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Passive treatment of acid mine drainage using South African coal fly ash in a column reactor.

By

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ABSTRACT

Fly ash (FA) and acid mine drainage (AMD) are two undesirable materials generated from combustion of pulverized coal for energy and mining activity respectively. Both waste materials have serious, negative impacts on the environment. Fly ash storage leaches a variety of contaminants into surface and groundwater and AMD contains high amounts of toxic metals besides the already dominant SO_4^{2-} concentrations.

Many studies had investigated AMD treatment using FA and successfully removed significant amounts of sulphate, as well as minor and trace elements. Hence AMD can be treated using coal fly ash in an active or passive system without addition of any other chemicals. This study had as of objectives the evaluation of the neutralization capacity of FA from two South African's power stations located in Mpumalanga which are Lethabo and Kendal with mine drainage water from the Mpumalanga coal fields using passive treatment.

The research program simulated ex-situ neutralization of AMD in a fly ash slurry followed by continued AMD contact, representing the potential for using spent material as mine annulus fill to reduce air and water content and further AMD generation. Both the fly ash and AMD were obtained from the Mpumalanga province in Eastern South Africa. A 3:1 slurry ratio of AMD to fly ash was mixed until pH stabilized. After mixing, the slurry was packed in columns and left for a duration of 24 hours for a good settling time before the hydraulic treatment. Thereafter the AMD was continuously passed through the columns using gravity flow. Samples of effluent were collected at set time intervals during the hydraulic treatment. These samples were used to determine the flow rate, pH of the leachates and some sent for analysis by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) and Ion Chromatography (IC) to determine the composition of the effluent water recovered.

The X-ray diffraction done on both coal fly ash sources shown a dominance of quartz and mullites,on the other hand the X-ray fluorescence demonstrate that Kendal and Lethabo coal fly ash belong to class F ash due to fact that the total composition of SiO_2, Al_2O_3 and Fe_2O_3 was exceeding 70% of the entire composition. Moreover, trace elements such as As, V, Ni, Mn, S, Sr, Cu, Y and Pb are found in the CFA used as well. The ICP-OES analysis showed that Eyethu AMD is very acidic with a pH of 2.23, with sulphate concentration of 2680 mg/L, displaying the existence of some metals some of which are Ca, Al and Fe. The neutralization process of Eyethu acid mine drainage using Kendal and Lethabo CFA was highlighted by the variation of pH from the time mine water was in contact with CFA, for the treatment with

Lethabo CFA the treated water had its pH raised from 2.23 to 12.65 and from 2.23 to 8.37 using Lethabo and Kendal CFA respectively and this phenomena was explained by the dissolution and hydrolysis of the oxide components such as CaO. This neutralization process was characterized by a strong buffer zone around the pH of 12.83 to 8.37 from the Lethabo leachate and between 8.37 to 7.28 for the leachate from Kendal column. This buffer zone is explained by the hydrolysis of Al^{3+} which forms a hydroxide phase until all the aluminum ion was totally hydrolyzed. Electrical conductivity was also observed to vary. An amount of 1440 g of Kendal fly ash was used in the columns and treated 15 bed volumes of Eyethu AMD before the CFA was exhausted and lost its neutralizing power in the case of Lethabo CFA, 13 bed volumes of AMD were treated with 1280g CFA before breakthrough was observed.

During treatment of Eyethu AMD with Lethabo and Kendal CFA the flow rate of the effluents water first increased during the first minutes of contact of AMD with CFA then started decreasing with time. The concentration of sulphate was reduced to up to 88% in the effluent from Lethabo CFA and 56% in the effluent from Kendal CFA. Some other metals such Fe, Mg, Mn, Al have been significantly removed from the AMD in the Lethabo and Kendal leachate. Furthermore, mass balance calculation were done around the columns in order to determine the moisture content and the % water recovery. From the calculation done it was shown that the column made of Kendal CFA can treat the AMD with a water recovery of 91.9% while Lethabo column could only recover 83.33% of the inlet water. In addition, Acid Base accounting tests were done in order to determine whether either Kendal or Lethabo CFA are from an acid generating or neutralizing rock. Test results have shown that both Kendal and Lethabo CFA are from an alkaline producing rock as their Net Neutralizing Potential and Neutralizing Potential Ratio were above 20 Kg/t $CaCO_3$.

LIST OF ABBREVIATIONS

ABA – Acid base accounting

ALD – Anoxic limestone drain

AMD – Acid mine drainage

AP – Acid potential

ASTM – American society for testing and materials

CFA – Coal fly ash

DWAF – Department of water affairs.

EC – Electrical conductivity

ED - Electro dialysis

EDR – Electro dialysis reversal

IC - Ion chromatography

ICP-OES - Inductively coupled plasma-optical emission spectrometry

IR – Infra red

LOI - Loss of ignition

MF - Micro filtration

MPA – Maximum potential acid

NF – Nano filtration

NNP – Net neutralization potential

NP – Neutralization potential

NPR- Neutralizing potential ratio

OLD – Open limestone drains

PRB – Permeable reactive barriers

RO - Reverse osmosis

SAPS – Successive alkalinity producing system

SRB - Sulphate reducing bacteria

UF – Ultra filtration

WHO - World Health Organization

XRD – X-ray diffraction

XRF – X- ray fluorescence

ℓ - Density

DECLARATION

I, E. B. Nkongolo declare that the contents of this thesis represent my own unaided work, and that the thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

Signed **Date**

DEDICATION

I dedicate this piece of work to my God for allowing me to get to this level and to my closest family for their tremendous support throughout the course of this study:

- Benjamin Nkongolo (Late Father)
- Therese Tshilanda Mulumba (Late mother)
- Emilie Kalonji (wife)
- Alain Tshilumba (brother)
- Evka Keyembe (Brother)

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CHAPTER ONE

1 INTRODUCTION

1.1 BACKGROUND

Mining industries represent an important source of metals as well as an essential economic activity for the regions where they are located. Minerals copiousness provided a mean of generating wealth. Minerals are sold on the free trade, this allowing countries that own them to acquire valuable currency compared to countries that do not have. In South Africa mining has been taking place for over 100 years. This mining activity in South Africa has positively impacted the economy of the country. Gold is the first mineral that was discovered in South Africa at Langlaagte farm in 1886. Its discovery opened up the door to gold mining which became the turning point of the South African economy (Bobbins, 2015).

However, mining activity has a negative impact on the environment and aquatic life by polluting water. Mining leaves voids, which are empty spaces underground. The fact that water flows through these voids that contain sulfur-bearing materials leads to the formation of solutions of net acidity called Acid Mine Drainage. From the equation 1.1 below it can be shown that sulphuric acid is generated through pyrite (FeS_2) oxidation in the presence of water and air with *Acidobacillus bacteria* as a catalyst. The sulphuric acid product of this reaction is at the origin of the chemical weathering of the surrounding rocks, thereby causing the leaching of radioactive elements and hypothetically toxic metals into water (Madzivire, 2012; Winde, 2010).

$$FeS_2 + \frac{7}{2}O_2 + H_2O \rightarrow Fe^{3+} + 2H^+ + 2SO_4^{2-} \ldots\ldots\ldots\ldots\ldots \text{Equation 1. 1}$$

AMD is found in underground activities of profound mines, in spite of the fact that this is for the most part of minor importance when a mine is in active production and water tables are kept artificially low by pumping. Nevertheless, when mines are closed and abandoned; and the pumps are turned off; rebounding of the water table will lead to the discharge of contaminated groundwater (Johnson & Hallberg; 2004). AMD is mostly characterised by a pH water 4 with a high concentration of Fe, Mn and Al cations and sulphate ions as

well as toxic metals of different composition depending on the types of starting mineral store (Fysion et al., 1994; Sheoran & Sheoran, 2005). The effluent produced is typically acidic and often comes from places where mining activities involving ore or coal have exposed rocks containing pyrite, a mineral that carries sulphur. Metal-rich drainage can also occur in mineralised areas not previously mined or in areas, which were mined and often abandoned, or in mines that are still active.
Most or all of this iron contain in AMD will precipitate to form the red, orange or yellow sediments at the bottom of mine-drainage streams (Gitari, 2006). Metals like copper, lead and mercury are dissolved into ground or surface water by the acid runoff. Moreover, AMD can contaminate ground water and disrupt development and reproduction of plants and animals that live in water. The corrosive effects of AMD on infrastructures, like bridges is also problematic. Acid mine drainage does not affect only the ecology aspect but the economy of the country as well. A area affected by acid mine drainage often has declines in prized recreational fish species such as trout, as well as a general decline in outdoor recreation and tourism, together with pollution of groundwater resources (Madzvire, 2009). The Witwatersrand basin gold fields, O'Kiep copper district, KwaZulu-Natal coal fields and Mpumalanga coal field are the areas mostly affected by acid mine drainage. The impact upon water resources has serious consequences for people health and well-being. South Africa is a water scarce country, the average rainfall in SA is below the world average. Water is unequally distributed across the country, with just more than 1200 Kl of available fresh water for each individual per year. South Africa is on the brink of the international definition for being in water crisis. This situation is about to depreciate more due to the climate change, with current evaluations indicating that the South Africa has warmed by around one degree Celsius in the past 30 years and that annual rainfall is predicted to go down by between 20 and 40 mm per annum staring from 2050. This proves that the fresh water supplies of South Africa are scarcity and will be more affected by the presence of acid mine drainage (Feris & Kotze, 2014). Solutions are needed in order to stop or reduce this pollution; several studies and different techniques or passive and active treatment strategies have been undertaken (Taylor and Murphy, 2005). Active and passive abiotic and biological techniques are among the techniques used to treat acid mine drainage in order to control pH and lower the concentration of toxic metal and sulphate content as well

as to reduce the acidity of the effluent water (Trumm, 2010; Hallberg & Johnson, 2004). The mining of coal has more than one negative environmental impact. Besides being the source of acid mine drainage, it has another impact by generating a lot of waste by-products through the combustion of coal for electricity generation. Among these wastes, the most notable is coal fly ash waste.

Fly ash is a major combustion residue generated through the combustion of pulverised coal and is a fine-grained, inorganic, spherical, glassy, powdery residue, which is resulting from inorganic minerals. CFA being generated as a waste product from coal combustion, is produced in huge amounts because of the high demand for energy throughout the world. CFA production is predicted to increase and the disposal of this waste by-product becomes a worrying issue. Therefore, several studies on the utilisation of CFA are being conducted in a way to beneficiate this waste material and to protect the environment. It has been made known that AMD can be treated using CFA using an active or passive methods (Sarkar et al., 2006; Nyambura et al., 2011; Gitari et al., 2008; Querol et al., 2002; Nyale, 2014).

1.2 PROBLEM STATEMENT

The world's dependence on coal for production of energy continues to increase through an increase of the population. South Africa has the largest coal reserves in Africa, mining 250 Mt of coal per year and exporting an amount about 71.4 Mt of it annually (Nyale, 2014; BP, 2010; DME, 2006). The coal mining activities release toxic metals into water sources, thus causes the pollution of surrounding water and threatens the health and safety of the surrounding environment after the mines have been closed down (Jaiswal & Shrivastva, 2012). Moreover, the burning of coal for energy generation comes with a cost to the environment due to the high volume of coal fly ash that is produced during this process. A huge amount of CFA is generated each year and it is not well disposed. CFA is usually stored in ash dams and as such has a huge risk of leaching toxic and trace elements once CFA is in contact with aqueous solution such as rain water. These problems will increase with the high demand of energy growing proportionally with the population growth. Several studies have been conducted in order to find a solution on how to reduce the negative impacts of AMD and CFA on the environment. This study will use a passive way to treat AMD with CFA, as this method is cost effective and does not require the addition of any other chemicals. It can provide a solution to minimizing the negative impacts of these two waste materials AMD and FA on the environment.

1.3 AIM AND OBJECTIVES

This study aims to investigate the neutralization capacity of Eyethu AMD while treating it with Kendal and Lethabo CFA, as well as majors and trace elements removal when passively treating Eyethu AMD with South African CFA. This aim will be achieved following the objectives below:

- Characterisation of Kendal and Lethabo coal fly ash using XRD and XRF analysis. The characterisation of the acid mine drainage using IC and ICP-OES tests in order to determine the cation and anion element present in the waste water.
- Understanding and monitoring the flow rate through the columns of fly ash from Kendal and Lethabo.
- Understanding the chemical, physical and mineralogical property of the solid residue produced by using XRD and XRF and determining the particle size and the chemical composition of the leachates.
- Understanding the degree of improvement in Eyethu water quality.
- Understanding how many bed-volumes of AMD can be treated by either Lethabo or Kendal ash.

1.4 RESEARCH QUESTIONS

This study will answer the following research questions:

1. What are the chemical and physical parameters of Eyethu AMD
2. What are the chemical, physical and mineralogical characteristics of fly ash obtained from Kendal and Lethabo power stations and?
3. What are the similarities and differences, in terms of chemical and mineralogical characteristics, of Kendal and Lethabo coal fly ash?

4. Can Eyethu AMD be treated using Kendal and Lethabo coal fly ash in passive methods?
5. To what extent is neutralisation and purification of Eyethu AMD achieved using Kendal or Lethabo coal fly ash?
6. How does the particle size impact on the treatment capacity of Eyethu AMD with Kendal or Lethabo ash?
7. What is the percentage water recovery of treated water from Kendal and Lethabo coal fly ash?

1.5 RESEARCH APROACH

A wide ranging literature review on the treatment of acid mine drainage with South African CFA was conducted. This research topic on the passive treatment of Eyethu AMD with Kendal and Lethabo coal fly ash is inspired by the work proposed by Gitari et al. (2013). The overall schematic representation of all the steps of the experiments and different techniques of characterisation test are represented in Figure 1.1 below.

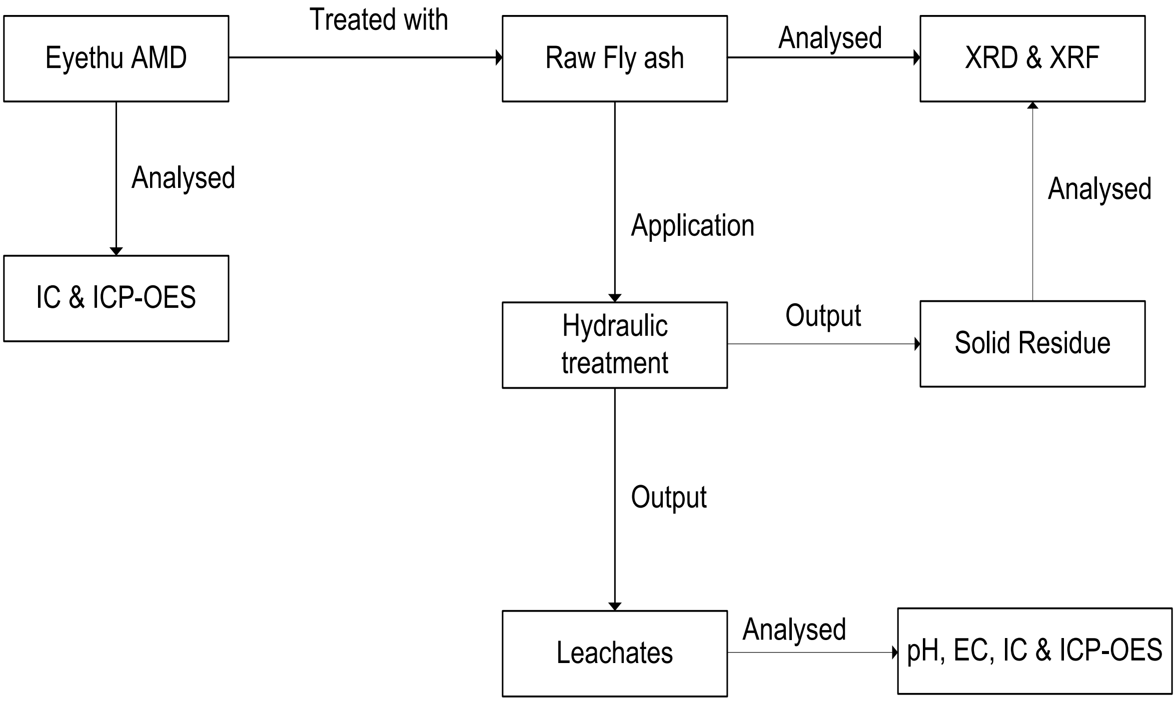

Figure 1. 1: Block flow diagram of the process

This study will focus on the treatment of Eyethu AMD with Kendal and Lethabo coal fly ash. Raw AMD will be characterised using IC, ICP-OES, physical parameters (pH and EC) and fresh coal FA will be characterised as well by using XRF and XRD. For the determination of the elemental composition, mineral phases and particle morphology before treatment. This will be followed by the mixing of Eyethu with each type of coal fly ash (Kendal and Lethabo) to be used for column packing. After the mixture has settled the columns will be connected to the hydraulic system that will allow fresh Eyethu AMD to flow through the column. It will be a down flow where AMD will be entering from the top of the columns and treated water (collected) at the bottom at different times throughout the experiment periods. Leachates or product water will be characterised using IC and ICP-OES in order to determine its elemental composition, physical parameters such as pH and EC and the elements that are removed. Moreover, solid residues will be characterised by XRF and XRD to investigate changes within the mineral phases during the treatment of AMD. The acid base accounting test will be determined on both Kendal and Lethabo CFA to determine the Net neutralizing potential and the neutralizing potential ratio of both CFAs. Furthermore, the mass balance calculations will be done to determine the percentage water recovery of the process.

1.6 Scope and delimitation

Kendal and Lethabo coal fly ash were the two type of fly ash those were used in this study among the types of CFA generated in South Africa and Eyethu acid mine drainage was the only AMD used in this study. Passive treatment was the only method that will be used to treat Eyethu AMD without any addition of other chemicals in this study to make the study cost effective. Solid residue produced during this study can be used in the synthesis of geopolymer but that will not be part of this study.

1.7 THESIS OUTLINE

- Chapter 2: Literature review

This chapter gives the background literature related to this study. The literature reviewed includes the mine water formation and composition; different mine water treatment technologies, FA formation and composition, different uses of FA, disposal methods of FA and the radioactivity of mine water.

- Chapter 3: Methodology

Chapter 3 details how the sampling of AMD and CFA were done, and explains all the experimental methodology and analytical techniques like X-ray diffraction (XRD), X-ray fluorescence (XRF) that were used on the fresh CFA and solid residue generated, and the test done on the AMD the pH, ion chromatography (IC), Inductively coupled plasma Optical Emission Spectroscopy (ICP-OES) and Electrical conductivity (EC) used within this study.

- Chapter 4: Results and discussion

The chapter four presents all the analytical results of the fresh CFA and solid residue as well as for the AMD and the treated water. It gives in details on the neutralisation process, the variation of pH over time, the concentration removal of the toxic metals during the treatment process, trends of sulphate concentration removal is being exposed as well, the volumetric flow rate, percentage removal, rate of removal of both heavy metals and sulphate. Furthermore, the mass balance calculation as well as the Acid Base Accounting test are presenting in this section.

