 2000. Leaching of chromium and barium from steel slag in laboratory and field tests-a solubility-controlled process. *Waste Management*, 20, 149-154.

48. Feng, D., Aldrich, C., Tan, H., 2000. Treatment of acid mine water by use of heavy metal precipitation and ion exchange. *Mineral Engineering*, 13, 623-642.

49. Feng, D., van Deventer, J. S. J. and Aldrich, C. 2004. Removal of pollutants from acid mine wastewater using metallurgical by-product slags. *Separation and Purification Technology,* 40, 61-67.

50. Fleischanderl, A., Pesl, J., Gebert, W., Heckmann, H., 1999. Converting wastes into profit: recycling of steel mill wastes through BOF/BF, RMF and COREX-technology. In: Learn strategies for coping with Steel Mill Wastes and Profiting from by-products. *Gorham/Intertech Consulting*, p. 15.

51. Francis, AA., 2004. Conversion of blast furnace slag into new glass-ceramic material. *J Eur Cream Soc*, 9[4], 2819-24.

52. Fregeau-Wu, E., Pignolet-Brandom, S., Iwasaki, I., 1993. Liberation analysis of slow-cooled steelmaking slags: implications for phosphorus removal. Proceedings of the 1st International Conference on Processing Materials for Properties, Sponsored by: TMS; MMIJ Publ by Minerals, Metals & Materials Soc (TMS), pp. 153-156.

53. Fripp, J., Ziemkiewicz, P.F., Charkavork, H., 2000. Acid mine drainage treatment - Technical Notes Collection. Vicksburg: Army Engineer Research and Development Center; Report No.: ERDC TN-EMRRPSR-14.

54. Fuerstenau, M., Zhong, K., Hu, W., Liu, Y., 1997. Remediation of heavy metal ionsutilizing cellophane. *Mineral Engineering*, 10, 1245-1251.

55. Furusawa, T. and Smith, J.M., 1973. Fluid-particle and intraparticle mass transport rates in slurries. *Industrial and Engineering Chemistry Fundamentals*, Volume 12, [2], 197-203.

56. Gaikwad, R.W., Misal, S.A., Dhirendra., Gupta, D.V. 2009. Removal of copper ions from acid mine drainage (AMD) by ion exchange resins, INDION 820 AND INDION 850. *Journal of applied sciences in environmental sanitation*, Volume 4 [2], 133-140.

57. Gazea, B., Adam, K., Kontopoulos, A., 1996. A review of passive systems for the treatment of acid mine drainage. *Minerals Engineering*, Volume 9 [1], 23-42.

58. Gerber, D.W., Burns, J.E., Stove, R.W., 1985. Removal of dissolved iron and manganese ions by sphagnum moss system, in: R. Brooks, D. Samuel, J. Hill (Eds.), Proceedings on Wetlands and Water Management on Mined Lands, Pennsylvania State University, PA, pp. 365-372.

59. Gibert, O., de Pablo, J., Cortina, J.L., Ayora, C., 2005. Municipal compost-based mixture for acid mine drainage bioremediation: metal retention mechanisms. *Appl, Geochem*, 20, 1648-1657.

60. Gomes, J. and Pinto, C. 2006. Leaching of heavy metals from steelmaking slags. *Revista del Metalurgia*. 42[6], 409-416.

61. Griffiths, D., 2005. Abandoned mine drainage. Environmental Agency.

62. Gupta, V. K., Ali, I., 2002. Adsorbents for water treatment: low-cost alternatives to carbon. In: Hubbard, A. T. (Ed.) Encyclopedia of surface and Colloid Science, Volume 1. Marcel Dekker, New York, pp. 136-166.

63. Hall, K.R., Egleton, L.C., Acrivos, A. and Vemeulen, T. 1966. Pore and solid diffusion kinetics in fixed bed adsorption under constant pattern conditions. *Industrial and Chemical Engineering Fundamentals*, 5, 212-223.

64. Hallberg, K.B. and Johnson, B.D., 2003. Passive mine water treatment at the former Wheal Jane tine mine, Cornwall: important biogeochemical and microbiological lessons. *Land Contamination and Reclamation*, Volume 11 [2], 213-220.

65. Hamilton, R.M., Bowen, G.G., Postlethewaite, N.A., Dussek, D.J., 1994. The abandonment of Wheal Jane, a tin mine in S.W. England. In: Proceedings of the 5th International Mine water Congress, Nottingham, UK, 543-551.

66. Hamilton, J., Gue, J., and Socotch, C. 2007. The use of steel slag in passive treatment design for AMD discharges in the Huff Run watershed restoration. Proceedings of the 28th West Virginia Mine Drainage Task Force Symposium.

67. Hammarstrom, J.M., Sibrell, P.L., Belkin, H.E., 2003. Characterization of limestone reacted with acid mine drainage in a pulsed limestone bed treatment system at the Friendship Hill National Historical Site, Pennsylvania, USA. *Appl, Geochem*, 18, 1705-1721.

68. Harsco Metals and minerals, 2013. Waste water treatment. [Available at: http://www.harsco-m.com/69/Waste-Water-Treatment.aspx: last accessed: 25/9/2012].

69. Helfferich, F. and Plesset, M.S., 1958. Ion exchange kinetics. A nonlinear diffusion problem. *Journal of Chemical Physics*, Volume 28 [3], 418-424.

70. Ho, Y.S., and Mckay, G. 1998. A Comparison of Chemisorption Kinetic Models Applied to Pollutant Removal on Various Sorbents. In:Transactions for Institution of Chemical Engineers (Trans IChemE).

71. Ho, Y.S., and Mckay, G. 1999. Pseudo second order model for sorption processes. *Process Biochemistry,* 34, 451-465.

72. Ho, Y. S. 2006. Review of second order models for adsorption systems. *Journal of Hazardous Materials,* B136, 681-689.

73. Hoehn, R.C. and Sizemore, D.R., 1977. Acid mine drainage (AMD) and its impact on a small Virginia stream. *Water Resources Bulletin*, Volume 13, 153-160.

74. Holley, C.A. 1985. Agglomeration of steel plant waste for recycling. Paper Presented at the 19th IBA Conference, Baltimore.

75. Hughes, P., 1994. Water pollution from abandoned coal mines. Library Research Paper 94/43.

76. Huifen, Y.,Wen, M., Weina, Z., Zhiyong, W. 2011. Steel Slag as Multi-functional Material for Removal of Heavy Metal Ions in Wastewater. International Conference on Computer Distributed Control and Intelligent Environmental Monitoring, pp.1287-1290.

77. Hustwit, C.C., Ackman, T.E., Erickson, P.E., 1992. The role of oxygen transfer in acid mine drainage (AMD) treatment. *Water Environ. Res*, 64, 817-823.

78. Inglezakis, V.J., Diamandis, N.A.D., Loizidou, M.D., Grigoropoulou, H.P., 1999. Effect of pore clogging on kinetics of lead uptake by clinoptilolite. *Journal of Colloid and Interface Science*, 215, 54-57.

79. Inglezakis, V.J., Loizidou, M.D., Grigoropoulou, H.P., 2001. Applicability of simplified models for the estimation of ion exchange diffusion coefficients in zeolites. *Journal of Colloid and Interface Science*, 234, 434-441.

80. Inglezakis, V.J., Zorpas, A.A., Loizidou, M.D., Grigoropoulou, H.P., 2003. Simultaneous removal of metals $Cu^{2+}$, $Fe^{3+}$ and $Cr^{3+}$ with anions $SO_4^{2-}$ and $HPO_4^{2-}$ using clinoptilolite. *Microporous and Mesoporous Materials*, 61, 167-171.

81. Jenke, D.R. and Diebold, F.E., 1983. Recovery of valuable metals from acid mine drainage by selective titration. *Water Res*, 17, 1585-1590.

82. Jochova, M., Puncochar, M., Horacek, J., Stamberg, K., Vopalka, D., 2004. Removal of heavy metals from water by lignite-based sorbents, *Fuel*. 83, 1197-1203.

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

84. Jusoh, A.B., Cheng, W.H., Low, W.M., Noraaini, A., Noor, M.J.M.M., 2005. Study on the removal of iron and manganese in groundwater by granular activated carbon. *Desalination*, 182, 347-353.

85. Kalyoncu, R.S., 1999. Slag-Iron and steel: U.S. *Geological Survey Mineral Commodity Summaries*, p. 94-95. [Available at: http://minerals.usgs.gov/minerals/pubs/commodity/iron_&_steel_slag/790400.pdf: last accessed: 4/10/2010].

86. Kim, D.-H., Shin, M.-C., Choi, H.-D. 2008. Removal Mechanisms of Copper using Steel-Making Slag: Adsorption and Precipitation. *Desalination,* 223, 283-289.

87. Koryak, M., Shapiro M.A., Sykora, J.L., 1972. Riffle zoobenthos in streams receiving acid mine drainage. *Water Research*, Volume 6, 1239-1247.

88. Kostura, B., Kulveitova, H., Juraj L. 2005. Blast furnace slags as sorbents of phosphate from water solutions. *Water Research*. 39 [9], 1795-802.

89. Kurniawan, T. A., Chan, G. Y. S., Lo, W. 2006. Comparisons of low-cost adsorbents for treating wastewaters laden with heavy metals. *Science of the Total Environment,* 366, 409-426.

90. Langmuir, I., 1918. The adsorption of gases on plane surfaces of glass, mica and platinum. *Journal of American Chemical Society*, 40, 1361-1403.

91. Lee, Y.E. and Kozak, D.S., 1993. The Role of Zinc in the Eruption of High Carbon FeMn Smelting Furnace. *Electric Furnace Conference Proceedings.* 51, 145-150.

92. Lide, D.R., 1997. Handbook of chemistry and physics, 78th edition.

93. Lopez, F. A., Perez, C., Sainz, E. 1995. Adsorption of $Pb^{2+}$ on Blast Furnace Sludge. *Journal of Chemical Technology and Biotechnology.* 62 [2], 200-206.