- Chapter 5: Conclusion and recommendation

This chapter provides thee conclusion obtained from this study, which could be drawn based on the results obtained. Furthermore, it gives the answers to the research questions that were firstly highlighted in Chapter 1 and it provides the recommendation and future work that can emanate from the findings undertaken in this study

CHAPTER 2

2 LITTERATURE REVIEW

This chapter offers a literature review that gives the genesis of acid mine drainage (AMD), its chemical composition, environmental impact and different methods of treatment. Furthermore, it describes the formation, properties, classification and environmental impacts of coal fly ash disposal and its various applications.

2.1 ACID MINE DRAINAGE (AMD)

AMD is a discharge waste that arises from mining activity. This waste is known as the biggest environmental issue created by the mining industry due to the toxicity and high acidity of this water (Gitari, 2006). AMD has a pH below 3 making it enormously acidic and enriched with Fe, Mn, Al and some other toxic metals such as pyrite (FeS_2). It does not have a specific composition but mined ore and the chemical additives used in the mineral processing and hydrometallurgical processing can determine AMD composition (Maleka, 2015). Therefore, AMD can be classified using other parameters rather than chemical composition. The parameters used in classifying AMD includes major and cations and anions, pH and alkalinity versus acidity of the mine water (Madzvire, 2009; Lottermoser, 2007). Figure 2.1 presents the image of acid mine drainage from the Witwatersrand region.

Figure 2. 1 :AMD from Witwatersrand (Source: of. 12.08.2019)

2.1.1 Formation of AMD

AMD is produced from natural weathering of FeS_2, which is a major constituent of both coal and base metals sulphide. The oxidation of FeS_2 to form AMD in the presence of water is been represented in a complex set of reactions as shown in equation below (Stumm and Morgan, 1981).

$$2FeS_2 + 7O_2 + 2H_2O \;--\!\!\rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+ \;\ldots\ldots\ldots\ldots\text{Equation 2. 1}$$

$$4Fe^{2+} + O_2 + 4H^+ --\!\!\rightarrow 4Fe^{3+} + 2H_2O \ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 2. 2}$$

$$4Fe^{3+} + 12H_2O \;\leftarrow\!--\!\!\rightarrow 4Fe(OH)_3 + 12\,H^+ \;\ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 2. 3.}$$

$$FeS_2 + 14Fe^{3+} + 8H_2O \;--\!\!\rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16\,H^+ \;\ldots\ldots\text{Equation 2. 4}$$

In Equation 2.1, FeS_2 reacts with O_2 and H_2O to produce Fe^{2+}, $SO_4^{2+}$and acidity (1). The conversion of Fe^{2+} to Fe^{3+} in Equation (2) has been named the rate defining step for the

overall sequence, since at pH value lesser than 5 under abiotic conditions the reaction rate is very low (Stumm and Morgan, 1996). Nevertheless, Fe-oxidizing bacteria, mainly *acidothiobacillus* sp, quicken the reaction rate by orders of magnitude, so the activities of the bacteria enhance the formation of AMD (Johnson and Hallberg, 2003). Furthermore, at this low pH, the solubility of several base metals such as Cu, Pb, Zn, Co, Ni, Al, Mn and Cd are enhanced by oxidation of pyrite and therefore AMD is characterised by higher concentrations of metal in solution. During 1990 and 1991, when monitoring AMD, the elemental concentrations in solution were reaching 111,000 mg/L, Fe, 760,000 mg/L, SO_4^{2-}, 9800 mg/L, Cu, 49,300 mg/L, Zn and 850 mg/L As (Nordstrom and Alpers, 1999). However, weathering and carbonation as well as dolomite minerals can help to consume acidity and by buffering the solution, contaminant metals can be removed (Dzombak and Morel, 1990). The third step (Equation 2.3) involves hydrolysis of Fe^{3+} to produce Fe $(OH)_3$ precipitates, which release additional acidity and are pH dependent. Therefore, at a low pH (3.5), the solid hydroxide does not form and Fe^{3+} will remain in the water until the pH has increased then it will precipitate as $Fe(OH)_3$. The fourth step involves the autocatalytic oxidation of additional FeS_2 by Fe^{3+} (Equation.2.4). The initial oxidation reactions in steps one and two generates Fe^{3+}. This cyclic propagation of acid generation by iron happens very rapidly and goes on until the supply of Fe^{3+} or FeS_2 is depleted. For the fourth reaction to take place oxygen is not required.
The overall sequence of pyrite reactions is among the most acid-producing in nature of any weathering process.

The dominance of acid producing minerals over acid neutralising minerals is the cause of AMD production in mine water. Acid base accounting (ABA) for acid producing minerals and acid neutralizing minerals can be used as an initial step to predict if a certain geology can produce AMD, neutral or alkaline mine water during and after mining (Skousen et al., 1990). Then, the sulphide is oxidized to elemental sulphur which dissolves in the oxygenated water to form sulphate and acidity and this enhances the leaching of toxic metals (such as Fe, Cu, Pb, Cd, Co, Cr, Ni and Hg), metalloids (As and Sb), other elements (Al, Mn, Si, Ca, Na, K, Mg and Ba) and sulphate iron from other minerals associated with the FeS_2 containing rock. AMD is characterized by low pH, high concentration of Fe and

Al (more than 100 mg/L), elevated amounts of Cu, Cr, Ni, Pb and Zn (bigger than 10 mg/L) and SO_4^{2-}(larger than 1000 mg/L) (Lottermoser, 2007).

AMD can cause pollution of the environment, and has affected a lot of countries, which have historic or current mining productions. In South Africa, mines such as that are are found in the Witwatersrand Basin have been operating for at least a century. This region is subdivided into western (Carletonville), eastern (East Rand), central (Johannesburg) basins and it was reported that the Wits basin has the potential to produce 350000 m^3 of AMD effluent per day (Manders and Herman. 1994). However, since the beginning of 2002, water has been decanting from the western basins into nearby rivers and dams, which causes pollution into the Krugersdorp game reserve and in the central basins. Herman et al. (1994), stated that AMD is one of the most difficult mine water waste to address. He further mentions that the post-closure decant from defunct coalmines were estimated to be 62 ML/d and approximately 50 ML/d of AMD is discharged into the Olifants river.

AMD formation materials, such as acidity and Fe, can devastate water resources by lowering the pH and covering the bottoms of the stream with $Fe(OH)_3$; creating the orange coloured "yellow boy" common in areas with uncontrolled mines. As acidity increases, small living creatures should withstand the harsh conditions. The corrosive acid water often damages culverts and bridge abutments, resulting in exposed structures having a shorter than normal life span. Small amounts of AMD can affect the life of streams because the metals, sulphates and/or other suspended solids precipitate out of the water and cover the rocks and gravel at the bottom of the stream. When this happens, it actually smothers the flora and fauna that live on and under the rocks because they can not get oxygen out of the water. High levels of Na make the water unacceptable for irrigation while hardness influences the toxicity of toxic metals such as Zn (Lottermoser, 2007).

2.1.2 Means of treatment

Acid mine drainage is treated to raise the pH of water, to lower the concentrations of toxic metal by precipitations or adsorption, to decrease aqueous sulphate concentration, to reduce the toxicity/bioavailability of metals in solution, to oxidize the elements in solution, to reduce species in solution and lastly to gather, dispose and isolate the metallic sludge produced. The effluent from treated AMD can be used for industrial and other utilities. The treatment of AMD is complex and very expensive and this is because of the complexity and diversity of AMD composition. AMD treatment methods can be generally classified into two categories: active and passive treatment. Passive treatment methods are a way of treating AMD by passing it through an environment where geochemical and biological process help to treat the mine water without any addition of a chemical but just a little resource input once in operation (Kalin et al., 2006; Madzvire, 2014). On the other hand regular reagent and labour inputs are required during active treatment of AMD.

2.1.2.1 Passive treatment

The passive treatment of mine water is the technique that uses natural resources to facilitate chemical and biological procedures to extract pollutants from mine water. The passive treatment is a process that does not require a continuous addition of chemicals and monitoring. There are different types of passive treatment methods of AMD. That will be explained below:

- **Constructed wetland**

Constructed wetlands are a complex ecosystem designed to promote oxidation process to precipitate undesirable metals and in turn increase the pH (Robb and Tobinson, 1995). The constructed wetland comes from an observation made in the early 1980s. From the observation it was shown that mine water quality significantly improved as it flowed through natural, sphagnum moss-dominated wetlands and this led to the idea that constructed wetland could be used to remedy AMD (Wieder and Lang, 1982). Constructed wetlands are complicated ecosystems consisting of water-saturated soil and sediments with supporting vegetation that have the ability to naturally improve water quality via a range of physical, chemical, microbial and plant-mediated processes. This action incorporates oxidation, reduction, precipitation, sedimentation, filtration, adsorption, complexation, chelation, active plant uptake of metals, microbial conversion and immobilisation mechanisms (Taylor and Murphy, 2005). This process functions by precipitating metal hydroxides, creating metals sulphides and absorbing few amounts of metal by the plant community (Skousen and Ziemkiewicz, 1995). They were successfully utilised in various locations to neutralise mine water, but they are frequently applied to coal mine drainage, which relatively contain small amounts of metals and maybe only mildly acidic to alkaline in comparaison to AMD from metals mines (Younger et al., 2002). Constructed wetland falls into two categories aerobic and anaerobic wetlands.

- **Aerobic wetland**

Aerobic wetland systems are designed to facilitate metal precipitation through oxidation process and are therefore usually shallow, vegetated and have predominant surface flow (Robb and Robinson, 1995). Aerobic wetlands are not profound, with depths no more than 30 cm. These processes are typically used once the entering mine water is net alkaline. Their principal use is just for aeration and metals precipiation from the alkaline mine water (Skousen and Ziemkiewicz, 2005). Skousen (2016) reported that this type of wetland promote oxidation of metals and hydrolysis, by this means producing precipitation and physical retention of oxyhydroxides of Fe, Al, and Mn as shown in Equations below:

$Fe^{3+} + 3H_2O \rightarrow Fe\,(OH)_3 + 3H^+$ ………………………………………..Equation 2. 5

$Al^{3+} + 3\,H_2O \rightarrow Al\,(OH)_3 + H^+$ …………………………………………...Equation 2. 6

$Fe^{2+} + \frac{1}{4}O_2 + \frac{5}{2}H_2O \rightarrow Fe\,(OH)_3 + 2H^+$ ………………………..Equation 2. 7

$Mn^{2+} + \frac{1}{4}O_2 + \frac{3}{2}H_2O \rightarrow MnOOH + 2H^+$ ……………………….Equation 2. 8

The equations 2.5 and 2.6 are hydrolysis reactions, which necessitate only the presence of water and sufficient alkalinity to neutralise the H$^+$ formed. Equation 2.7 and 2.8 need the presence of oxygen to oxidise the metal prior to hydrolysis. The four equations generate acidity (Madzivire, 2010).

Successful metal subtraction or removal is dependent of dissolved metal concentrations, dissolved oxygen content, pH and net acidity of the mine water, the presence of active microbial biomass, and retention time of the water in the wetland. total acidity or alkalinity and pH of the water are mainly important because pH has an influence on both solubility of metal hydroxide precipitates and the kinetics of the oxidation and hydrolysis of metals. Consequently, aerobic wetlands are preferable to be used in conjunction with water that contains net alkalinity to deactivate the acidity of metals (Skousen, 2016).

- **Anaerobic wetland**

An anaerobic system is a system that requires water from mines to run through an organic layer under anaerobic conditions. The organic material must have sulphate-reducing bacteria for metal sulphide precipitates to form (Robb and Robinson, 1995). Anaerobic wetlands are also called compost wetlands; this is the most used passive treatment for net acidic mine water, While alkalinity in the wetland must be developed and added into the water before dissolved metals can precipitate. The wetland substratum may contain a calcareous layer at the bottom, or it may be mixed between the organic matter. Wetland plants are then transplanted into the substrate of organic matter. Insoluble precipitates such as hydroxides, carbonates and sulphides constitute a significant metal sink in the wetlands. About 50 to 70 percent of the total Fe derived by wetlands from AMD is contained as ferric hydroxides (Calabrese *et al*. 1991; Henrot and Wieder 1990; Wieder 1992). The availability of dissolved oxygen and the initial oxidation state of Fe in the AMD are the point of dependence of ferric hydroxide formation. Wieder (1993) reported significant retention of ferric hydroxides in surface sediments of anaerobic wetlands.

- **Successive alkalinity producing systems**

Successive alkalinity producing systems (SAPS) are another form of passive treatment that put together the use of anoxic limestone drain (ALD) and an organic substrate into one system (Kepler and McCleary, 1994). In SAPS, mine water is channelled through alternating series of wetlands of anaerobic and aerobic conditions. The wetlands that constitute the SAPS are made up of organic matter that removes O_2, creates a good environment for sulphate reducing bacteria (SRB) and converts Fe^{3+} to Fe^{2+}. Madzivire (2013) stated that water that enters the limestone region is O_2 and Fe^{3+} free preventing armouring of limestone with $Fe\ (OH)_3$. Alkalinity is generated through SRB or limestone dissolution in wetlands followed by metal removal in the aerobic ponds as a result of oxidation, hydrolysis, and precipitation and settling. Figure 2.2 gives a diagram of SAPS.

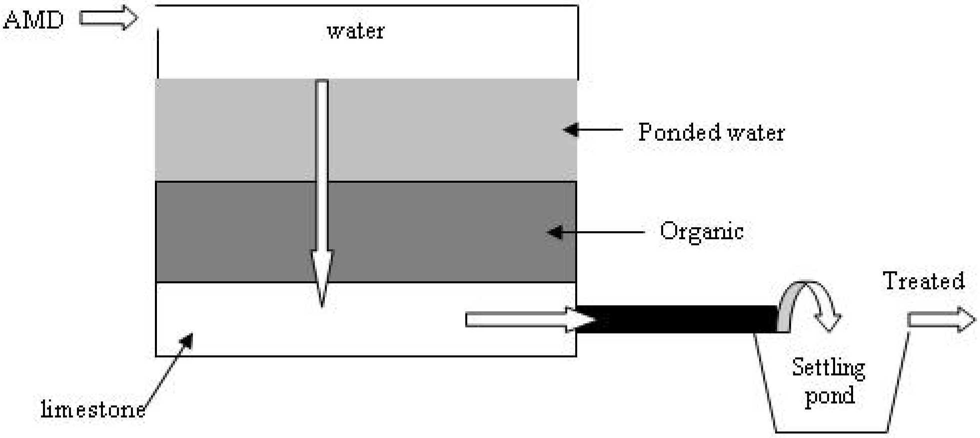

Figure 2. 2: **Successive alkalinity producing systems diagram**

Sulphates are removed either by bacterial action or by precipitation as gypsum in cases where the alkalinity is produced by limestone dissolution (Keplar and McCleary, 1994; Narin and Mercer, 2000). Nairn and Mercer (2000) have described the operability of SAPS techniques as that, proton acidity formed by aerobic metal removal mechanisms in the ponds will be buffered and waters may be discharged into the environment, if enough alkalinity is produced in the vertical-flow wetlands. But if there is not enough buffering space, AMD may be directed to another set of vertical-flow wetlands and aerobic ponds. Therefore, this sequence may be repeated until the water quality meets the standards for it to be released into the environment. Wieder (1992), Documentation that the process and efficacy of AMD care vary seasonally and with the age of wetlands. Aerobic and anaerobic wetlands are the most productive for the treatment of limited, moderately water quality AMD flows.

- **Open limestone**

Limestone drains are one of the passive chemical methods to remediate mine water. To make up open limestone drains (OLD), open ditches are filled with crushed limestone. Mine water flows over the limestone resulting in the dissolution of calcite ($CaCO_3$), which is the major mineral in limestone. The dissolution of $CaCO_3$ produces alkalinity thereby neutralizing the pH. This results in the increase in pH, HCO_3^-, OH^- and Ca^{2+} as stated in the reactions that follows (Stumm and Morgan, 1996; Cravotta and Trahan, 1999):

$CaCO_3 + H^+ \leftrightarrow Ca^{2+} + CO_2 + H_2O$ ……………………………………….…Equation 2. 9

$\mathrm{Ca}CO_3 + H_2O + CO_2 \leftrightarrow CCa^{2+} + 2HCO_3^-$ ……………….…………..…..Equation 2. 10

$CaCO_3 + H_2O \leftrightarrow Ca^{2+}\ HCO_3^- + OH^-$ …………………….……………..Equation 2. 11

The pH raise of the mine water results in the removal of soluble Al, Fe and Mn due to precipitation as hydroxides. Sulphate ions react with Ca^{2+} that dissolves from limestone to form gypsum (Mukhopadhyay et al., 2007; Ziemkiewicz et al., 1997; Nairn et al., 1991).

$Fe^{3+}(aq) + 3HCO_3^-(aq) \rightarrow Fe(OH)_3\,(s) + 3CO_2(G)$ ………………..Equation 2. 12

$Al^{3+}(aq) + 3HCO_3^-(aq) \rightarrow Al(OH)_3(s) + 3CO_2(g)$ ……………..….Equation 2. 13

$Ca^{2+}(aq) + SO_4^2\,(aq) \leftrightarrow CaSO_4.2H_2O\,(s)$ ……………..………..………..…Equation 2. 14

Open limestone systems work effectively when mine water flows over a long distance before exiting the treatment system. This is due to the fact that Fe and Al precipitate from the mine water, the limestone gets coated or armoured by the metal hydroxides thereby reducing the solubility of limestone and the system becomes ineffective over time and needs replacement.

- **Anoxic limestone**

Anoxic limestone drains (ALD) are buried cells or calcareous trenches in which anoxic water is deposited before it is exposed to atmospheric O_2. The limestone liquifies in acid water, increasing pH, and adding alkalinity. Under anoxic conditions, the limestone does not coat or armour since Fe^{2+} is not oxidized and cannot precipitate as Fe(OH)2 at pH lower than 6.0. Once the water containing excess alkalinity reaches aerobic conditions at the ground surface, Fe^{2+} is oxidized and precipitated together with Mn^{2+} and Al^{3+} while the water remains close to pH 6 (Brodie *et al*., 1990). The oxidation of Fe^{2+} produced solid Fe $(OH)_3$ and consequent hydrolysis (Madzivire, 2009).

$\mathrm{Fe}^{3+} + 3\mathrm{HCO} \rightarrow \mathrm{FeOH}\ (\mathrm{s}) + 3\mathrm{CO}$ … … … … … …Equation 2. 15

It has been observed that, clogging of limestone pores with precipitated Al and Fe hydroxides occurs, if appreciable dissolved Fe^{3+} and Al^{3+} are present (Faulkner and Skousen 1995; Watzlaf *et al.,* 1994). For high sulphate concentration water (>1,500 mg/L), gypsum ($CaSO_4.2H_2O$) may also precipitate (Nairn et al*.,* 1991).

- **Reactive barriers**

Permeable reactive barriers (PRBs) can be classified as chemical or biological passive treatment depending on the reactive material used. Building PRBs involves digging a trench in contaminated groundwater flow path. The void is filled with reactive materials (a mixture of organic solids or limestone gravel or zero valent iron) that are sufficiently permeable to allow unimpeded flow of the groundwater, and landscaping of the disturbed surface (Younger et al., 2002).

Alkalinity is generated due to dissolution of limestone or microbiological process or the oxidation of zero valent iron according to the following equations within the PRB. Metals are removed as sulphides, hydroxides and carbonates (Younger et al., 2002; Gavaskar, 199).