94. Lopez-Delgado, A., Perez, C. and Lopez, F. A. 1998. Sorption of Heavy Metals on Blast Furnace Sludge. *Water Research,* 32 [4], 989-996.

95. Lung, T.N., 1986. The history of copper cementation on iron, the world's first hydro metallurgical process from medieval China. *Hydrometallurgy,* 17, 113-129.

96. Lynch, B, 2003. The remediation of acid mine drainage using column flotation. The University of Birmingham, Thesis.

97. McBride, G. B., Alexander, R.B., Elliott, A.H., Shankar, U.2000. Regional scale modelling of water quality. *Water Atmos*, 8, 29-31.

98. McGinness, S., 1999. Treatment of Acid Mine Drainage. Research Paper 99/10. House of Commons, London.

99. Mack, B., and Gutta, B. 2009. An analysis of steel slag and its used in acid mine drainage (AMD) treatment. [Available at:

http://www.asmr.us/Publications/Conference%20Proceedings/2009/0722-Mack-WV.pdf:

last accessed: 20/5/2012].

100. Makkonen, H.T., Heino, J., Laitila, L., Hiltunen, A., Poylio, E., Harkki, J. 2002. Optimisation of steel plant recycling in Finland: dusts, scales and sludge. *Resources, Conservation and Recycling*, 35, 77-84.

101. Manchisi, J., Rowson, N.A., Simmons, M.J.H. 2013. Kinetics of Metals Adsorption in Acid Mine Drainage Treatment with Blast Furnace Slag. School of Chemical Engineering, University of Birmingham.

102. Marcus, Y., 1991. Thermodynamics of Solvation of Ions. *Journal of Chemical Society, Faraday Transactions*, 87, 2995-2999.

103. Maslehuddin, M., Alfarabi, AM., Sharif, M., Shameen, M., Ibrahim, M., Barry, MS. 2003. Comparison of properties of steel slag and crushed limestone aggregate concretes. *Construct Build Mater*, 17[2], 105-112.

104. Matlock, M.M., Howerton, B.S., Atwood, D.A., 2002. Chemical precipitation of heavy metals from acid mine drainage, *Water Res*, 36, 4757-4764.

105. Mecalf and Eddy.2003.Wastewater Engineering: Treatment, disposal and reuse, *Mc Graw Hill,* New york.

106. MEND Treatment committee. 1991. Study on metals and recovery/recycling from acid mine drainage, PHASE IA Literature survey, Mineral Sciences Laboratories. Canada. [Available at: http://www.mend-nedem.org/reports/files/3.21.1a.pdf last accessed:16/03/2011].

107. Michalakos, G.M., Nieva, J.M., Vayenas, D.V., Lyberatos, G., 1997. Removal of iron from potable water using a trickling filter, Water Res. 31, 991-996.

108. Mikhail, S.A. and Turcotte A.M., 1997. Thermal reduction of steel-making secondary materials, Basic-oxygen-furnace dust. *Thermochimica Acta*, 311, 113-119.

109. Modis, K., Adam, K., Panagopoulos, K., Komtopoulos, A., 1998. Development and Validation of a geostatistical model for prediction of acid mine drainage in underground sulphide mines. J.Trans. Instn. Min. Metall. (Sect A: Min. Industry), A102-A107.

110. Mohan, D., and Chander, S., 2001. Single component and multi-component adsorption of metal ions by activated carbons. *Colloid. Surf*, 177, 183-196.

111. Mohan, D., and Chander, S., 2006. Removal and recovery of heavy metal ions from acid mine drainage using lignite-A low sorbent. *Journal of Hazardous Materials*, 137[3], 1545-1553.

112. Moreno, N., Querol, X., Ayora, C., 2001. Utilization of zeolites synthesised from coal fly ash for the purification of acid mine waters. *Environmental Science and Technology*, 35, 3526-3534.

113. Motsi, T., Rowson, N.A., Simmons, M.J.H., 2010. Adsorption of heavy metals from acid mine drainage (AMD), by natural Zeolite. The University of Birmingham, Thesis.

114. Motz, H., Motz, J., Geiseler, J. 2001. Products of steel slags an opportunity to save natural resources. *Waste Management*, 21, 285-293.

115. Mueller, D., 2005. An overview of steel slag for mine drainage remediation. Pittsburgh, PA. [Available at: http://www.techtransfer.osmre.gov/arsite/workshops/2005/mwt/Presentations/PDFs/3hMueller.pdf: last accessed:12/8/2010].

116. Nantumbwe, B.B., 2007. Removal of metals from mine water and synthetic metal solutions using calcium alginate beads. The University of Birmingham, Thesis.

117. Nassar, M.M., Ewida, K.T., Ebrahiem, E.E., Magdy, Y.H., 2004. Adsorption of iron and manganese ion using low cost materials as adsorbents, *Adsorpt. Sci. Technol*. 22, 25- 37.

118. National River Authority, 1999.

119. Nieto, J.M., Sarmiento, A.M., Olias, M., Canovas, C.R., Riba, I., Kalman, J., Delvalls, T.A., 2007. Acid mine drainage pollution in the Tinto and Odiel rivers (Iberian Pyrite Belt, S.W. Spain) and bioavailability of the transported metals to the Huelva Estuary. *Environmental International*, 33, 445-455.

120. Nightingale, E.R.J., 1959. Phenomenological theory of ion solvation. Effective radii of hydrated ions. Department of Chemistry, University of Nebraska.

121. Nyirenda, R.L., 1991. The processing of steelmaking flue dust: A review. *Minerals Engineering*, 4 [7-11], 1003-1025.

122. Ochola, C. and Moo-Young, H.K. 2005. "Reclaimed Limestone Residuals (RLR) for the Treatment of Acid Mine Drainage". Proceedings International Conference on Energy, Environment, and Disaster.

123. Okumura, H., 1993. Recycling of iron-and steelmaking slags in Japan. In: Proceedings of the 1st International Conference on Processing Materials for Properties, Sponsored by: TMS; MMIJ Published by Minerals, Metals & Materials Soc (TMS). pp. 803-806.

124. Omer, Y., Altunkaynak, Y., Guzel, F., 2003. Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite. *Water Research*, 37, 948-952.

125. Papageorgiou, K.S., Katsaros, K.F., Kouvelos, P.E., Nolan, W.J., LeDeit, H., Kanellopoulos, K.N., 2006. Heavy metal sorption by calcium alginate beads from Laminaria digitata. *Journal of Hazardous Materials*, B137, 1765-1772.

126. Personal communication, G. Ghataora, April 17, 2011.

127. Peters, Mark A. Process for recovering zinc from steel-making flue dust. United States patent application 4071357. 1978-01-31.

128. Pickles, CA.2000. Recovery of metal values from EAF dust. In: Steel Mill Wastes & By-products, Atlanta, USA, Gorham Conference, p. 44.

129. Plasari E., and Muhr H.2007. Development in precipitation engineering for process intensification in the environmental protection and other purification industrial activities. *Chemical Engineering Transactions*, 11, 65-70.

130. Polat, M., Guler, E., Akar, G., Mordogan, H., Ipekoglu, U., Cohen, H., 2002. Neutralization of acid mine drainage by Turkish lignitic fly ashes; role of organic additives in the fixation of toxic elements. *Journal of Chemical. Technology Biotechnol,* 77, 372-376.

131. Proctor, D.M., Fehling, K.A., Shay, E.C. 2000. Physical and chemical characteristics of blast furnace, basic oxygen furnace, and electric arc furnace steel industry slags. *Environmental Science and Technology,*34[8], 1576-1582.

132. Proctor, D., Shay, E., Fehling, K., and Finley, B. 2002. Assessment of human health and ecological risks posed by the uses of steel industry slags in the environment. *Human and Ecological Risk Assessment,* 8, 681-711.

133. Qiu, H., Lv, L., Pan, B.C. 2009. Critical review in adsorption kinetic models. *Journal of Zhejiang University Science A,* 10 [5], 716-724.

134. Rehmat A. and Mensinger MC. 1996. Recovery of direct reduced iron from blast furnace dust. In: Second international symposium on extraction and processing for the treatment and minimisation of wastes. pp. 27-30.

135. Richardson, J.F., Harker, J.H., Backhurst, J.R., 2002. Coulson & Richardson's Chemical Engineering Volume 2, Fifth edition, Butterworth Heinemann.

136. Rios, C.A., William, C.L., Roberts. 2008. Removal of heavy metals from acid mine drainage (AMD) using coal fly ash, natural clinker and synthetic zeolites. *Journal of hazardous materials*, Volume 153[1-3], 23-35.

137. Robinson, R., Fenwei, SU., Hans-Olof L., 2003. Recycling of Sludge and Dust to the BOF Converter by Cold Bonded Pelletizing. *ISIJ International*, 44 [4], 770-776.

138. Russell, C.S. and Vaughan, W. 1976. Steel production. Baltimore and London: The Johns Hopkins University press.pp.21-32 & 103-128.

139. Ruthven, D.M., 1984. Principles of adsorption and adsorption processes. A Wiley–Interscience Publication, John Wiley and Sons Inc.

140. Sag, Y., and Aktay, Y.2000. Mass transfer and equilibrium studies for the sorption of chromium ions into chitin. *Process Biochemistry*, 36, 157-173.

141. Sanchez, E., Lopez-Pamo, E., Santofimia, E., Aduvire, O., Reyes, J., Barettino, D., 2005. Acid mine drainage in the Iberian Pyrite Belt (Spain): Geochemistry, mineralogy and environmental implications. *Applied Geochemistry*, 20[7], 1320-1356.

142. Santos, R., Machado, R., Correia, M.J.N., 2004. Treatment of acid mining waters. *Mineral. Engineering*, 17, 225-232.

143. Santona, L., Castaldi, P., Melis, P., 2006. Evaluation of the interaction mechanisms between red muds and heavy metals. *Journal of Hazardous Materials*, 136[2], 324-329.