$2Fe + O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4OH^-$ … … … … … … … … … … … … … ….Equation 2. 16

$Fe + 2H_2O \rightarrow Fe^{2+} + H_2 + 2OH^-$ ………………………………………………Equation 2. 17

2.1.2.2 Active treatment

Active treatment requires continuous inputs such as artificial energy, biochemical or chemical reagents and regular maintenance of a water treatment plant by a skilled group of individuals (Younger et al., 2002)

The advantage of using active treatments methods is, they have the capability to handle any change in the mine water quality and quantity due to the precise process control in response to these changes. It does not require a huge quantity of land compared to passive treatment. The active treatment methods have a disadvantage in that the sludge and brine, which are produced as waste materials are more expensive to handle and dispose. The cost of nonstop energy input, reagents and the need for skilled work to operate and maintain the treatment plant make the techniques more expensive (Madzivire, 2009). Different neutralisation technologies that can be applied for the treatment of mine water are necessary because of the vast differences in chemistry of acidic waters and the variety of physical, chemical and biological methods other options for separating metals from mine water. Any suitable method of treatment can be picked based on: the quality of mine water, its quantity, the desired treated water quality and the cost of the treatment techniques.

2.1.2.3 Chemical treatment

This is the most common method of treating AMD requiring the addition of a chemical neutralizing agent (Coulton et al., 2003). These alkaline materials that are added to AMD will increase its pH, speed up the rate of chemical oxidation of ferrous iron (for which active aeration, or addition of a chemical oxidizing agent such as hydrogen peroxide, is also necessary), and lastly causing many of the metals that are present in solution to precipitate as hydroxides and carbonates at different pH values. Fe^{3+}, Al^{3+}, $Mn^{2+}$and Mg^{2+} precipitate at pH values 3, 6, 9 and 11 respectively. Barium salts such as $Ba(OH)_2$, BaS and $BaCO_3$ are also used for treatment of mine water specifically for SO_4^{2-} precipitation. The production of an iron-rich sludge that could also contain numerous other metals, relying on the chemistry of the mine water treated, is the result of this process, but this process is not cost effective depending on the chemical to be used and it requires equipment and maintenance.

- **Chemical compound used in AMD treatment**

Typical chemical compounds used during chemical treatment of AMD are listed in Table 2.1. The alkali requirements is the amounts of alkali needed per unit of acidity and it has as unit $CaCO_3$ (ton / ton of acidity). The efficiency of neutralization estimates the chemical's relative effectiveness in neutralizing acidity (Cherry, 2012).

Table 2. 1: Chemical compound used during AMD treatment (Cherry, 2012)

Common name	Chemical name	formula	Alkali Requirements	Neutralization efficiency
Limestone	Calcium carbonate	$CaCO_3$	1.00	30%

Hydrated lime	Calcium hydroxide	$Ca(OH)_2$	0.74	90%
Pebble quicklime	Calcium oxide	CaO	0.56	90
Soda ash	Sodium carbonate	Na_2CO_3	1.06	60
Caustic soda (solid)	Sodium hydroxide	$NaOH$	0.80	100
20% liquid caustic	Sodium hydroxide	$NaOH$	784	100
50% Liquid caustic	Sodium hydroxide	$NaOH$	256	100
Ammonia	Anhydrous ammonia	NH_3	0.34	100

I. Lime/ limestone

For decades, this chemical has been used to raise the pH and remove metals from the AMD. It is cost effective and does not cause any handling problem. Regrettably, its low solubility and tendency to develop an external coating, or armour of $Fe(OH)_3$ when added to AMD causes successful application to be limited. In cases where pH is low and mineral acidity is also relatively low (low metal concentration), finely-ground limestone may be dumped in streams directly or the limestone may be ground by water-powered rotating drums and metered into the stream. Limestone can also treat AMD in anaerobic (anoxic limestone drains) and aerobic environments (open limestone channels).

II. Hydrated Lime

In the treatment of AMD, hydrated lime $Ca(OH)_2$ is a generally used chemical. It is sold as a powder that tends to be hydrophobic, and to disperse it in water extensive mechanical mixing is required. Hydrated lime is mainly useful and cost effective in large flow, high acidity situations where a lime treatment plant with a mixer/ aerator is constructed to help dispense and mix the chemical with the water (Skousen and Ziemkiewicz, 1996). This chemical has limited effectiveness if a very high pH is needed to remove ions such as Mn. Lime treatment systems operators also increase the application of lime, as the Mn water levels of increase. However, because of the lime dissolution kinetics, increasing the lime rate increases the amount of unreacted lime entering the metal floc settling bath Pebble Quicklime

Pebble quicklime (CaO) is used in combination with the Aquafix Water Treatment System applying a water wheel concept (Jenkins and Skousen, 1993). The movement of the water wheel dictate the amount of chemicals to be applied, which causes a screw feeder to dispense the chemical. The hopper and feeder can be installed in less than an hour. Due to the reactivity of CaO, this system was initially used for small and/or periodic flows of high acidity. Newly, however, water wheels have been attached to large bins or silos for high flow/high acidity situations. Preliminary tests have shown an average of 75% cost savings over NaOH systems and about 20 to 40% savings over NH_3 systems.

III. Soda ash

Soda ash (Na_2CO_3) is usually used to neutralise AMD in remote areas with low flow and low amounts of acidity and metals. Selection of Na_2CO_3 for AMD treatment is usually based on convenience rather than chemical cost. Soda ash comes as solid briquettes and is fed by the use of buckets or barrels into water. The number of briquettes to be used each day will be determined by the flow rate and the quality of water to be treated. The bin system has one problem: The briquettes absorb moisture, causing them to expand and stick to the corners of the bin. This delays the briquettes from dropping into the AMD stream. For short-term treatment at isolated sites, Some operators use a very simpler system employing a wooden box or barrel with holes that allows water inflow and outflow for short-term treatment at isolated sites. Barrel is filled with briquettes regularly by the operator, and they place the barrel in the flowing water. This system provides less control of the amount of chemical used.

IV. Caustic soda (NaOH)

Caustic soda is frequently used in remote locations (e.g., where electricity is unavailable), and in low flow, high acidity situations. Most of the time caustic soda is used in AMD solution when Mn concentrations are high. The system can be gravity fed by dripping liquid NaOH directly into the AMD. This chemical is very soluble in water, it does disperse rapidly, and raises the pH to 14 of the water quickly. NaOH should be used at the surface of ponded water due to the fact that this chemical is denser than water. The major weaknesses of using liquid NaOH for AMD treatment are high cost (it is expensive) and causing handling problem.

V. Ammonia

Ammonia or anhydrous (NH_3 or NH_4OH) is a very hazardous chemical that needed to be handled with careful attention (Hilton, 1990). Ammonia is a gas at ambient temperatures, it is soluble in water and reacts rapidity. It is stored as a liquid after being compressed but returns to the gaseous state when released. Ammonia acts as a strong base and can raise the pH of receiving water to 9.2. At pH 9.2 so easily, in the solution water ammonia buffers the solution to further pH increases, and consequently to elevate the pH beyond 9.2. very high amount of NH_3 is added to the solution. The reason why ammonia is used in treatment of AMD is, it raises pH of water so quickly and it is not expensive compared to other chemicals used such as NaOH (Skousen et al., 1990). Using ammonia to treat AMD presents some disadvantages such as, hazards related to the handling of this chemical, nitrification is so uncertain, denitrification and acidification downstream and lastly the consequences of excessive application rates (Faulkner, 1990). Particular training and experience are important for the safe use of NH_3 to reduce its hazardous effect. It is recommended to conduct extra analyses such as temperature, total NH_3-N, and total acidity for discharge water and receiving streams. Although ammonia can be effective for the removal of Mn in numerous cases, this recommending careful monitoring and attention, and over application of ammonia often occurs. Consequently, in situations where Mn is the ion of primary concern (low Fe, high Mn water). a different chemical may be more appropriate (Adlem, 1997; Maree et al., 1989).

- **Membrane treatment**

Membrane treatment eliminates contaminants by selectively allowing only certain ions to pass through the pore of the membranes by size exclusion. This industrial method of treatment started back in the 1960s for dialysis and in 1970 progressed to pressure driven or asymmetric techniques. Membrane treatment are classified as a secondary process of treating mine water. This is because these systems involve pre-treatment of mine water in order to remove solids that are suspended to reduce fouling of membranes.

Allison and Engineer (2005) stated that electro dialysis reversal (EDR) was developed in the early 1970s, and this process is a mechanical improvement of the ED process where the polarity of the applied DC power is sporadically reversed. The reversal process consecutively exposes the membrane surfaces and flow compartments to the concentrate and the desalting streams. Figure 2.3 shows the EDR process. EDR quickly became the principal form of electro dialysis used for AMD, and this is due to the fact that water recovery capability was improved, and continuous chemical addition to the concentrate stream for scaling control is not needed for most systems (Allison and Engineer, 2005), ,

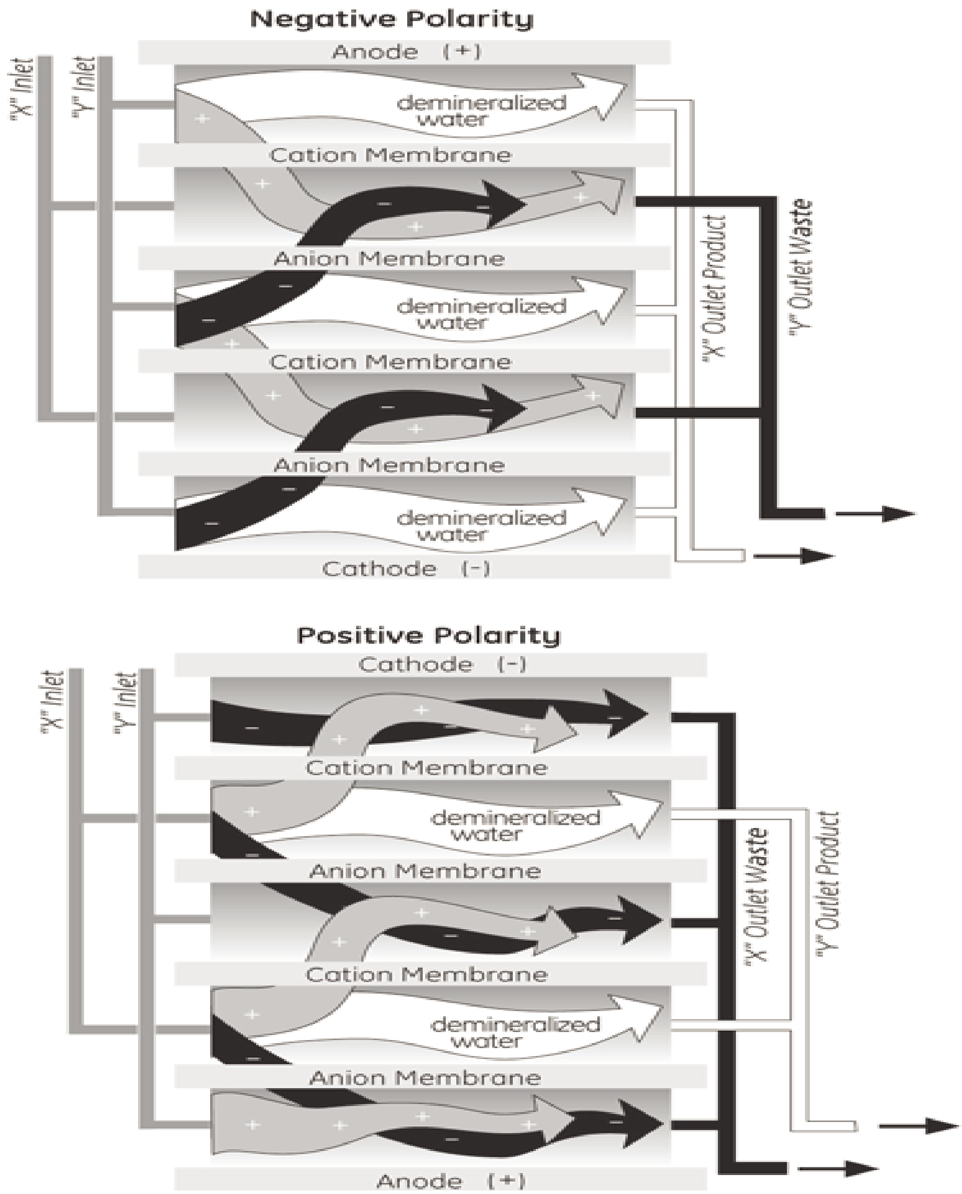

Figure 2. 3: EDR operation

More recently, the development of asymmetric (pressure driven) membranes which involve reverse osmosis, microfiltration, ultrafiltration and nanofiltration has received attention. These membranes were able to develop more rapidly than the dialysis techniques. An asymmetric membrane is a succession of associated layers of materials, having an asymmetric structure, a thin layer of thickness approximately 50 µm supported by a thicker layer greater than 100 µm (Rurales and Eau, 2002). The four types of pressure driven processes are described by Trussell-tech (2016) as follows:

- Microfiltration (MF) membrane

Microfiltration is the purification of water by passing it through membranes with pore size ≥ 0.1µm and < 0.45µm. Removal of bacteria is achieved but viruses, colloids, colour and solutes remain in the water.

- Ultrafiltration (UF) membrane

Ultrafiltration involves passing contaminated water through membranes with pore sizes ranging from 0.01 µm and 0.1 µm. The water that is treated using this process is free from colloids and microorganisms, with only solutes remaining. Ultrafiltration and microfiltration are used as pre-treatment options for nano-filtration and reverse osmosis (RO) treatment process of mine water to produce drinking water.

- Nanofiltration (NF) membrane

Nano filtration uses a pressure gradient to separate ions through a porous membrane. The pores on nano-filtration membranes are greater than 0.001 µm and less than 0.01 µm. Nano-filtration is capable of separating bigger divalent anions, such as sulphate and organic molecules, from water and monovalent small cations (Kentish and Stevens, 2001).

- Reverse osmosis (RO) membrane

RO membrane is a pressure driven membrane process where the solution is transferred through a semi-permeable membrane (pore size < 0.001 µm). During RO a substantially high pressure difference across the membrane is necessary to outforce the osmotic pressure difference between the salt free permeate and the saline reject solution (brine). The smaller water molecules are accurately pushed through the semi-permeable membrane, whereas the larger solute species are retained. This process is the “reverse” of natural osmosis, which involves water diffusion from a dilute to concentrated region through a semipermeable membrane.

Kentish and Stevens (2001), state that the principle by which these membranes choose or reject ions, are based on size and electrical charge. MF and UF membranes were gradually used in the salt removal process to protect RO, NF and ED membranes from solids that were suspended and bigger colloidal material that are disadvantageous to their performance. Additionally, the MF and UF membranes are not capable of rejecting salts and, resulting in that, both are only pertinent to desalination membrane systems as a pre-treatment process (Trussell-tech, 2016). NF membranes are visualised as tight UF membranes that not only reject materials such as suspended solids, colloidal material, bacteria, based upon size exclusion, furthermore remove hardness namely multivalent ions; this is based upon a charge repulsion mechanism. Nevertheless, NF membranes reject monovalent salts. Therefore, a majority of detoxification is performed by non-porous RO membranes that deliver a physical barrier to a wide range of contaminants, including monovalent ions.

According to Trussell-tech (2016), for removing a numerous inorganic contaminants such as antimony, arsenic, barium, fluoride, nitrate, nitrite, boron, selenium, radionuclides, and emerging contaminants, including endocrine disrupting compounds, and several pharmaceutical compounds RO was designated as the best available technology by EPA.

- **Ion exchange**

Ion exchange is known as a charged ion reversible interchange (cation and anion) for a correspondingly charged iron, between a solid material (the iron exchanger) and the surrounding liquid, in which there is no permanent change in the structure of the solid (Kitchener, 1957; Madzivire, 2015). Ion exchange reflects the idea of the water that flows through a layer of ion exchange material, where undesirable ions are removed and replaced with less offensive ones. Demineralization is changing all anions with OH^- and all cations with H^+. Ion exchange processes bear a resemblance to the sorption process, that during these two process, a dissolved species is used up by a solid, however the main difference between the two phenomena is that ion exchange unlike sorption, is a stoichiometric method where every detached ion from the solution is replaced by an equivalent amount of another species of the same sign. Or else, in sorption there is no replacement of a solute which is taken up (Madzivire, 2010). Ion exchangers are used as storage batteries, they must be regenerated periodically to restore their exchanger capacity; these systems are capable of removing selected ions almost completely if they are properly designed and operating. As a wastewater treatment process, ion exchange was discovered to be effective and feasible. In an ion exchanger, some absorbents such as activated carbons, alumina, silica, bentonite and peat can be used to remove metal ions (Gaikwad et al., 2010). Ion exchange resins with better sorption capability and adsorbents can benefit from such non-specific adsorbents (Kim et al., 2002).

Ion exchangers have a unique characteristic property that can be attributed to a distinctive feature in their arrangement. They are made up of a framework, kept together by chemical bonds or lattice energy and The most specific constituents of minerals are the which is compensated by ions of opposite sign also referred to as counter-ions (Kitchener, 1957).

The rate of exchange once an exchanger is in contact with a solution of swapping ion can be controlled by the following three steps (Kentish and Stevens, 2001):

- **Film diffusion** is controlled by the rate of progress of an ion through a film of water molecules, which by feature the surface charge on the exchanger can be viewed as stagnant;
- **Particle diffusion** is guarded by the progress of ions inside the exchanger;
- **Chemical reaction** is measured by bond formation.

Ion exchange processes require very little energy, cheap regenerants and when well-maintained, resin beds can be used for many years before replacement is required (New Zealand Institute of Chemistry, 2002)**.** Even though various ion exchange processes come out to be theoretically efficient at meeting the targeted water quality, few have proven to be economically feasible (Taylor and Murphy, 2005)

2.2 COAL FLY ASH (CFA)

2.2.1 Introduction

Coal is the most bountiful fossil fuel on the planet (Williams, 2001; Nyale 2012). It is a multifaceted mixture of organic matter and is mostly composed of two major solid components organic part and inorganic one. Coal is an easily combustible rock that contains 50 % or more by mass and 70 % by volume of carbonaceous material (Schopf, 1956). Coal is formed in environments that boost plant growth and under depositional conditions that favour preservation of dead plants. According to Speight et al. (2005) coal formation involves the decomposition and alteration of distinct organic and inorganic entities by compaction caused by high pressure and temperature. Nevertheless, the organic and inorganic components are derived from decaying of vegetation but in some cases woody precursors play a significant role during coal formation (Crelling et al., 2010). The non-combustible substances of coal are made of inorganic components and they are bonded originally as mineral matter such as crystals or fragments (McLennan et al., 2000). The mineralogy of the constituent of coal is depended on the geology of the surrounding environment of the coal formation. The clay minerals, illite and kaolinite; sulphides such as pyrites and marcasite; carbonates like dolomite, ankerite, calcite and siderite and quartz are the most common mineral found in CFA. Clay minerals make up 60-90 % of the total mineral matter and quartz is found in almost all coal and can comprise from 1 to 20% of the inorganic compounds presents in the coals (Rao and Gluskoter, 1973). Numerous trace elements are found within coal deposits, ranging from a few percent of the total composition to a fraction of a part per million (ppm) (Gitari, 2013). Coal has been classified based on its properties that depend on the origin and geological age. The nature of the coal matrix determines its specific physical and chemical properties. Various methods of classifying coal have been chosen such as: coal type depending on the origin, coal rank depended on the degree of maturity or, metamorphism and lastly coal grade, which depends on the amount of impurities present such as ash or sulphur (Maleka, 2015, Crelling et al., 2010). Moreover, coal can also be classified based on rank into four groups that are Anthracite, bituminous, subbituminous and lignite coal based on the percentage of carbon content and the heating value the amount of energy released when burned, the reserve of coal in South Africa are estimated at 53 billion tonnes, an average value of 224 million tons of marketable coal are produced annually, uplifting South Africa economy and making it the fifth largest coal producing country in the world. 23% of the produced coal is being exported internationally making South Africa the third largest coal exporting country in the world and the 53% of the coal produced is used for electricity generation where electricity produced through coal combustion covers 77% of the country’s primary energy needs (Eskom, 2017). The burning of coal for electricity production comes with the emanation of solid residue referred to as by-products. Among these by-products there is CFA, bottom ash, boiler slag, flue gas desulphurization material, fluidized bed combustion ash and scrubber residues (Hower, 2012).