144. Sensel, M.E., and Myers, K.J. 1992. Add some Flavor to your Agitation Experiment. *Chem. Eng. Ed.*, 26[3], 156.

145. Serbent H., Maczek H., Rellermeyer H. 1975. Large-scale test for the treatment of BF sludge and BOF dust according to waelz process. In: Iron making proceedings. 34, 194-205.

146. Sharma, KK., Swaroop, S., Thakur, DS., 1993. Recycling of LD slag through sinter route on direct charging in blast furnace at Bhilai Steel Plant. In: Proceedings of national seminar on pollution control in steel industries; pp.72-79.

147. Shchukin Yu.P., Kaporulin V.V., Novikov V.S. and Marsuverskii B.A., 1991. Influence of Various Factors on Behavior of Zinc in Blast Furnace. *Steel in the USSR.* 21 (5), 189-193.

148. Shen, H., and Forssberg, E., 2003. An overview of recovery of metals from slags. *Waste management*, 23[10], 933-949.

149. Sheremata T., and Kuyucak N., 1996. Value recovery from acid mine drainage, MEND project 3.21.2a, Pointe-Claire, PQ, Noranda Technology Center. Pointe Claire, Quebec, Canada.

150. Shevko, VM., Tomilin, IA., Nikanorov, AD., Pominov, VD., Kabylbekova, BN. 1993. Pilot plant testing of oxidising chlorination roasting of blast furnace and steel making sludges. pp. 5-93.

151. Simmons, J., Ziemkiewicz, P., and Black, D. C., 2002. Use of steel slag leach beds for the treatment of acid mine drainage. *Mine Water and the Environment.* 21, 91-99.

152. Singer, P.C. and Strumm, W., 1970. Acid mine drainage: the rate determining step. *Science*, 167, 1121-1123.

153. Skousen, J. and P., Ziemkiewicz. 1996. Acid Mine Drainage Control and Treatment. 2nd Ed. National Research Center for Coal and Energy, National Mine Land Reclamation Center, West Virginia University, Morgantown, pp. 362.

154. Skousen, J., Rose, A., Geidel, G., Foreman, J., Evans, R., Hellier, W., Members of the Avoidance and Remediation Working Group of ADTI, 1998. Handbook of technologies for avoidance and remediation of acid mine drainage. The national Mine Land Reclamation Centre, West Virginia.

155. Skousen, J.G., Sexstone., A., Ziemkiewicz, P.F. 2000. Acid mine drainage control and treatment. Reclamation of Drastically Disturbed Lands. Chapter 6, pp.1-32.

156. Sposito, G. 1989. The chemistry of soils. New York: Oxford University Press.

157. Sprynskyy, M., Boguslaw B., Terzyk, A.P., Namiesnik, J., 2006. Study of the selection mechanism of heavy metal ($Pb^{2+}$, $Cu^{2+}$, $Ni^{2+}$ and $Cd^{2+}$) adsorption on clinoptilolite. *Journal of Colloid and Interface Science*, 304, 21-28.

158. Steffen, Robertson and Kirsten, Inc., 1989. Acid Drainage Draft Technical Guide, Volume 2 – Summary Guide.

159. Swash, P.M. and Monhemius, A.J., 2005. Characteristics and stabilities of residues from the Wheal Jane constructed wetlands. *Science of the Total Environment*, 338, 95-105.

160. Tarleton, A.L., Lang, G.E., Wieder, R.K., 1984. Removal of Iron from acid mine drainage by sphagnum peat: results from experimental laboratory microcosms, in: D. Graves (Ed.), Proceedings of the Symposium on Surface Mining, Hydrology, Sedimentology and Reclamation, University of Kentucky, Lexington, KY, pp. 413-420.

161. Thakur, P.K., 2000. Utilisation of steel melting slag to generate wealth from waste. Proceedings of the Conference on Environmental Management in Metallurgical Industries. BHU, Varanasi India, pp. 187-193.

162. Topkaya, Y., Sevinc, N., Gunaydin, A. 2004. Slag treatment at Kardemir integrated iron and steel works. *Int. J. Miner. Process*, 74, 31-39.

163. Uno S., Umetsu Y., Ohmizu M., Munakata S. 1997. Dezincing equipment and operation based on wet classification of wet-cleaned BF dust. *Nippon Steel Tech Rep*, 13, 80-85.

164. USEPA. Technical document of acid mine drainage prediction. Office of Solid Waste, Washington, USA; 1994. p. 48.

165. Utgikar, V., Chen, B.-Y., Tabak, H.H., Bishop, D.F., Govind, R., 2000. Treatment of acid mine drainage: 1. Equilibrium biosorption of zinc and copper on non-viable activated sludge. *Int. Biodeterior*, 46, 19-28.

166. Vadapalli, VR., Petrik, L.,Fester, V., Slatter, P., Sery, G. 2007. Effect of fly ash particle size in its capacity to neutralise Acid Mine Drainage and influence on the rheological behaviour of residual solids. *WoCA*. [Available at: http://www.flyash.info/2007/8vadapalli.pdf: last accessed: 24/10/2011].

167. Van-Herck, P., Vandecasteele, C., Swennen, R., Motier. 2000. Zinc and lead removal from blast furnace sludge with a hydrometallurgical process. *Environ Sci Technol*, 34[17], 3802-8.

168. Valenzuela, F., Cabrera, J., Basualto, C., Sapag-Hagar, J., 2005. Kinetics of copper removal from acidic mine drainage by a liquid emulsion membrane. *Minerals Engineering*, 18, 1224-1232.

169. Wang, J.W., Bejan, D., Bunce, N., 2003. Removal of arsenic from synthetic acid mine drainage by electrochemical pH adjustment and co-precipitation with iron hydroxide. *Environ. Sci. Technol*, 37, 4500-4506.

170. Weber Jr., T.W., Chakravorti, R.K., 1974. Pore and solid diffusion models for fixed bed adsorbers. *J. Am. Inst. Chem. Eng*, 20, 228-238.

171. Webster, J.G., Swedlund, P.J., Webster, K.S., 1998. Trace metal adsorption onto an acid mine drainage iron (III) oxy hydroxy sulphate. *Environ. Sci. Technol*.32, 1361-1368.

172. White, D.A., and Siddique, A.A., 1997. Removal of manganese and iron from drinking water using hydrous manganese dioxide. *Solvent Extr. Ion Exc*, 15, 1133-1145.

173. Whitehead, P.G., Cosby, B.J., Prior, H., 2005. The Wheal Jane wetlands model for bioremediation of acid mine drainage. *Science of the Total Environment*, 338, 125-135.

174. Whitehead, P.G., Hall, G., Neal, C., Prior, H., 2005. Chemical behaviour of the Wheal Jane bioremediation system. *Science of the Total Environment*, 338, 41-51.

175. Wilkin, R.T., and McNeil, M.S., 2003. Laboratory evaluation of zero valent iron to treat water impact by acid mine drainage. *Chemosphere*, 53, 715-725.

176. Wingenfelder, U., Hansen, C., Furrer, G., Schulin R., 2005. Removal of heavy metals from mine waters by natural zeolites. *Environmental Science and Technology,* 35, 4606-4613.

177. Wong, M.H., Luk, K.C., Choi, K.Y., 1977. The effects of zinc and copper salts on Cyprinus carpio and Ctenopharyngodon idellus. *Acta Anatomica*, 99, 450-454.

178. World Coal Institute, 2010. [Available at: http://www.worldcoal.org/coal-the-environment/coal-mining-the-environment/ last accessed: 11/10/2011].

179. Xinchao W., Roger C., Viadero J. and Karen M., 2005. Recovery of Iron and Aluminum from Acid Mine Drainage by Selective Precipitation. *Environ. Eng. Sci,* 22[6], 745-755.

180. Xu, C.Y., Schwartz, F.W., Samuel, J.T., 1997. Treatment of acid mine water with calcite and quartz sand. *Environ. Eng. Sci*, 141, 141-152.

181. Yadev, U.S., Das, B.K., Kumar, A., 2001. Recovery of mineral value from integrated steel plant waste. In: Barbosa, J.P., et al. (ED.), Proceedings of the VI Southern Hemisphere Meeting on Mineral Technology, Volume 2, 719-725.

182. Yan, J., Moreno, L., Neretnieks, I., 1999. The long-term acid neutralizing capacity of steel slag. *Waste Management,* 20, 217-223.

183. Younger, P.L., Banwart, S. A., Hedin, R. S., 2002. Mine Water: Hydrology, Pollution, Remediation. The Netherlands: Kluwer Academic Press.

184. Zabban, W., Fithian, T., Nabevak, D.R., 1972. Converting AMD to potable water by ion exchange treatment, Coal Age 107-111.

185. Zamzow, M.J., Eichbaum, B.R., Sandgren, K.R., Shanks, D.E., 1990. Removal of heavy metals and other cations from waste water using zeolites. *Separation Science and Technology*, 25 [13-15], 1555-1569.

186. Zawani Z., Luqman Chuah A. and Thomas Choong S. Y,. 2009. Equilibrium, kinetics and thermodynamic studies: adsorption of remazol black 5 on the palm kernel shell activated carbon (PKS-AC). *European Journal of Scientific Research,* Volume 37, [1], 67-76.

187. Zeydabadi, BA., Mowla, D., Shariat, MH., Fathi Kalajahi.,1997. Zinc recovery from blast furnace flue dust. *Hydrometallurgy*, 47[1], 133-25.

188. Zhou, Y.-F.; Haynes, R. J. 2010. Sorption of heavy metals by inorganic and organic components of solid wastes: Significance to use of wastes as low-cost adsorbents and immobilizing agents. Critical Reviews in Environmental Science and Technology, 40[11], 909-977.

189. Zhou, Y.-F. and Haynes, R. J. 2010. A Comparison of Inorganic Solid Wastes as Adsorbents of Heavy Metal Cations in Aqueous Solution and Their Capacity for Desorption and Regeneration. *Water Air Soil Pollut*, 218, 457-470.

190. Ziemkiewicz, P., Skousen, J., Brant, D., Sterner, P., Lovett, R.J., 1997. Acid mine drainage treatment with armoured limestone in open channels. *Journal of Environmental Quality*, 26, 1017-1024.