2.2.2 Formation of coal fly ash

The chemical composition of CFA shows that it is made up of a numerous elements from a significant portion of the periodic table. Some of these elements contained in CFA such as As, Hg, Cd and Ba are poisonous to humans, frequently producing cancer and neurological illness (Gottlieb et al., 2010). In South Africa CFA is being produced in huge quantities with an estimated value of more than 36.22 Mt of fly ash produced annually (Eskom, 2011). Only a small percentage of this waste material is being used efficiently for production of cement and bricks in the construction industry. The remainder is carried by pipes in a watery slurry and disposed into large ash dams (Petrik et al., 2004, Van Hamburg et al., 2004). The disposal of CFA in ash dams or dumps create a huge environmental problem because of the high leaching of salts and trace elements such as B, Pb, Hg, and Cd, As etc. when CFA is infiltrated with rain water (Mattigod et al., 1990; Adriano et al., 1980). Leaching of these salts and toxic elements leads to groundwater and surface water contamination, thereby threatening humans, plants and aquatic life (Carlson and Adriano, 1993). However, CFA contains some elements that are deemed beneficial to plants development but these benefits are of negligeble value compared to the negative environmental impact caused by CFA. According to Du Plessis et al., (2014), toxic and trace elements presence in CFA made it potential hazardous material. Toxic elements are concentrated on the surface of the CFA amorphous particles (Bhanarkar et al., 2008; Shama and Kalra, 2006).

2.2.3 Properties of coal fly ash

The chemical composition and properties of CFA depend on the physio-chemical properties of coal, the coal burning process, the source of coal used during the combustion process, the collection method, storage and climate (Saikia et al., 2006, Adriano et al., 1980; Young, 1993). According to Nyale et al., (2014) CFA is mostly composed of the following oxides group SiO_2 (58.44%), Al_2O_3 (31.25%), CaO (3.21%), and Fe_2O_3 (3.09%). The chemical composition of fly ash is typically composed of elements such as Si, Ca, Al, Fe, Mg, C and many trace elements such as Co, Cd, As, Se, Zn, Mo, Mn, Pb, B, Cu and Ni that are in the ash. Due to their high melting point and the short time during which the ash particles actually remain in the furnace during combustion, the inorganic minerals liquefy and become fluid or volatile or react with oxygen during the combustion process because of the high temperature. On cooling; the components form crystalline solids, spherical amorphous particles or condense as coating on the particles (Kutchko and Kim, 2006).

CFA does have a variable colour that varies from light grey to dark grey, depending on the quantity of unburnt carbon after combustion (Madzivire et al., 2010; Mainganye, 2012;). According to Fisher et al, (2010) CFA is abrasive, alkaline and refractory in nature. It generally consists of spherical micro-particles; these spherical particles are glassy and mostly transparent, indicating complete melting of silicate minerals (Fisher et al., 1978). The particle size of CFA is in the range of 0.01 to 200 μm, with specific surface area and specific volume ranging from 21 to 3.0 m^2/ Kg and 170 to 100 m^3/ Kg respectively. CFA surface area depends on the combustion conditions not on the type of coal from which it was obtained (Sarbak et al., 2004). According to Izidoro et al., (2012) the specific surface area of CFA may vary between 1.4 to 30 m^2 / g. CFA generated from the combustion of bituminous coal is finer in texture compared with that produce from lignite coal (Ahmaruzzaman. 2010). According to Basu et al., (2009), the bulk density of fly ash is generally low (1.01 – 1.43 $g.cm^{-3}$), as well as the hydraulic conductivity and specific gravity (1.6 – 3.1 $g.cm^{-3}$), whereas mean particle density for both non-magnetic and magnetic particles are 2.7 g cm^{-3} and 3.4 g cm^{-3} individually and the moisture retention in CFA is in the range of 6.1% at 15 bar to 13.4% at 1/3 bar.

2.2.4 Classification of coal fly ash

The American Standard of Testing and Measurement (ASTM) C 618 classifies CFA into three categories, Class F, Class C and Class N based on the chemical composition (ASTM C-618, 1993). Moreover, it is significant to bear in mind that the ASTM C-618 classification system is also based on the use of CFA as a pozzolan or mineral admixture in concrete (Nyale, 2014). Class F has the total amount of oxides of Si, Al and Fe by mass of ≥ 70 %, while in Class C fly ash the total amount of the oxides of Si, Al and Fe is between 50 and 70 %. The class F CFA is obtained from the burning of anthracite and bituminous coals, the group in which South African CFA belongs. Class C CFA is produced from combustion of lignite and sub-bituminous coals. Class N CFA is composed of raw or calcined natural pozzolans such as opalinecherts and shales, tuffs, diatomaceous earths, volcanic ashes, and pumicites (Nayak, 2007). The table below shows the chemical specifications for the different classes of CFA as required by ASTM C-618.

Table 2. 2: CFA classification according to ASTM C-168

Chemical specification	F	C	N
(SiO_2 + Al_2O_3 +Fe_2O_3) minimum %	70	50	70
Sulphur trioxide (SO_3), maximum %	5	5	4
Calcium oxide (CaO)	<10 >20		
Moisture content , maximum %	3	3	3
Loss of ignition (LOI), maximum %	6	6	10

2.2.5 Application of CFA

The ever-growing population causes an increased demand for electricity that result in the continuous burning of coal to meet this goal. Due to the burning of coal, huge quantities of CFA is produced and only a small amount of it used and the rest is disposed in ash dams and dumps (Mahlaba et al., 2011b). Thus, research should focus on utilization of this waste rather than disposing it. A good understanding of chemical composition, mineralogy, surface chemistry and reactivity of CFA can help in order to come up with utilization options. Finding uses of CFA can facilitate its disposal and minimize its negative environmental impacts (Steernari et al., 1999). In some places, CFA was found to be effective, despite the high concentration of trace elements and the increased mobility of these elements for weather conditions. CFA has been used in the treatment of acid mine water (Madzivire, 2009), synthesis of zeolites (Musyoka, 2009), synthesis of geopolymer (Nyale, 2011), in backfilling of mine voids (Vadapalli et al., 2012) and because of its physical properties such as water holding capacity, its bulk density and pH CFA has been used as well in agriculture as an amendment in soil due to the fact that it comprises almost all needed plant nutrients (Gupta et al., 2012). The picture below displays the summarized application of CFA in different sectors depending on its chemical and physical properties (Wang and Wu, 2006)

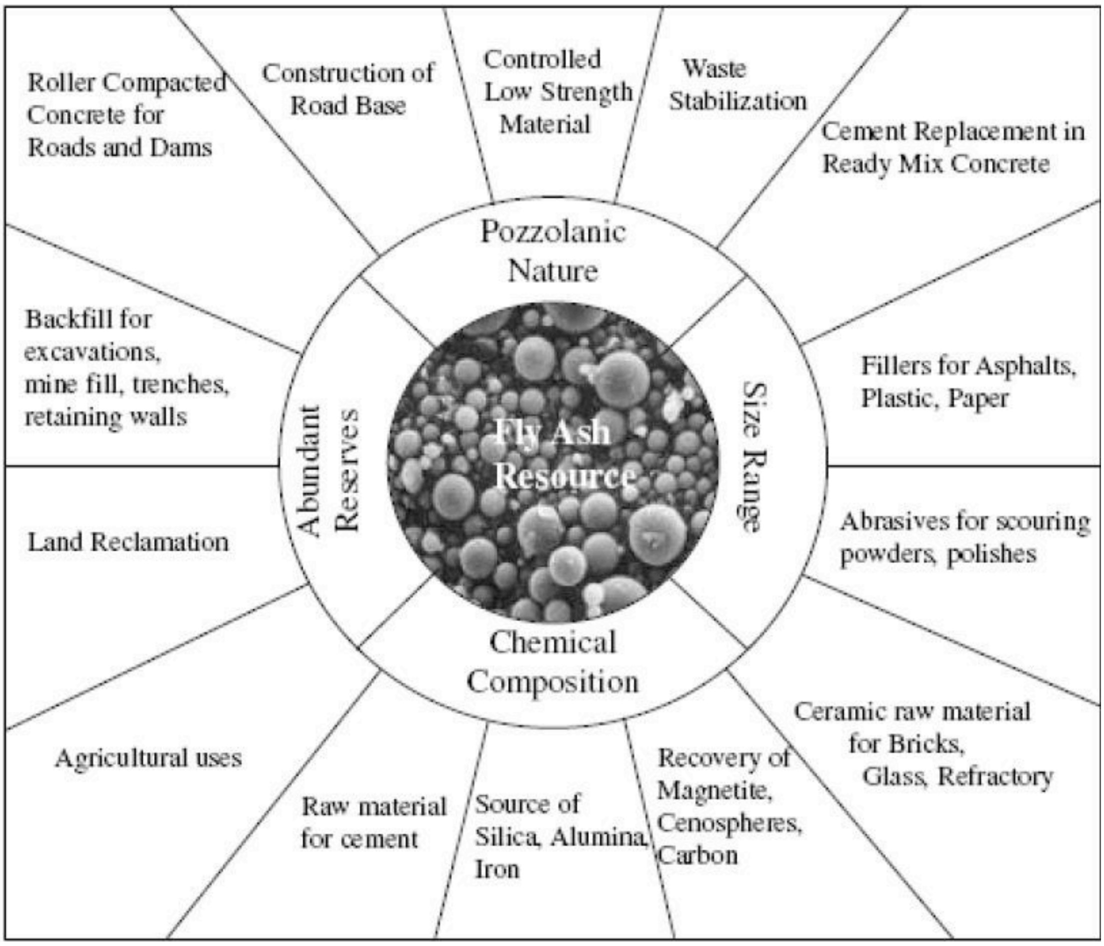

Figure 2. 4: **CFA utilisations (Source: Nyale, 2011)**

- Cement and concrete making

South African CFA was found to be a strong additive to Portland cement and has a number of positive effects on the resulting concrete including a drop in the concrete water demand (Campbell, 1999; Foner et al., 1999). The pozzolanic activity of CFA depends on factors such as chemical composition of the ash, the mineral phase composition, the glass structure and fineness of the ash. The advantage of adding of CFA into ordinary Portland cement is the improvement of the compressive strength and the increase of the cement's resistance to chemical corrosion (Tkaczewska et al., 2012). Moreover, the small particle size of the CFA particle, decreases the air entrainment in the concrete compared to the aggregate. By reacting with calcium hydroxide in the cement to form stable cementitious silicate hydrate gel, CFA further increases corrosion resistance and entry of corrosive liquids. The less soluble calcium silicate hydrate reduces the possibility of calcium hydroxide leaching from the concrete (Fatoba, 2007). The reaction products also result in the filling of capillary voids in the concrete mixture, which reduces the concrete's permeability (Halstead, 1986; Taylor, 1998). The use of CFA as admixture for concrete has several advantages on the resulting concrete including improved consistence, lower heat of hydration, higher strength and durability performance (Jones et al., 2006). According to McCarthy and Dhir, (1999), CFA can be used as a binder in concrete due to its cementitious or binding characteristics.

- Treatment of acidic soils

CFA addition to soils has been observed to increase its water-holding capacity and this has contributed to the increased utilization of CFA. Fly ash is used alone or mixed with organic or inorganic materials in the reclamation of mine spoil or damaged soil. Certain characteristics of CFA make it favourable for agricultural application; these include favourable pH, significant concentrations of many essential plant nutrients, low bulk density and silt-sized particles (Nyale, 2014; Ram & Masto, 2010). However this application is limited due to the fact that CFA has the capability to release trace metals and/or soluble salts to the surrounding environment. For this process to be more efficient it requires the addition of certain inorganic or organic alterations which will render CFA metals and other salts ions biologically inactive (Ram & Masto, 2010).

- Treatment of AMD

CFA has been used in the treatment of AMD due to its neutralisation capacity (Petrik et al., 2004) and as an absorbent and also used as a precursor for activated carbon for water purification (Mishra et al., 2010). This neutralisation of AMD using CFA is always a cost effective process due to the fact that both are waste materials and CFA is an economically viable absorbent with good adsorption efficiencies in certain applications, compared to commercial activated carbon (Mishra et al., 2010, Ayanda et al., 2014).

2.3 ACID MINE DRAINAGE TREATMENT WITH COAL FLY ASH

Numerous studies were conducted on the usage of CFA as an adsorbent for the treatment of AMD. Gitari (2006) states that, CFA can successfully be used to neutralize acid mine drainage (AMD) by reacting different amount of CFA with solution of AMD. It has been shown that these two waste materials have the potential to neutralize each other leading to precipitation of alumino-silicates and iron compounds. Hendriks (2005), states that, the incentive for the co-disposed process is mainly due to the highly neutralizing capacity of CFA, brought about mainly by its free sub-micron CaO particles which upon contact with the AMD, induced considerable pH rise in the AMD, through hydration and as such, functioned as a pH buffer, with the overall result being the precipitation of various mineral and metal species. From all these investigations the following findings were made:

- The formation of ettringite (calcium-aluminium-sulphate-hydrate) at pH 10-12, which is known to be potentially very important hydrous oxide adsorbent material.
- CFA addition increased the solution pH within the first 30 minutes due to the hydration of free lime (provided by the sub-micron CaO particles).
- Other minerals also observed to form included 2-line ferrihydrate at pH between 5 and 8.
- Gypsum (hydrated calcium) formation occurred at pH in the range of 5 and 6, this compound is known due to its ability to serve as solid precipitant for sulphate.

Reardon et al. (1995) treated AMD with CFA, and observed that most unstable phases dissolve when CFA is brought into contact with water. The more stable and less soluble secondary phases precipitate. Furthermore, some of the primary phases of CFA, specifically the glass and crystalline aluminosilicate particles, dissolve very slowly. Secondary hydrous aluminosilicate products are very insoluble and build up as alteration rinds on the surfaces of the primary phases. This further impedes the breakdown of the primary phases as the flow of ions and water between these phases is dominated by the diffusion of the pore water.

A series of neutralization reactions of AMD with CFA, lime and limestone was carried out by Klink (2004), where the neutralization potential of CFA was compared with lime and limestone. It was found that a given amount of lime or limestone had a higher neutralisation potential than the same amount of CFA but is more costly. However that study did not clearly show the mechanisms involved in the removal or release of major and minor elements during the neutralization process. A better understanding of CFA and AMD's role in the neutralization process will greatly help improve this treatment. Moreover, the fate of trace metals removed from the AMD as precipitates in the solid residues will probably dictate their long term behaviour on disposal.

Van den Berg et al. (2001) carried out a site specific study of the use of CFA to control water quality in opencast coal mines on the Highveld region (South Africa). The study investigated Matla, Hendrina and Duvha CFA and water from Rietspruit, Optimum and Middleburg South collieries. The study involved column leaching tests, samples from the ash dams, groundwater samples and historical records. A major finding was that the safe application of CFA depended on the relationship between the acid generating capacity of the mine spoil and the base potential of the CFA. If the pH of the combined leachate from the CFA and mine spoil was sufficiently high, then elements contained within the CFA were not mobilized. The report also indicated that ash should be placed above the final decant level of the mine. Otherwise, heavy metal mobilization would occur. The report contained a review of overseas experience which indicates the possibility of using CFA to remediate AMD underground, or as a barrier to control AMD at reclaimed surface sites, or as an ameliorant mixed with mine spoil and deposited above the decant point). Gitari et al., (2006) also investigated the columns leaching treatment of AMD with CFA, with a focus on the evaluation of the leachate chemistry and contaminants attenuation in AMD by CFA and its derivatives (Gitari et al; 2006).

2.4 COLUMN LEACHING

According to Mills (1998) the column leaching procedure is generally utilised to study the weathering of coal combustion by-products, waste rock, ore or tailing or in order to determine the kinetic behaviour of such materials. In both case the objective was monitoring the effluent water (leachate) quality with time by periodic sampling. Columns are of laboratory, pilot plant or site scale, with sample size ranging from a few kilograms to hundreds of kilograms. There are generally two types of columns set-ups, for sub-aerial and sub-aqueous test work procedures. They are typically 76, 102 or 152 mm in diameter, and from about 1 m to more than 3 in height. There is little if any standardization of column test work procedure, thus allowing significant flexibility in size and material for the making of columns. Column set-up, design, diameter and length differ in the different studies and for different tested materials.

Many researchers have used leaching columns to study AMD generation, weathering of CFA, stability of contaminants immobilized by microbial reduction in an inert substrate, performance of reactive barriers and environmental stability assessment of OPC stabilized industrial waste (Stewart et al., 1997; Dudas, 1981, Kanungo and Mohapatra, 2000; Catalan et al., 2004; Komnitsas et al., 2004; Warren and Dudas, 1984). If the column penetration rate is varied to simulate site conditions, the leachates analysis from a column test work gives a better indication of the quality of water that is expected (Price, 1997). According to Dudas (1981), even though a number of short-term leaching, extraction, and equilibrium studies demonstrated numerous of the initial dissolution characteristics of CFA, the information obtained may not accurately represent the long term dissolution behaviour and concomitant environmental hazards or benefits of CFA. Leaching column tests provide the best estimate of field weathering conditions (Bradham and Carrucio. 1990; Perry, 1985)

2.5 MASS BALANCE

Material balance includes applying the law of mass conservation specifying that mass can not be lost or produced during a chemical reaction and that the total mass of the remains remains unchanged (Himmelblau and Riggs, 2004; Felder and Rousseau, 2005). Material balance includes calculations of the quantities of all materials that enter and leave any system as input and output. The main idea behind material balance calculations is to solve a number of independent equations that involve a number of unknowns of compositions and mass flow rate of streams that enter and leave the system or process. A process is described as one or several operations in which physical and chemical treatments are performed and at the end of which a desired product is produced (Felder, 1986). A process can be clarified as batch, continuous or semi batch and is either in steady states or unsteady state. The system is defined as either an arbitrary portion of a process, or a whole process to be analysed. A system is determined by a system boundary and can be closed or open. A closed system is one in which material neither enters or leaves the vessel system or an open system in the other hand is the one determined by inlet and outlet stream meaning the material crosses the system boundary. Material balance is calculated using the general equation 2.18 below:

$INPUT + GENERATION - OUTPUT - CONSUMPTION = ACCUMULATION \dots\dots\dots\dots\dots$Equation 2. 18

The input stream represents the materials that enter the system boundary, generation represents what is produced within the system after the reaction has taken place, output represents the stream of the materials that leave through the system boundary, Consumption is what is consumed inside the system and accumulation is the build-up within the system (Felder and Rousseau, 2005).`

A batch process is a process which does not have an inlet and outlet stream (a closed system, the feed materials are placed into the system (this can be a reactor, filter or mixer among others) before the system starts operating. The materials in a batch system are held for a period of time during which the necessary physical or chemical modifications occur. No material will go beyong the system boundary during this time. The mass balance equation for a batch process is as follows:

$INPUT\ (initial\ quantity) = OUTPUT\ (final\ quantity) \dots.\dots\dots\dots\dots\dots\dots\dots$Equation 2. 19

A semi-batch process only has the inlet stream but not the outlet and the final product is collected at the end of the experiment or process.