191. Ziemkiewicz PK, and JG Skousen. 1998. The use of steel slag in acid mine drainage treatment and control. In: Proceedings, 19th Annual West Virginia surface Mine Drainage task force symposium, Morgantown, West Virginia.

192. Zunkel, AD., and Schmitt RJ., 1996. Dealing with EAF dust: environmental regulations and treatment processes. In: 9th International Mini-mill Conference, 12-14 March 1996, Cincinnati, USA Metal Bulletin Monthly's. p.23.

# APPENDICES

# <u>APPENDIX A</u>

**Atomic absorption spectroscopy (AAS)**

Atomic absorption spectrometry (AAS) is an analytical technique that measures the concentrations of elements and metals. Atomic absorption is very sensitive and it can measure down to parts per billion. The technique makes use of the wavelengths of light specifically absorbed by an element. Atoms of different elements absorb characteristic wavelengths of light. For example with copper, a lamp containing copper emits light from excited copper atoms that produce the right mix of wavelengths to be absorbed by any copper atoms from the sample (Tissue, 1996).

Since samples are usually liquid, the metal atoms or ions must be vaporized in a flame. In AAS, the sample is atomised and converted into ground state free atoms in the vapour state. The vaporised atoms absorb ultraviolet or visible light and make transitions to higher electronic energy levels. The metal concentration is determined from the amount of light absorbed by the vaporised atoms (Tissue, 1996). The amount of light absorbed by the atoms is simply the total amount of light produced at the light source (lamp) minus the total amount received by the detector, See Figure A1.

A calibration curve must be constructed for concentration measurements by running several samples of standard solutions of selective metal ions ($Cu^{2+}$, $Fe^{3+}$, $Zn^{2+}$ and $Mn^{2+}$) at known concentrations. The amount each standard solution absorbs is compared with the calibration curve and this enables the calculation of the respective metal ions concentrations in the unknown sample.

**Figure A1: Schematic of atomic absorption spectrometer.** (Reprinted from: http://toolboxes.flexiblelearning.net.au/demosites/series5/508/PMLTEST506/42step01.htm)

The process of lighting the AAS flame involves switching on first the fuel then the oxidant and finally lighting the flame. After only a few minutes the flame is stable. Deionized water can be aspirated between samples. Shutdown involves aspirating deionized water for a short period and then closing the fuel.

**Function of the hollow cathode lamp**

The light source is usually a hollow-cathode lamp of the element that is being measured. It provides the analytical line for the element of interest. Lasers are also used in research instruments. Since lasers are intense enough to excite atoms to higher energy levels, they allow AAS and atomic fluorescence measurements in a single instrument. The disadvantage of these narrow-band light sources is that only one element is measurable at a time.

**Function of the atomizer**

AAS requires that the metal atoms be in a gaseous phase. Ions or atoms in a sample must be vaporised in a high-temperature source such as a flame (2100–2400K) or graphite furnace. Flame AAS can only analyse solutions, while graphite furnace AAS can accept solutions, slurries, or solid samples.

**Function of the nebulizer**

It sucks up liquid sample at a controlled rate and creates a fine aerosol for introduction into the flame.

**Function of the Flame**

AAS uses a slot type burner to increase the path length, and therefore to increase the total absorbance (Beer-Lambert law). Sample solutions are usually aspirated with the gas flow into a nebulising/mixing chamber to form small droplets before entering the flame. Table A1 presents examples of different fuels used to produce a flame for the AAS.

**Excitation**

A flame provides a high-temperature source for desolvating and vaporising a sample to obtain free atoms for spectroscopic analysis. As stated above in atomic absorption spectroscopy ground state atoms are desired. For atomic emission spectroscopy the flame must also excite the atoms to higher energy levels.

**Light separation and detection**

AAS use monochromators and detectors for UV and visible light. The main purpose of the monochromator is to isolate analytical lines photons passing through the flame and removes scattered light of other wavelengths from the flames. Simple dedicated AAS instruments often replace the monochromator with a band-pass interference filter. Photomultiplier tubes are the most common detectors for AAS.

The atomic absorption spectrometer (AAS) used in this study uses an air – acetylene flame to vaporise solution samples and single element hollow cathode lamp as a light source.

| Fuel | Oxidant | Temperature, K |
|---|---|---|
| Hydrogen | Air | 2000-2100 |
| Acetylene | Air | 2100-2400 |
| Hydrogen | Oxygen | 2600-2700 |
| Acetylene | Nitrous Oxide | 2600-2800 |

**Table A1: Examples of common fuels used in AAS and the temperature of the flames they produce.**

**Sample analysis**

The atomic absorption spectrometer (AAS) had to be calibrated for each metal before analysing any sample. This was achieved by passing samples of known concentration through the AAS. These samples were made from standard metal solutions which were diluted to the required metal concentration. The results of analysing these diluted standard solutions gave a calibration curve for each metal.