A continuous process (flow process) is a process during which the inlet and outlet materials are unceasingly entering and leaving the system boundary. A continuous process can be classified into two groups as either a steady state or an unsteady state process. The steady state process is a process in which all the operating conditions such as temperature, pressures, compositions and flow rates among others remains constant with throughout the reaction while unsteady state process is the opposite of the steady state as some operating parameters vary with time, and the flow rate of the stream entering and leaving the system does change with time as well (Felder and Rousseau, 2005)

The mass balance can be performed using flow rates, mole fraction, mass fraction, mass and moles. The mass or material balance can be applied on a single unit or to an overall balance around the system. An elemental balance can be conducted for each specific element within all the streams or for the entire stream (Himmelblau and Riggs, 2004). For this study, the use of material balance was to determine the mass of treated water, solid residue generated and lastly the mass of water and solid in the slurry in the inlet and outlet streams.

2.6 ACID BASE ACCOUNTING (ABA)

Acid-base accounting (ABA) is an analytical tool used before coal mining to determine the acid- or alkalinite-producing potential of overburden rocks (Skousen et al., 2001). This process was first developed by Dr. Richard M. Smith and associates from the West Virginia University in the late 1960s. ABA was originally designed to discern layers that could be used as topsoil replacements or as hard resistant rock for valley fillings in the overburden. Nevertheless, since the method detected acid-and alkaline-producing materials in the overburden, this method was the first available technology to estimate the amount of acid-producing materials before mining (Skousen et al., 1990). ABA has been widely adopted as a method of overburden characterization and estimation of the quality of drainage after mining (Sobek et al., 2000).

ABA was initially developed for measuring neutralization potential (NP), sulphur content, net neutralization potential (NNP) and maximum potential acid (MPA) of individual overburden strata. ABA is mostly calculated using the method of total S (sulphur) determination according to the stoichiometric equation below from which the percent of sulphur (% S) that is present in the rock is determined and is then multiplied by a constant (31.25) to determine the MPA and NP and other unknown.

$$FeS_2 + 2CaCO_3 + 3.75\ O_2 + 1.5\ H_2O \rightarrow Fe(OH)_3 + 2SS_4^{-2} + 2Ca^{+2} + 2CO_2 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\text{Equation 2. 20}$$

First-order classification, which specifies the acid-neutralizing and acid-generation potentials of rock, and the difference or Net neutralizing potential is calculated. Different methods were developed to determine the ABA test such as ABA methods by Sobek et al in 1978, a modified ABA method used by Lawrence & Wang in 1997, the B.C Research initial test method among others but for the case of this study ABA method was the only one used. This method is still much-used methods, it estimates the acid potential based on the sulphur content. Once the %S is determined the other unknowns such as acid potential (AP), Neutralizing potential (NP), Net neutralizing potential (NNP), Neutralizing potential ratio (NPR) and Rock types can be determined as well. The analysis of ABA data for use in predicting water quality post-mining requires various assumptions. Assumption number one, all sulphur in a sample will react to form acid. Assumption number 2, all material in the sample that consumes acid in the laboratory will generate alkalinity in the field. Assumption number 3, the reaction rate of sulfur will be equivalent to the dissolution rate of the neutralizing material. Assumption number four (last), NP and %S below certain thresholds do not influence water quality. It is impractical to believe that these assumptions are correct in the natural environment this putting to question the ability of ABA to accurately predict post-mining drainage quality (DiPretoro and Rauch, 1988; Erickson and Hedin, 1988)

The classification of materials in terms of their acid-mine drainage (AMD) potential is done base on the net neutralising potential value, the ABA results are presented in terms of its NNP, %S and NP:AP ratio as follows: a rock is theoretically considered to have a net potential for acid drainage only if his NNP < 0 kg $CaCO_3$/t. A rock with NNP > 0 kg $CaCO_3$/t rock will have a net potential for the neutralization of acidic drainage. The uncertainty related to the exposure of the carbonate minerals or the pyrite for reaction, had made the interpretation of whether a rock will be net acid generating or neutralizing is more complex. Studies had revealed that a range from -20 kg $CaCO_3$/t to 20 kg $CaCO_3$/t exists that is defined as a “grey” area in determining the net acid generation or neutralization potential of a rock. A material is classified is Rock type III only if his NNP value is above the range from -20 kg $CaCO_3$/t to 20 kg $CaCO_3$/t. No Potential for Acid Generation and material with an NNP below this range classified as Rock Type I - likely Acid Generating.

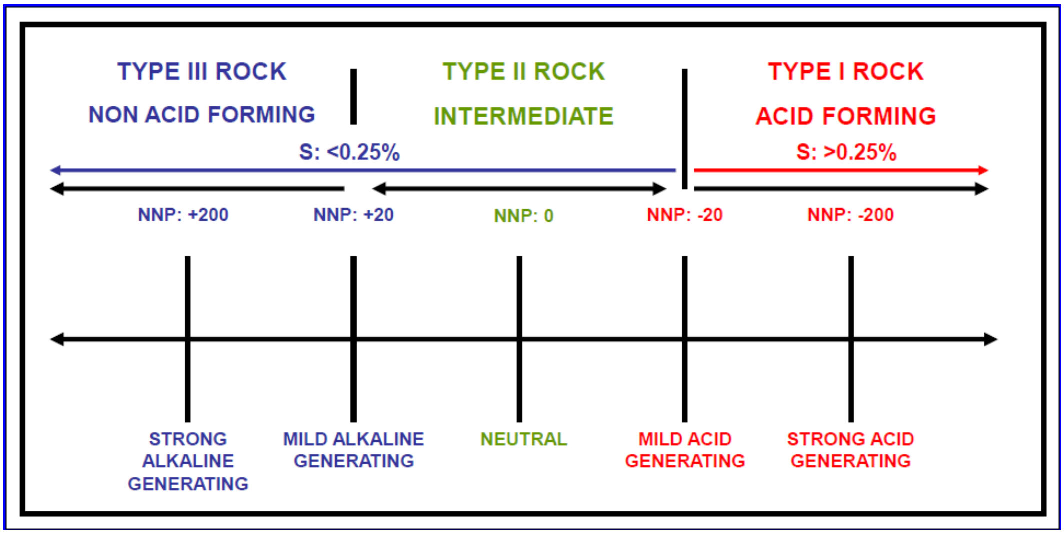

Figure 2. 5: Schematic drawing of type of the rock

2.7 SUMMARY

The mining of coal results in open mines that cause the formation of AMD through oxidation of pyrites in presence of oxygen and water, leading to the contamination of ground water, which has a negative environmental impact. On the other hand, the increase in population causes energy production to increase to meet the energy demand, resulting in a huge amount of CFA being produced causing a disposal problem. The impact of coal fly ash disposal on the environment, especially on the groundwater cannot be underestimated. Several methods have been used to treat AMD using coal fly in order to reduce their negative environmental impact, among these methods there is an active methods of treatment which requires a chemical plant, equipment, maintenance and labour, this method requires capital making it not cost effective. This study will use a passive method of treatment, which does not require a chemical plant for treatment, labour and maintenance and it is energy free treatment and the operation can take place on site where the CFA is produced and treated water can be reused for instance in combustion plant for the cooling system in the heat exchanger unit.

CHAPTER THREE

3 METHODOLOGY

3.1 INTRODUCTION

This section provides the materials and chemicals utilised in this study. Detailed information about the origin of the raw materials such as Eyethu acid mine drainage as well as Kendal and Lethabo CFA used are presented in this chapter. Moreover, this chapter outlines the sampling, storage procedures of raw materials, experimental procedures as well as the analytical techniques used to characterize raw materials, treated water and solid residue produced during treatment period.

3.2 STUDY AREA

The acid mine drainage (AMD) used in this study was from Eyethu coal mine in the Mpumalanga Province and the coal fly ash samples were from Kendal and Lethabo power station located in the Mpumalanga Province, South Africa. Figure 3.1 is the map of South Africa presenting the locations where the samples were collected.

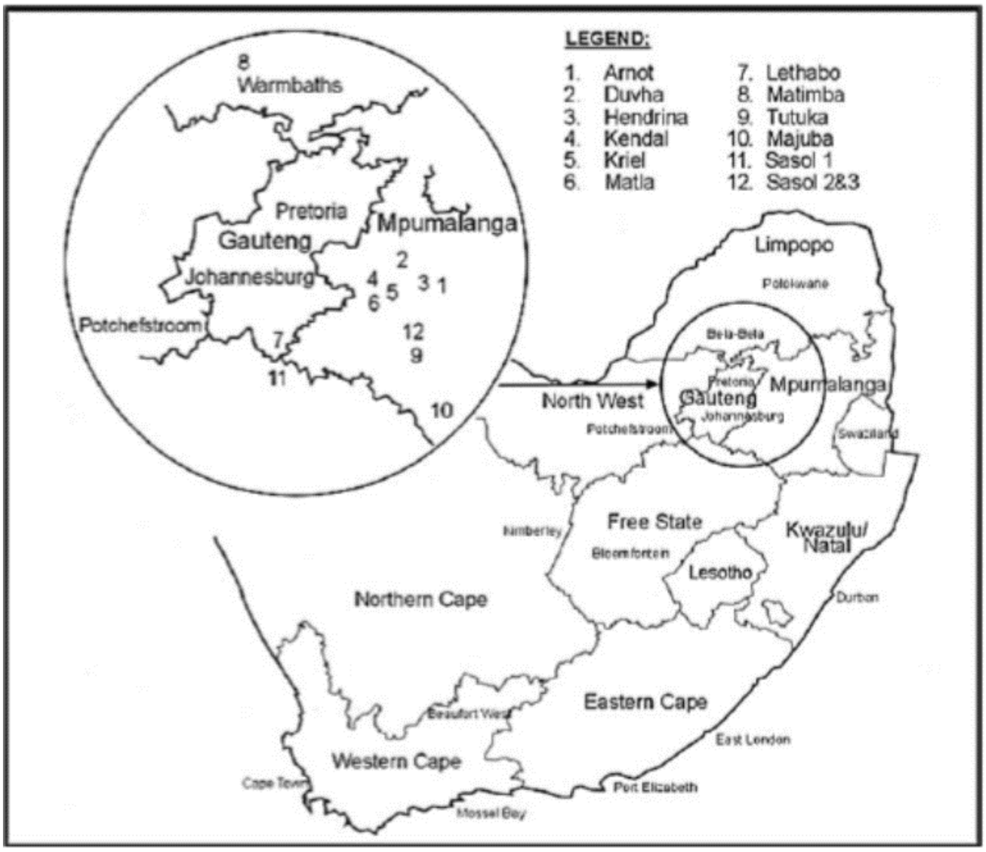

Figure 3. 1: Coal power plants in South Africa (Source:)

3.3 MATERIALS AND CHEMICALS USED

The CFA samples used in this study were collected from the ash hoppers from Kendal and Lethabo power stations. Kendal power station is one of the biggest power generating stations in South Africa and it is the largest indirect dry-cooled power station in the world. Kendal power station, located in Mpumalanga province, started full operation in 1983. Lethabo power station is a large coal fired power station owned by Eskom, which produces an average of 20 000 tons of ash daily. Lethabo power station, located in the Free State province, was constructed in 1980 and started full operation in 1985. The coal fly ash was sampled from the ash hoppers, kept in a sealed tight plastic container and kept at room temperature in a dark place to avoid contact with light and air which can cause a change in composition. The AMD sample was collected from Eyethu coal mine located in the

Mpumalanga province in 25 L container and filtered through a 0.45 µm syringe filter. The AMD used was from Eyethu coal mine in the Mpumalanga province. Kendal and Lethabo power station are presented in Figure 3.2 and 3.3.

Figure 3. 2: Kendal power station (Source: Eskom.co.za: access 10/10/2019)

Figure 3. 3: Lethabo power station (Source: Eskom.co.za: access 10/10/2019)

3.4 EQUIPMENTS AND MATERIALS USED

For the case of this study, no chemicals were used during treatment process except of sulphiric acid, which was used during ICP-OES test. Table 3.1 below presents the list of equipment and raw materials used in this study :

Table 3 1: Equipment and raw materials used

Equipment	Description	Suppliers
Mixer	A mixing machines whith 6 impellers, rotating at 120 rpm	UWC facilities
Columns	Columns were made of Perspex tubes, Internal diameter 9 Cm and 20 Cm long.	UWC facilities
Pipes	PVC pipes	UWC facilities
Raw materials		
Eyethu AMD	Liquid	Eyethu coal mine
CFA	Solid	Kendal amd Lethabo power stations.

3.5 METHODS

3.5.1 Experimental approach

Figure 3.4 is the overall schematic representation of all the steps involved during the treatment of Eyethu AMD with Kendal and Lethabo CFA and different characterization techniques used in this study.

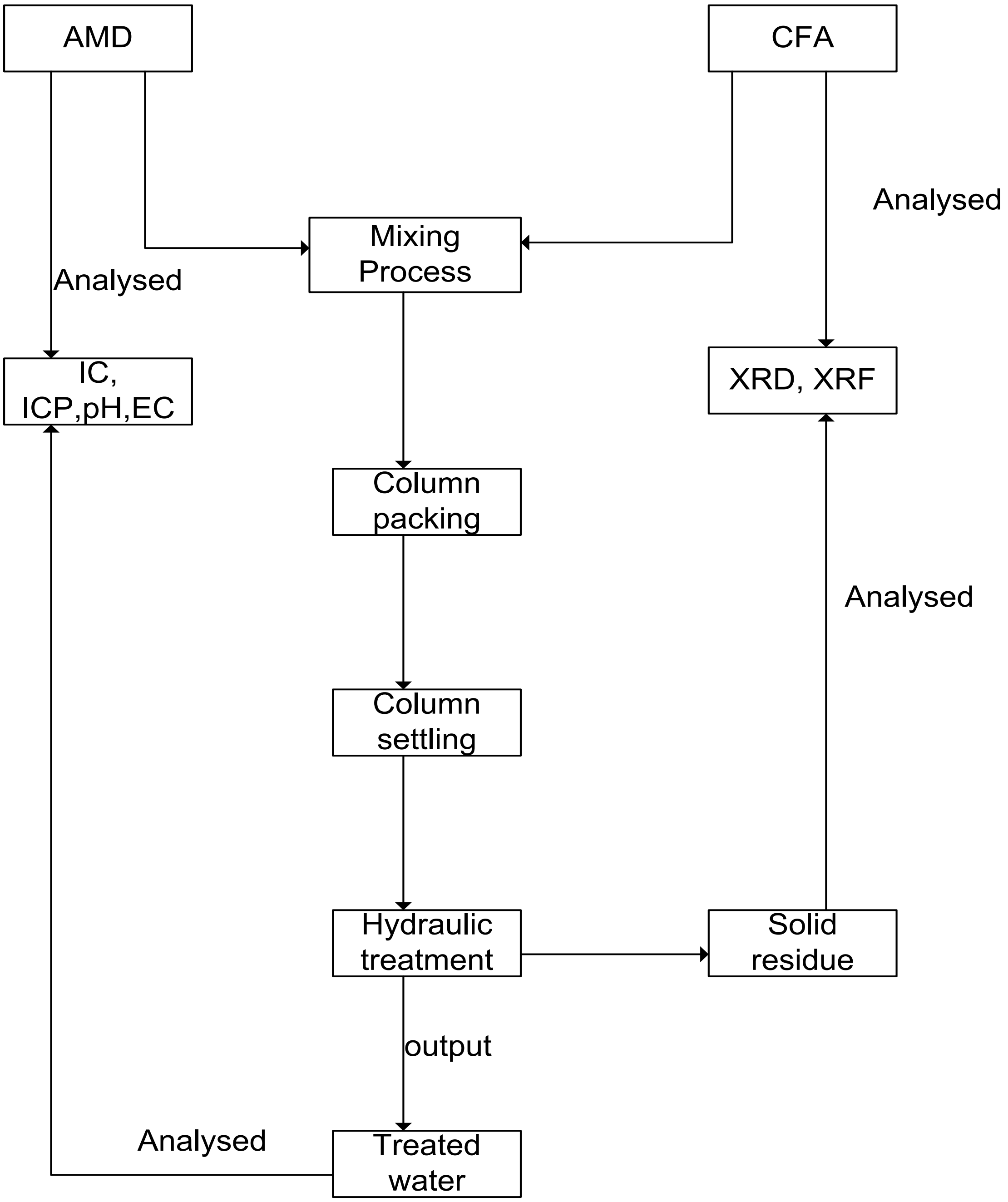

Figure 3. 4: Block flow diagram of the process

3.5.2 Mixing process

This process was done by mixing Eyethu AMD with the coal fly ash samples from Kendal and Lethabo separately in a 600 mL beaker at a ratio of 3:1. To fill up a column made of Eyethu AMD mixed with Kendal CFA the amount of fly ash used was1440 g and 4320 mL of AMD were used, for Lethabo columns 1280 g of fly ash and 3840 were used. A certain amount of coal fly ash was poured into AMD according to the ratio and the mixture was then stirred by means of a magnetic stirrer for a period of 30 minutes. The mixing stage was undertaken for pre-treatment prior to column packing. Figure 3.5 below displays the mixing stage and the instrument used.

Figure 3. 5: Mixing equipment

3.5.3 Column packing and settling

The columns were made of Perspex tubes of 9 cm internal diameter and were 20 cm long. The columns had two shut-off valves, one at the bottom and another one on top, which had as duty to control the inlet and outlet flow of water. Two white caps having small holes at the center, covered inside by two plastic netting cut into disc that were used to prevent the slurry from running out of the column. After the mixing stage was completed the slurry was poured into a column for it to settle. This was repeated until each of the columns were completely filled up with AMD-fly ash slurry (no open space was allowed above the packed slurry in the column). The columns were made by mixing AMD with coal fly ash at the ratio of 3:1 as shown Section 3.4.2 above. The slurry was then left to settle for 24 hours. Lastly, the columns were then connected to the system for hydraulic treatment as shown in Figure 3.6.

Figure 3. 6: Columns settling

3.5.4 Hydraulic system

Two hosepipes were connected to each column; one as inlet and the other as outlet flow. As shown in Figure 3.7 the inlet hose pipe was taking the AMD from the reservoir container into the column. The column set-up was a down-flow system where the AMD flowed into the column from the top, passing through the slurry and then exited at the bottom where the outlet hose was connected to the collection bottle. Filtered samples of the effluent were collected at different times and sent for analysis by IC and ICP-OES respectively. It was a continuous system where the AMD was pumped into the column using a peristaltic pump at a specific flow rate of 12mL/h for a period of 21 days and the effluent (treated water) was collected from the bottom of the column.

Figure 3. 7: Hydraulic column leaching system

3.5.5 Effect of time during treatment process

Two sets of experiments were conducted while monitoring time in order to determine the impact of time during neutralisation process. Samples have been collected at different time, starting from time zero till the end of the experiment. Furthermore, the collected samples were sent for test in order to determine pH and EC measurement, in additional to run IC and ICP-IOES test of the recovered water. This was done on the leachates from Kendal and Lethabo columns.

3.5.6 Effect of pH in treated water

During treatment process, variation of pH was observed as the neutralisation and some metals removal were pH dependant. A time was set at which samples of treated water should be taken from the column made of Eyethu AMD with Kendal CFA as well as for Eyethu AMD with Lethabo CFA. At every given time pH was recorded using pH meter as highlighted in Section 3.6.1 and IC and ICP-OES analysis was done to determine change in concentration of each cation and ion present in the treated water.

3.5.7 Engineering parameters

Engineering parameters such as Volumetric Flow rate, percentage removal and rate of removal were calculated as follows: The volumetric flow rate of the effluent leachate from the columns was calculated over time, by recording a volume of the effluent at a specific time. The volumetric flow rate was calculated by dividing the volume recorded by the time during which it was recorded. The percentage removal of the metals from Eyethu AMD was calculated by using the equation below:

$$\%\ \text{removal} = \left(\frac{\text{conc of ionic species in raw sol.} - \text{conc.of ionic species at a given time}}{\text{conc.of ionic species in raw sol.}}\right) * 100 \ldots\ldots\ldots\ldots\ldots \text{Equation 3. 1}$$

The rate of removal or rate at which metals were removed from Eyethu AMD was determined using the following equation:

$$Rate\ of\ removal = \frac{concentration\ of\ elements\ \left(\frac{mol}{L}\right)}{Time\ (s)} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 3. 2}$$

3.5.8 Acid-base accounting

The percent of sulphur (% S), acid potential (AP), neutralisation potential (NP), net neutralisation potential (NNP), neutralising potential ratio (NPR) of the rock material was worked out in this test. The assumption was made that pyrite was the only sulphide in the rock the AP is determined by multiplying the percentage sulphur (%S) with a factor of 31.25 which is based on the oxidation reaction of pyrite. The AP was measured in kg $CaCO_3$/t rock this indicating that the theoretical amount of calcite neutralized by the acid produced. The percent sulphur (%S) was determined through an infrared (IR) detector after sample combustion in an Eltra furnace. The total %S was determined after heating the furnace to ±2200°C and the sulphide %S was determined at 1 000°C. The sulphide %S was used to determine the acidification potential of the samples and the acid potential of the sample was therefore not overestimated. The NP (Neutralization Potential) was calculated by treating a sample with a known excess of standardized hydrochloric or sulphuric acid (the sample and acid are heated to ensure reaction completion). Standardized sodium hydroxide was used to back-titrate the paste in order to determine the amount of unconsumed acid. NP unit is kg $CaCO_3$/t rock to represent the amount of calcite theoretically present to neutralize the acidic drainage, NNP is determined by subtracting AP from NP.

3.5.9 Mass balance calculation

The material balance was done around the column and the overall balance was also done for the entire process. The mass balance concerned for the case of Kendal column 1280g of the fly ash with 300 L (283.5 Kg) of the AMD, and for the case of Lethabo columns 1440g of CFA with 275 L (259.88 Kg) of Eyethu AMD. The slurry produced were then weighed for the overall mass balance calculation. Furthermore, sample of slurry from both columns were dried and used for moisture content determination. Three slurry samples were collected after treatment and weighed directly and the mass recorded as wet weight of sample, these weighed samples were then dried at 100 ºC using an oven for 24 hours. The samples were allowed to cool. The cooled samples were weighed again, and recorded as the dry weight of sample.

3.6 ANALYTICAL TECHNIQUES USED

3.6.1 Electrical Conductivity and pH

The pH analysis is based on electrical measurement involving tow electrodes; an indicating electrode and a reference electrode. The pH of a solution is defined as a measure of the concentration of hydrogen ion H^+ in solution. The pH meter converts the potential (voltage) ratio between a reference half-cell and a indicating half-cell to pH values. MoreoverThe pH meter senses the potential change and calculates [H+] that which is unspecified. The measurements were conducted at ambient temperature.

Electron conductivity is used to measure the total concentration of inorganic substances in water which relies on the presence, mobility and valence of the species in solution. Furthermore, EC, is usually measured in mS/cm or µS/ cm. The instrument used to measure the electrical conductivity of the samples is Hanna HI 991301 pH meter with portable pH/EC/TDS/ Temperature probe. The analysis was done at room temperature where the meter was standardized before the test by using a standard of 12.88 mS/cm. For the case of this study pH and EC of raw Eyethu AMD were determined before the neutralisation process, for the covered or treated pH and EC measurement were recorded every time when the sample was gathered and the final reading at the end of the experiment.

3.6.2 Ion Chromatography AND Inductively Coupled Plasma-Optical Emission Spectromery

Ion chromatography (IC) is a technique that is used to separate, identify and quantify inorganic cations, anions and low molecular weight water soluble organic acids and bases. This technique is a method of liquid chromatography using ion-exchange resins to isolate atomic or molecular ions based on their interaction with resins, as the affinity of ion-exchange resins varies with different metal ions. The aqueous samples are analyzed in parts-per-million (ppm) or parts-per-billion quantities. The anions and cations that can be detected during this analysis are fluoride, chloride, nitrite, nitrate, sulphate, lithium, sodium, ammonium, and potassium using conductivity detectors. This technique was used to analyze the fresh Eyethu AMD as well as the treated water, a 0.45 µm membrane filter were used to filter the samples and to remove suspended solids and then diluted with de-mineralized water to obtain EC values between 50 and 100 µS/ cm. The instrument used was a Dionex DX-120 ion chromatography with Ion Pac AS14a column and AG14-4 mm guard column.

ICP-OES analysis was conducted to analyze the major and trace elements contained in Eyethu AMD and the leachates or treated water. Samples were prepared through digestion with 2% nitric acid at 10 times and 100 times dilution. Analysis was performed in triplicate for accuracy of the result. The instrument used was a Varian 710 ES. A spectra scan multi element range was used for the standards. The machine used for this analysis has a high solids torch and an axial torch and it was calibrated daily prior of its operation and accuracy was checked by analyzing quality control standards for all the elements analyzed.

3.6.3 X-ray Diffraction

The mineral phases present in the raw Kendal and Lethabo CFA and in the solid residue produced after treatment were determined using XRD analysis. The samples of coal fly ash and solid residue were oven dried for 24 hours at 60° C to remove water. Analysis were made using a multi-purpose X-ray diffractometer D8-Advance from Bruker operated in a continuous θ-θ scan in locked coupled mode with Cu-K$_{\alpha}$ radiation. The sample was mounted in the center of the sample holder on a glass slide and levelled up to the correct height. The analysis were run within a range in 2θ defined by the user with a typical step size of 0.034° in 2θ. to record diffraction data at a typical speed of 0.5 sec/step which is equivalent to an effective time of 92 sec/step for a scintillation counter, a position sensitive detector, Lyn-Eye, was used. Data are background subtracted so that the phase analysis is carried out for diffraction pattern with zero background after the selection of a set of possible elements from the periodic table. Phases are identified from the match of the calculated peaks with the measured ones until all phases have been identified within the limits of the resolution of the results. The specifications of instrument are as described in Table 3.2:

Table 3 2: XRD instrument description

Instrument	Measurements	Software
Manufacturer: BRUKER AXS (Germany) Diffractometer: **D8 Advance** Measurements: continuous Θ-Θ scans in locked coupled mode Tube: Cu-Kα radiation ($\lambda K\alpha_1$=1.5406Å) Detectors: LynxEye (Position sensitive detector)	Tube voltage: 40kV Tube current: 40mA Variable slits: V20 variable slit 2Θ Range available: 0.5° to 130° Increment $\Delta 2\theta$: 0.034° Measurement time: 0.5 sec/step (long enough for good statistics)	ICDD: PDF database 1999 Data evaluation: EVA software from BRUKER

3.6.4 X-ray Fluorescence

The elemental composition of Kendal and Lethabo fly ash as well as the elemental changes that occurred in the recovered solid residue after treatment with Eyethu AMD were determined using XRF technique. This technique is advantageous because it is non-destructive, multi-elemental, fast and cost effective. Moreover, this technique gives a uniform detection limit through a large portion of the periodic table and is valid to a wide range of concentration, it can analyse many elements in the periodic table starting from Beryllium (Be) with atomic number 4 to Uranium (U) with atomic number 92 at trace levels (Czichos et al., 2006). The CFA and solids residue samples were dried using an oven at 105°C for at least 4 hours then cooled in a desiccator for plus minus 30 minutes of time, then crushed until 2 mm, then split into approximately 100 grams using a rotary splitter. Lastly the sample was milled to 80% < 75 micron. Philips PW 1480 X-ray spectrometer were used to determine the oxides of the major elements namely SiO_2, Al_2O_3, Fe_2O_3, CaO, TiO^2, MgO, K_2O, P_2O_5, MnO and Cr_2O_3 of each sample. The instrument was fitted with a chromium tube, five analysing crystals and the detectors being a combination of gas-flow proportional counter and a scintillation detector. EPA (2004), states that the XRF technique can analyse elements from ppm to per cent levels.

3.7 SUMMARY

This chapter has given an overall overview of the sampling techniques, analytical techniques as well as the experimental methods and the equipment and raw material used in this study. The following Chapter will discuss in details the analytical and the experimental results obtained from this study.

CHAPTER FOUR

4 RESULTS AND DISCUSSION

4.1 INTRODUCTION

This chapter presents and discusses the results obtained from the experimental work conducted during this study as explained in chapter three. The following parameters of the results will be detailed: chemical, physical composition and morphology of raw materials as well as of solid residue using X-ray diffraction (XRD), X-ray fluorescence(XRF), Ion chromatography (IC) and inductively coupled plasma-Optical emission spectrometry(ICP-OES) of the raw AMD and treated water produced, pH and EC variation, the neutralisation reaction of AMD using CFA, major and trace elements removal, sulphate removal from the AMD and the % removal of elements, rate of removal and the volumetric flow rate, mass balance and the acid-base accounting test.

4.2 CHARACTERISATION OF AMD AND CFA BEFORE TREATMENT

This section presents results obtained from ICP-OES and IC of Eyethu AMD before treatment, and the XRD and XRF results of fresh Kendal and Lethabo CFA. Moreover, it provides acid-base accounting calculation as highlighted in Chapter 3, Section 3.5.

4.2.1 Eyethu AMD analysis

The mine water used in this study was from Eyethu coal mining. It was characterised using IC and ICP-OES to determine the alkalinity and elemental composition as described in chapter 3, Section 3.6.2.

4.2.2 pH and electrical conductivity

The characterisation of Eyethu AMD using IC and ICP-OES is presented in Table 4.1. The electrical conductivity and pH measurement of Eythu AMD were done following the method highlighted in Chapter 3, Section 3.6.1 (number of samples analysed =3).

Table 4. 1: **ICP-OES results of Eyethu AMD before treatment**

Parameters	Unit
pH	2.23
EC	1.8
Chloride (mg/L)	28.28
Sulphate (mg/L)	2680
Na (mg/L)	219.6
Al (mg/L)	120
Mg (mg/L)	112.5
Fe (mg/L)	100.3
Ca (mg/L)	36.62
Mn (mg/L)	32.84
Si (mg/L)	13.53
K (mg/L)	11.14
Zn (mg/L)	6.71
Ni (mg/L)	1.65
Co (mg/L)	1.623
Sr (mg/L)	0.61
Cu (mg/L)	0.05
Pb (mg/L)	0.01
Mo (mg/L)	0.005
Be (mg/L)	0.005
Cd (mg/L)	0.005
Cr (mg/L)	0.005
Pb (mg/L)	0.005

From the result it was shown that Eyethu AMD is very acidic with a pH of 2.23 and contained high sulphate concentration of 2680 mg/L much greater than the given range for irrigation and potable water given by DWAF. The pH value of the water from Eyethu coal mine is not within the DWAF limit for irrigation or potable water and Can then be classified as acid mine drainage, since the pH is less than 6 (Younger et al., 2006). The very low pH could be due to the high concentration of Fe, Al and Mn which produce so many protons during the formation of their respective hydroxides according to Equations 4.1, 4.2 and 4.3 (Younger et al., 2002).

$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$ ……………………………………………………..Equation 4. 1

$Al^{3+} + 3H_2O \rightarrow Al\,(OH)_3 + 3H^+$ ……………………………………………………. …..Equation 4. 2

$Mn^{2+} + 2H_2O \rightarrow Mn(OH)_2 + 2H^+$ ……………………………………………………. …Equation 4. 3

Based on the relative abundance and level of weathering of pyrite and calcite neutralisation, the pH of mine water can be pushed to acidic or alkaline mode. Acidity of Eyethu water can also be explained by the geology of the bedrock of the coal mine, which is pyrite dominating bedrock hence the oxidation of pyrite produces an acidic water. A scarcity of calcareous minerals and the absence of carbonate buffering in these AMD samples suggest the acidic pH importance. Electrical conductivity and the chemical composition is mostly dominated by the presence of sulphate The high sulphate concentration in mine water gives it a noticeable taste, and it can cause laxative effects to individual who have not adapted to the to the water (WHO, 2011). The high concentration of sulphate in the acid mine drainage is explained by the typical of leachate from sulphide rich coal mine tailing and opencast mine lake (Uhlmann et al., 2004) and chloride ions, as well as the high concentration of Ca, Al, Mg, Fe, Na, Mn,Si and K. The acidity of the mine water characterised by its pH, making it unsuitable for domestic, agricultural and industrial use (DWAF, 1996; WHO, 2011). AMD can not be released into the environment and therefore represents a liability for the mine, which requires treatment before to be released into the environment.

4.2.3 Coal fly ash analysis

The XRD and XRF results of raw Kendal and Lethabo CFA are presented in Figures 4.1and Figure 4.2, and Table 4.2 below. The results are found following the methods explained in Chapter 3, section 3.6.3 and Section 3.6.4.

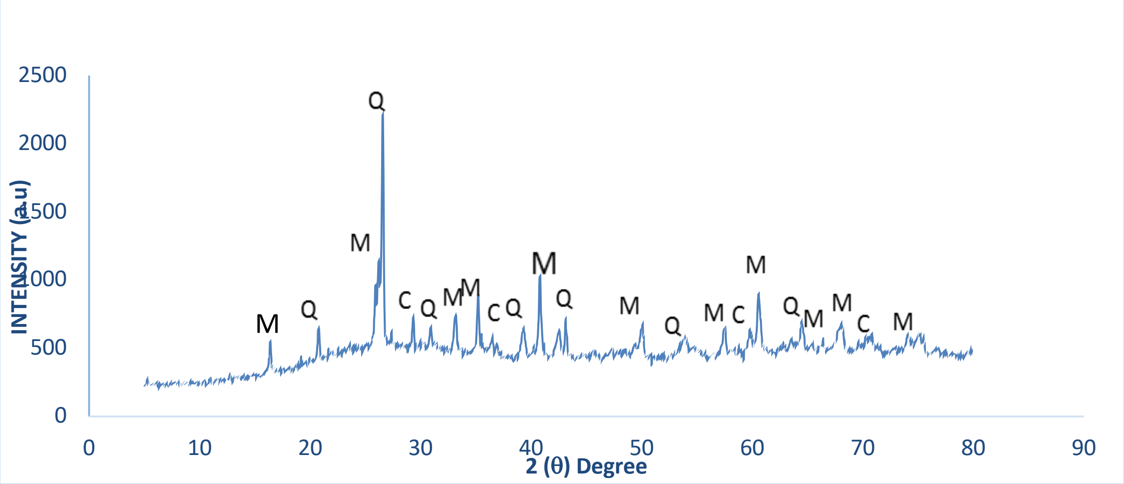

Figure 4. 1 X-ray diffraction of raw Lethabo CFA. (Q=quartz, M=mullite, C= calcite) n=3

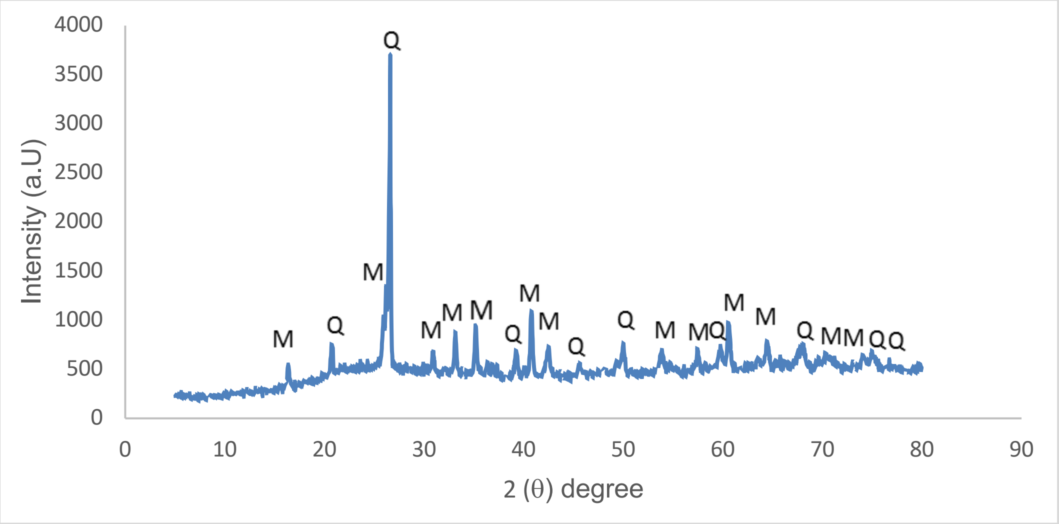

Figure 4. 2: X-ray diffraction of fresh Kendal CFA before treatment. (Q=quartz, M=mullite, C= calcite) n=3

The results showed that quartz ($Al_2Si_2O_{13}$) and mullite (SiO_2) were the only or dominant crystalline phases that make up Lethabo coal fly ash while Kendal coal fly ash was made up of ($Al_2Si_2O_{13}$), mullite (SiO_2) and calcite ($CaCO_3$) and microcline intermediate. Rao & Glusker (1970) states that these are the common mineral phases found in fresh coal fly ash. Mullite is formed when Kaolinite found in the parent coal undergoes phase transformation under an elevated temperature in the range of 1200- 1400° C. Quartz from parent coal survives the combustion conditions therefore it is found unchanged in fly ash, quartz does not undergo any phase transformation, even at the extreme temperatures in a typical combustion chamber, thus it is found unchanged in the fly ash (Bandopadhyay, 2010) and Calcite is as well generating from parent coal. The mineral phases found by XRD were compatible with the significant Si, Al and Ca levels present in the fresh fly ash.From the XRD results it was observed that Lethabo CFA contains another crystalline phase which is lime which was not present in Kendal CFA. Furthermore, lime is used to neutralise acidic solutions (Gitari et al, 2006). The presence of lime in Kendal CFA made it a suitable neutralizing agent.