The errors in analysing copper, iron, zinc and manganese was approximately ±6.65%, 6.67%, 5.77% and 5.59% respectively. Figure A2 presents the typical calibration curves for copper, zinc, manganese and iron used in this study.
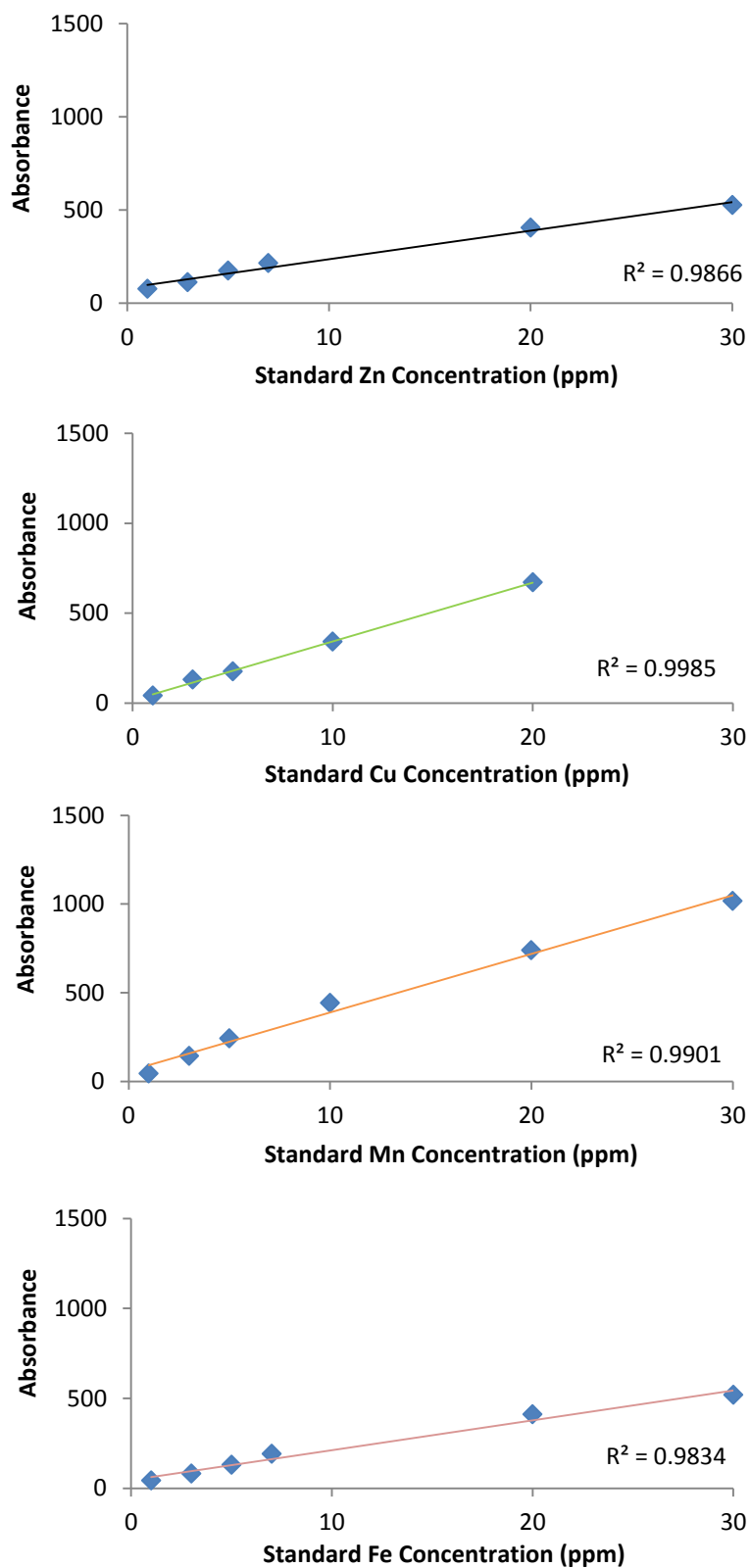
**Figure A2: Typical calibration curves for zinc, manganese, copper and iron obtained using the AAS.**

# <u>APPENDIX B</u>

**Proposed design of a passive AMD treatment reactor vessel**

Flow rate into passive treatment plant = 6 L/s
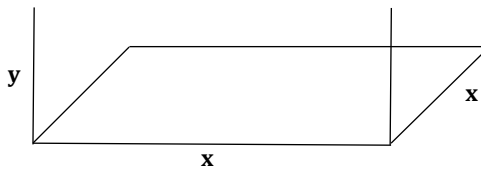
Residence time = 5 hours

*Calculations:*

$Q = V / RT$

Total volume (V) passed in 5 hours = 108 m$^3$

Assuming the tank has a square base and a height that is half of the length of one side of the square base:



Where $y = x / 2$,

Hence, volume of tank = $x^2y$

Volume, m$^3$ = 108 = $x^2y = x^3/2$

The dimensions of the reactor is:

The value of $x = 6$ m

And, $y = 3$ m

*Material of Construction:*

The vessel will be constructed using concrete; this is resistant to the acidic nature of AMD and results in a longer life of the reactor vessel.

# APPENDIX C