The Raw Kendal and Lethabo coal fly ash chemical compositions are presented in Table 4.2. The X-ray fluorescence of both Kendal and Lethabo CFA were obtained following the procedures described in Chapter 3, Section 3.6.4. The analyse was done in triplicate for accuracy purpose.

Table 4. 2: XRF of fresh Kendal and Lethabo CFA (major elements) n=3

Species	Major elements % W/W	
	Lethabo CFA	Kendal CFA
SiO_2	52.78 ± 0.22	52.78 ± 0.21
Al_2O_3	29.24 ± 0.23	29.17 ± 0.28
CaO	5.85 ± 0.184	4.61 ± 0.09
Fe_2O_3	4.11 ± 0.074	3.47 ± 0.03
TiO_2	1.63 ± 0.023	1.59 ± 0.027
MgO	1.55 ± 0.182	1.04 ± 0.182
BaO	0.16 ± 0.99	0.12 ± 0.99
K_2O	0.8 ± 0.01	0.77 ± 0.01
Na_2O	0.54 ± 0.006	0.27 ± 0.006
MnO	0.25 ± 0.02	0.3 ± 0.02
SO_3	0.24 ± 0.01	0.19 ± 0.12
Cr_2O_3	0.03 ± 0.008	0.03 ± 0.07
V_2O_5	0.02 ± 0.41	0.02 ± 0.41
LOI	3.24 ± 0.53	0.69 ± 0.53
Total	99.875	99.875

The major oxides dominating Kendal coal fly ash are SiO_2, Al_2O_3, CaO and Fe_2O_3. The American Society for Testing and Materials (ASTM, 1988), states that, if the mean sum of these 3 oxides SiO_2, Al_2O_3, and Fe_2O_3 is greater than 70 % by mass of total CFA composition and the CaO mean mass is lesser than 10% the fly ash will be classified among class F fly ash therefore Kendal fly ash belongs to Class F fly ash, due to the fact that the mean sum of SiO_2, Al_2O_3 and Fe_2O_3 was 86.13 by mass % and CaO 5.84 % XRF value given in Table 4.2. Comparing the two coal fly ash Lethabo and Kendal from XRF results, it can be seen that Lethabo has a high concentration of Al_2O_3, CaO and Fe_2O_3

comparing to Kendal CFA. Moreover, CaO is available for neutralisation as it increases the alkalinity of the acidic solution, as well as MgO which can also contribute for neutralization of mine water (Gitari et al., 2006). The presence of BaO in CFA made it important as it removes sulphates from mine water (Wilsenach, 1986) The Loss on ignition (LOI) in Lethabo CFA is greater with 3.24 % by mass compared to the one in Kendal CFA which is 0.69 % by mass. This is to explain that the percentage of unburned carbon in Lethabo CFA is greater than in Kendal CFA. Furthermore, this variation in the loss of ignition (LOI) can be allocated to the physical combustion parameters that are different, parameters such as temperature used by the power stations and to the oxidation of combustible constituents of coal. As it has been explained in a study done by Falcon and Ham (1988), that apart from the initial external heat supply during coal burning, combustion of coal could be activated by the internally generated thermal energy and it is the result of the oxidation of the combustible constituents of coal in the presence of heat.

Besides the oxides, Kendal and Lethabo CFA present a high concentration of minor and trace elements such as S, Sr, V, Mn, Th, Pb and Y among others as presented in Table 4.3.The minor elements from coal fly ash were analysed using ICP-OES following the method.

Table 4. 3: Minor elements contains in Kendal and Lethabo CFA (n=3)

Species	Minor elements (ppm)	
	Lethabo CFA	Kendal CFA
S	1079.2 ± 8.54	1101.22 ± 7.84
Sr	941 ± 7.02	1264 ± 5.22
V	152.2 ± 1.00	100.7 ± 3.85
Mn	92.4 ± 3.85	139.9 ± 1.00
Th	29.0 ± 3.45	23.4 ± 3.45
Pb	20.2 ± 3.17	20.2 ± 6.87
Y	15.7 ± 2.25	15.7 ± 7.1
Cu	13.1 ± 1.18	13.9 ± 3.4
Ni	9.8 ± 2.42	7.2 ± 2.42
Zn	9.7 ± 2.61	9.7 ± 2.61
As	6.3 ± 0.99	8.1 ± 0.99
Sc	6.0 ± 0.21	7.0 ± 0.21
Se	5.0 ± 6.34	6.0 ± 7.24
Co	3.9 ± 4.53	5.5 ± 3.23
Mo	3.8 ± 3.19	2.8 ± 3.19
Be	1.5 ± 3.54	1.9 ± 3.54
Cd	1.3 ± 0.56	1.8 ± 0.56
Re	ND	ND

S, Sr, V and Mn were the most dominant element contained in Kendal and Lethabo CFA. These minor elements contained in Kendal and Lethabo CFA are the incombustible materials that get concentrated in CFA during the combustion process and have the ability to leach out of fly ash and can affect ground water causing some environmental problem such as health risk to the surrounding ecosystem as highlighted in Chapter 2, Section 2.3.2. Eary et al. (1990) testified that Mo concentrations in the CFA are higher than values generally found in coals and soils, showing that the combustion processes tends to enrich the CFA with the minor elements. The concentration of S, Sr, V and Mn were higher in Kendal CFA than in Lethabo CFA as presented in the Table 4.3.

4.2.4 Acid-base accounting

The Acid-Base Accounting test results for both Kendal and Lethabo CFA samples are given in Table 4.4. This test was done based on the methodology presented in Chapter 3, Section 3.5.8. The sulphur percentage (% S), the acid potential (AP), the neutralization potential (NP), the net neutralizing potential (NNP) as well as the neutralizing potential ratio (NPR) were all determined analytically.

Table 4. 4: ABA test results

ABA test Modified Sobek method	Sample identification	
	Kendal CFA	Lethabo CFA
Paste pH	11.4	9.8
%S	0.03	0.021
AP	0.94	0.66
NP	24.5	30.8
NNP	23.56	30.14
NPR	26.1	46.87
Rock types	III	III

From the paste pH which is 11.4 for sample from Kendal CFA and 9.8 for Lethabo CFA sample. It can be said that Kendal and Lethabo CFA are from a non-acid generating rock according to the categorizing samples guidelines (Price et al., 1997).

Table 4. 5: Paste pH value range in determination of acid generating mine water

Final pH	Acid Generating Potential
≥ 5.5	Non-acid generating
3.5 to 5.5	Low risk acid generating
≤ 3.5	High risk acid generating

The total % S was used in the calculation of the AP according to the assumption that was made stating that pyrite is considered as the only source of acid from Equation 2.20. The constant 31.25 was used in the calculation to convert the %s into Kg/t of $CaCO_3$. The neutralization potential was found to be 24.5 and 30.8 for Kendal and Lethabo sample respectively, this showing that these CFA are from a non-producing rock. Depedro and Rauch (1988), states that a rock with a NP <20 produces alkaline water, and the one with NP > 20 has a possibility to produce acid drainage water. Rock type determines the type of water that can be generated from a specific area as elaborated in the table above, so from the NPR results obtained it can be seen that Kendal and Lethabo CFA are from rock type III as the NPR values are above 20, this explaining that this rock cannot produce acid drainage water. The NNP value was found to be superior to 0, this showing that the Kendal and Lethabo CFA are potentially acid neutralizing, according to Price et al. (1997), sample with NNP less than 0 is potentially acid generating. If the sample has a NNP of greater than 0, it is potentially acid neutralizing but there is a range for NNP from -20 to +20 Kg/t $CaCO_3$ within which the system or sample can either become acidic or remain neutral. The type of rock was determined from the NNP value according to the schematic description below.

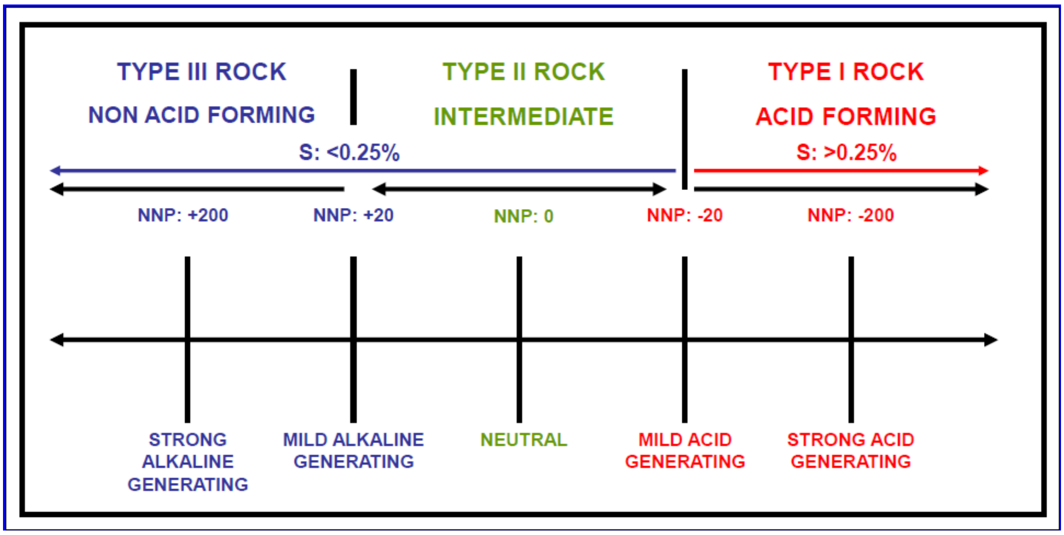

Figure 4. 3: Net neutralizing schematic description

4.3 EYETHU AMD TREATMENT WITH KENDAL CFA

This section provides results obtained from neutralisation process of Eyethu AMD with Kendal CFA as explained in Chapter 3. The neutralisation process was done while monitoring two parameters: time and pH variation as described in Chapter 3, Section 3.4 and 3.5.

4.3.1 Effect of time

The neutralisation process was monitored throughout the experiment and parameters such as time, EC and pH were scrutinised. The variations of pH and EC over time during treatment of Eyethu AMD with Kendal CFA are presented in Figure 4.4. The pH and EC were measured three times for accuracy and average values were used as presented in Figure 4.4.

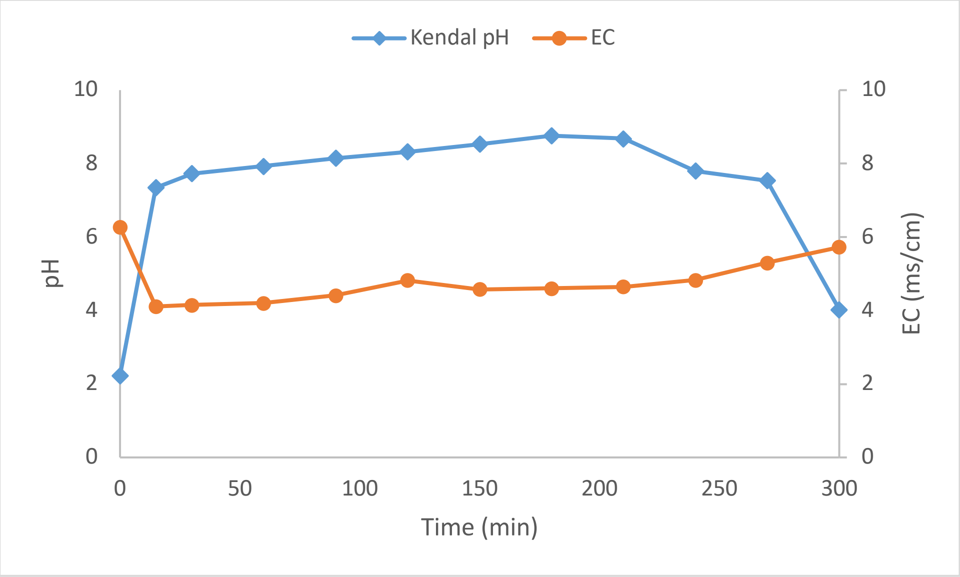

Figure 4. 4: pH and EC trend of Eyethu AMD with Kendal CFA

During treatment process of Eyethu AMD with Kendal coal fly ash. It was detected that within the first 60 minutes of contact of AMD with coal fly ash, the pH changes remarkably from 2.23 to 8.72 of the mixture of the AMD with the Kendal coal fly ash. The increase of pH once AMD was in contact with coal fly ash was explained by the dissolution and hydrolysis of the oxide components such as CaO and Fe_2O_3. The highest pH observed was 8.75 of leachate from Kendal column. The pH was decreasing with time after reaching the highest value. Approximately 13 bed volumes of Eyethu AMD were treated by 1280g of Kendal CFA, this giving a precision on the amount of Kendal CFA that can be used to treat a certain amount of Eyethu AMD which was one of the discovery of this study. This neutralisation process was characterized by a great buffer zone around the pH 8.72 to 7.28 for the leachate from Kendal columns. This buffer zone is explained by the hydrolysis of Al^{3+} forming a hydroxide phase until all the Al^{3+} is totally hydrolysed. Fe^{3+} undergoes hydrolysis as well which caused the buffering of pH in this region. Moreover, Fe^{2+}oxidation and hydrolysis and subsequent precipitation as hydroxide buffers pH. The hydrolysis of AMD constituent like Al^{3+}, Fe^{3+}, Fe^{2+} and Mn^{2+} play a major role of offsetting the increase of pH during the treatment. The EC of the mine water decreased when AMD was treated with CFA from 5.98 mS/m to 2.12 mS/m after 180 min. The metals precipitate out of solution in the form of their hydroxides $(FeOH)_3$, $Al(OH)_3$, $Mn(OH)_2$ and $Mg(OH)_2$)and is pH dependent (Madzivire et al 2010). From the literature, it can be seen that Kendal CFA can neutralise Eyethu AMD. The study done by Madzvire (2009) had proven that acid mine water can be treated by fly ash. In her study, Madzvire treated circumneutral mine water from Middleburg coal mine with Hendrina CFA at different ratio.

4.3.2 Effect of pH

During treatment of Eyethu AMD with Kendal CFA, pH of treated water was changing with time. The change of pH was causing the decrease of metals concentration. Metals concentration in treated water samples collected at different time were determined using ICP-OES as described in Chapter 3, samples were done in triplicates and average values are presented in Figure 4.5 below.

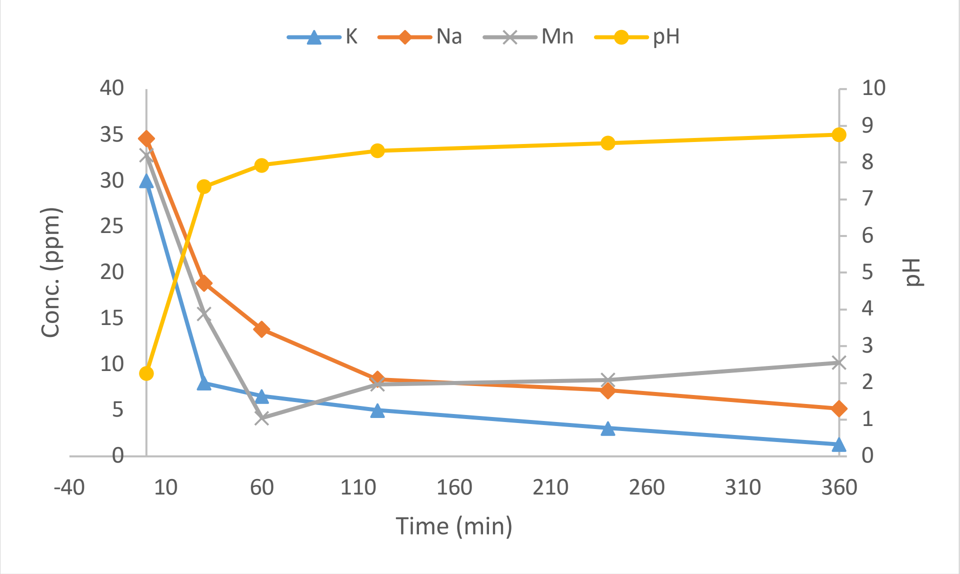

Figure 4. 5: Concentrations of K, Na and Mn at different time and pH

Eyethu AMD with Kendal CFA treatment, showed a decrease in metals concentration such as Fe, Mn, Mg and Al. These metals have shown high percentage removal all depending on the variation of pH (Madzivire et al., 2010). The major and trace element removal are pH dependent. The contact of QMD with CFA causes several process including the change in pH of the solution because acid waters are highly reactive, Main mineral phases dissolved and secondary mineral phases formed. The change in pH is the most important process or parameter caused by the dissolution of CFA and pH governs the mechanism of elimination of predominant toxic elements (Cravotta and Trahan, 1999; M Erol et al., 2005, Gitari, 2006). The pH of minimum solubility of the hydroxides of some metals such as Fe^{3+} is 3.0; Mn (8.41 to 9.0) and of Zn^{2+} (6.0 to 6.5) this explains the percentage mentioned in Chapter 4, section 4.8.2 (Jenke et al., 1983). Fe was first element removed from the AMD and then showed a complete removal of 100% at pH value of 8.32.

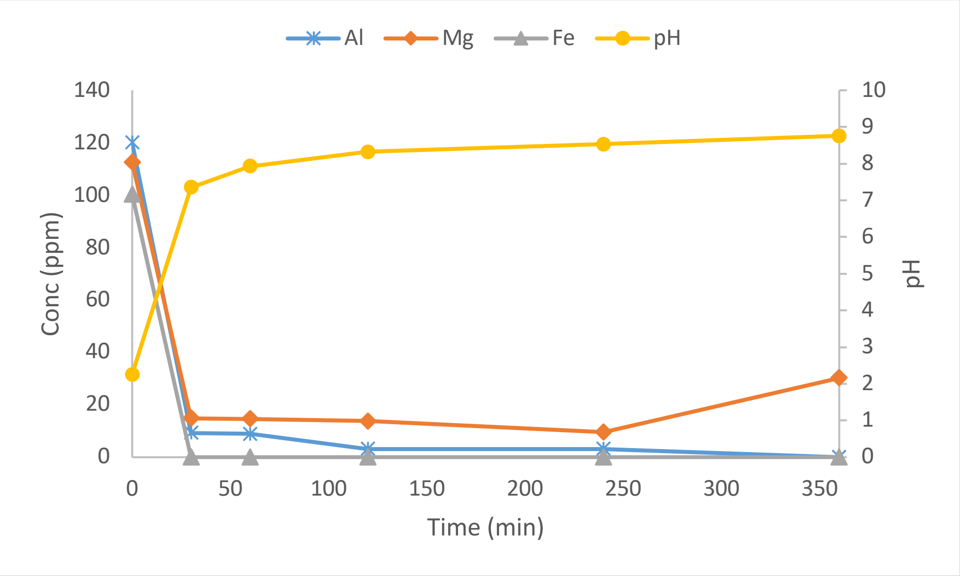

Figure 4. 6: Variation of Al, Mg and Fe concentrations during treatment of Eyethu AMD with Kendal CFA

Al on the other hand was completely removed from the solution at pH 8.53, Mn concentration decreases as well with time and pH of 8.65, but could not get a maximum removal during the treatment this is explained by the fact that manganese are completely removed from the solution only at pH greater than 9, which is the pH of minimum solubility of his hydroxides (Britton, 1956). Mg gets its highest percentage removal when the pH was 8.69. Other metals were completely removed from the solution.

4.4 EYETHU AMD NUTRALISATION WITH LETHABO CFA

This section gives the results obtained from treatment of Eyethu AMD with second set of coal fly ash used in this study that is Lethabo CFA. The same parameters pH and Time were observed in order to draw a conclusion based on the results obtained from treatment with the two types of CFA used in study to treat Eyethu AMD as explained in Chapter 3, Section 3.4 and Section 3.5.

4.4.1 Effect of time

Eyethu AMD was treated with Lethabo CFA using the same methodology as described in Chapter 3. The leachate was collected from columns at different time to measure the pH and EC values of each sample. EC and pH values were taken three times and the average values are presented in Figure 4.7 below.

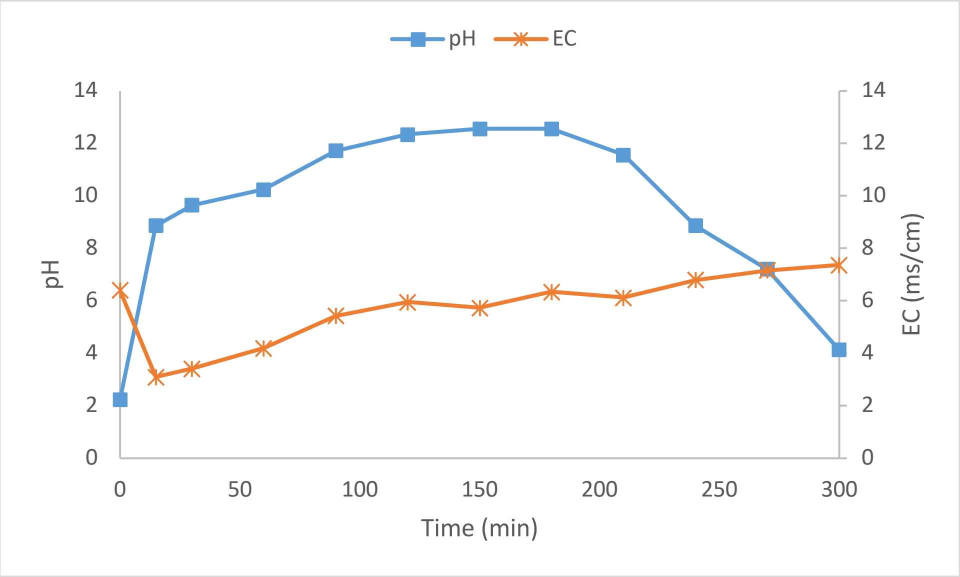

Figure 4. 7: pH and EC reading of leachates from Lethabo CFA column

Treatment of Eyethu AMD with Lethabo coal fly ash was highlighted by the formation of alkaline solution within the first hour of contact as presented in Figure 4.7. The XRF result of Lethabo coal fly ash (Table 4.3) showed the presence of SiO_2, Al_2O_3 and CaO, the dissolution of these oxides was responsible for the increase in pH. For the case of Lethabo CFA 15 bed volumes of Eyethu AMD was treated before 1440g of fly ash get exhausted and lost its neutralising capacity over the AMD. A buffer zone was observed around pH value of 8.37 to 12.28. The EC of the mine water decreased when AMD was treated with CFA from 5.98 mS/m to 2.12 mS/m after 180 min. The metals are known to precipitate out of solution as hydroxides $(FeOH)_3$, $Al(OH)_3$, $Mn(OH)_2$ and $Mg(OH)_2$) and is pH dependent (Madzivire et al 2010).

4.4.2 Effect of pH

Variation of pH during treatment of Eyethu AMD with Lethabo CFA was causing the decrease of metals concentration. The concentration was determined using IC and ICP-OES following the method explained in Chapter 3, Section 3.5. Samples were taken in triplicate and the average values of variation of concentration of some selected metals over time and pH are presented in Figures 4.8.

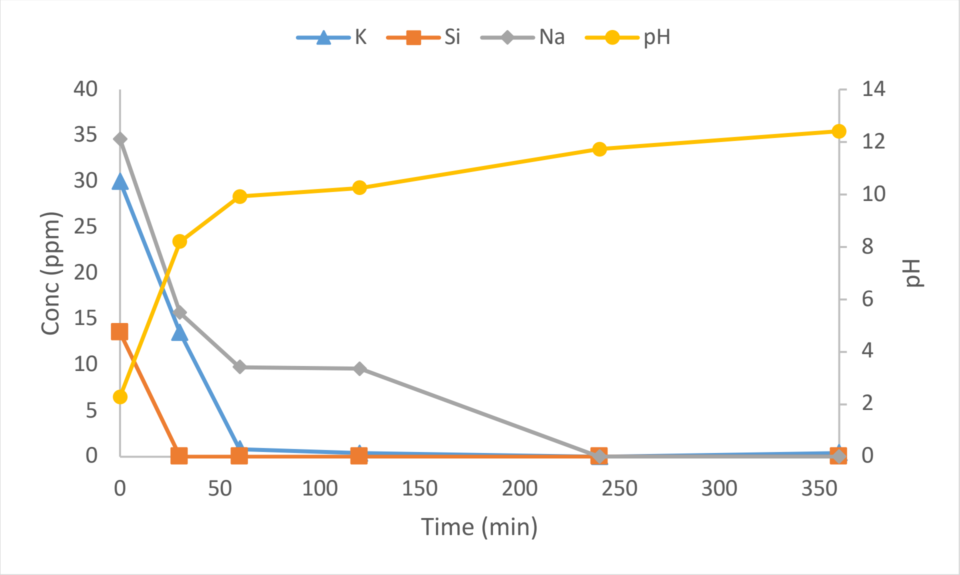

Figure 4. 8: Some selected metals removal trend of treated water from Lethabo CFA column

The increase in pH was causing the removal of some metals or decrease of their concentration. Metals such as K, Si and Na their concentration were completely reduced. Furthermore, these metals were removed from the solution when the solubility of their respective oxides was attained. Britton (1956), stated that the hydroxides of Fe^{3+}, Zn^{2+} and Ni^{2+} solubility are attained at these pH value 3, 8 and 6.66 respectively. During treatment of Eyethu AMD with Lethabo CFA pH value attained covers the optimum hydroxide precipitation pH range of some metals.

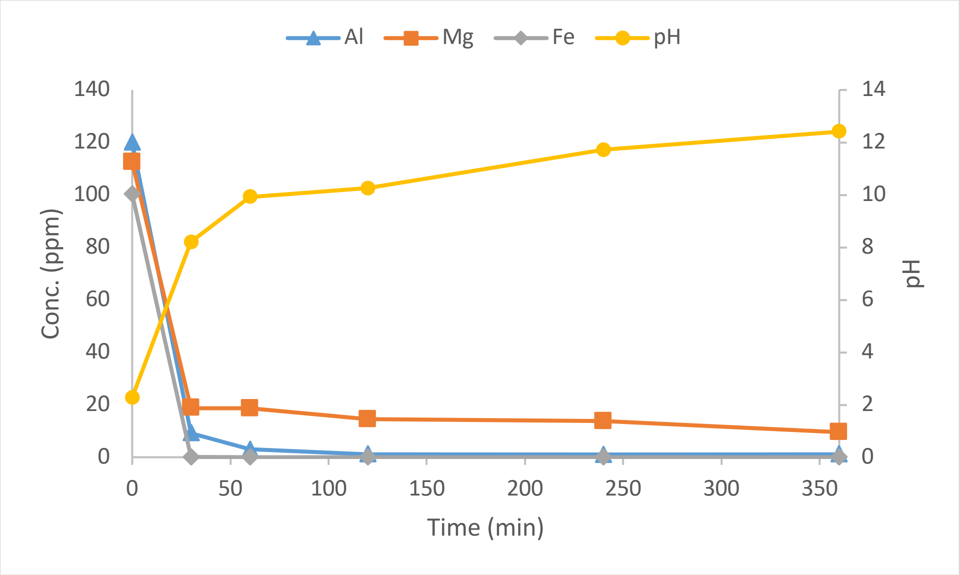

Figure 4. 9: Al, Mg and Fe concentrations variation during treatment of Eyethu AMD with Lethabo CFA

Fe species in AMD are usually in the ferric state (Fe^{3+}) because of the oxygenation by turbulence. Nevertheless, deep water that has not been disturbed can have Fe in the ferrous (Fe^{2+}) state (Stumm et al., 1996). Most dominant Fe in this AMD was in the ferric state from ICP-OES results given in Table 4.1. With the increase of the pH reaching 12.28 iron precipitated as oxyhydroxide compounds (FeO (OH)) and amorphous ox hydroxides is formed when iron undergoes hydrolysis. A large amount of iron was removed while reacting acid mine drainage with Lethabo coal fly ash. The Equation 4.4 demonstrates the process of iron precipitation. The formation of Fe oxyhydroxides does affect the mobility of some other metals such as Mn, Ni, As and Mo through sorption or co-precipitation (Packter at al., 1985; Wei et al., 2005).

$$Fe^{3+} + 2OH^{-} \rightarrow FeOOH + H^{+} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{Equation 4. 4}$$

Aluminum removal was observed to be nearly 100%. As the FA were exposed to AMD a decrease in the concentration of aluminum was detected and is explained by the increase of pH and the precipitation out of the solution of aluminum oxide as was observed in this study. Moreover, the formation of the amorphous phase can be noted as responsible for aluminum concentration decrease in the process water recovered .The precipitation equation of aluminum is presented in the equation 4.5.

$$Al^{3+} + 3OH^{-} \rightarrow Al\,(OH) \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.\ldots \text{Equation 4. 5}$$

4.5 CALCIUM AND SULPHATE CONCENTRAION VARIATION DURING TREATMENT OF EYETHU AMD WITH BOTH KENDAL AND LETHABO CFA

This section displays the results of the variation of Ca and sulphate concentration obtained from ICP-OES of the recovered water for both Kendal and Lethabo CFA at different time as explained in Chapter 3, Section 3.5.2. Figure 4.10 and Figure 4.11 present Ca concentration and pH variation over time of the recovered water from Kendal and Lethabo columns.

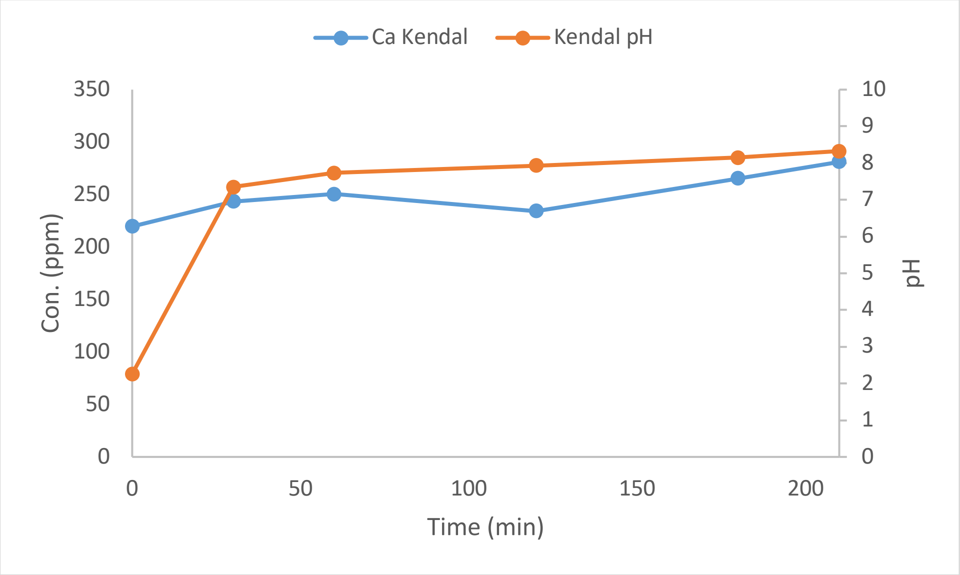

Figure 4. 10: Ca concentration variation over time and pH during treatment of Eyethu AMD with Kendal CFA

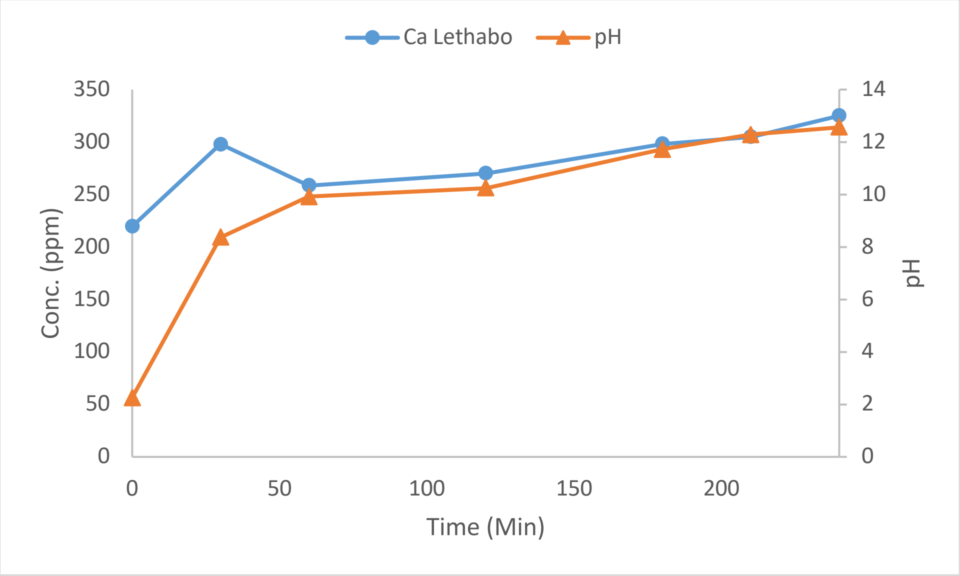

Figure 4. 11: Ca variation during neutralisation process of Eyethu AMD with Lethabo CFA

From Figure 4.10; it can be seen that Ca concentration showed an increase during treatment of Eyethu AMD with both Kendal and Lethabo CFA until the pH reaches its maximum point during this process, this was explained by the fact that Ca has been released from fly ash through the solubility of its corresponding salt that was on the surface of CFA. The free lime dissolve once FA was in contact with AMD this causing an increase in Ca concentration. Of all the metals that leached out in the solution only Ca^{2+} had its concentration, increasing in the solution and this is explained by the dissolution of calcium oxide which causes the decrease of sulphate concentration, according to Equation 4.9 below:

$Ca^{2+} + SO_4^{2-} + H_2O \rightarrow CaSO_4.2H_2O$.....................Equation 4. 6

Sulphate concentration variations are presented in Figure 4.12 and Figure 4.13 for both recovered water from Kendal and Lethabo CFA columns.

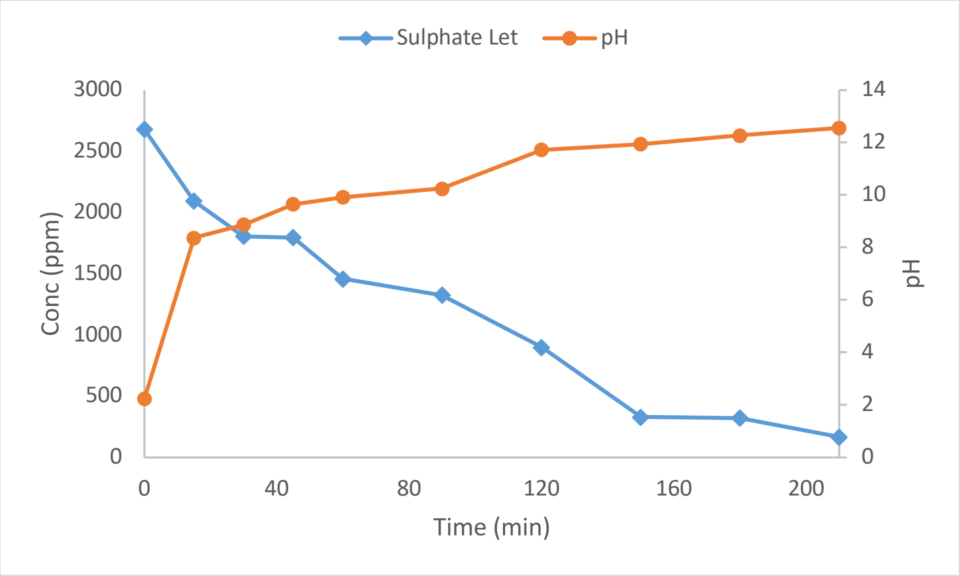

Figure 4. 12: Variation of sulphate concentration during treatment of Eyethu AMD with Lethabo CFA

The sulphate concentrations of leachates or recovered water from Lethabo columns showed a decrease to a value in the range given by DWAF for irrigation and potable water Table 4.9.

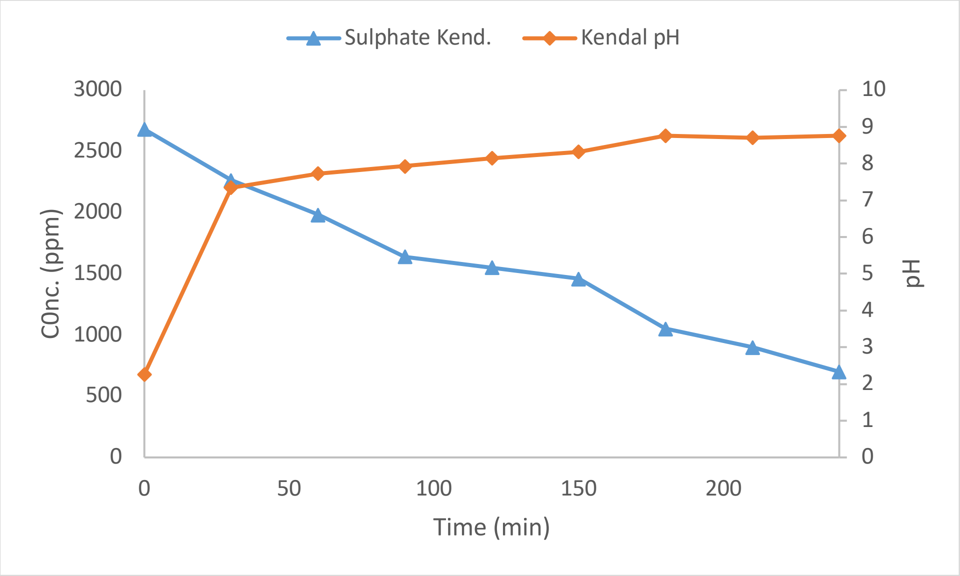

Figure 4. 13: Variation of sulphate concentration during treatment of Eyethu AMD with Kendal CFA

From Figure 4.12 and Figure 4.13 it was seen that sulphate concentration was decreasing with time. The reduction or removal of sulphate from the solution during treatment process is pH dependent (Gitari et al., 2006). Sulphate removal is inversely proportional to the change in pH. Sulphate concentration decreases with an increase of pH over time, which indicates that sulphate concentration decrease was caused the formation and precipitation of a secondary mineral phase. Among these mineral phase there is gypsum which is being formed through the dissolution of CaO from coal fly ash in the presence of the acidic mine drainage as shown in the XRD result of solid residue Figure 4.14. Moreover, the formation of barite ($BaSO_4$) and celestite ($SrSO_4$) caused by the dissolution of Ba and Sr salts from fly ash and their consequent interactions with SO_4 is well known as the cause of a decrease in SO_4 concentration. The increase in pH caused Fe^{3+} to precipitate and formed amorphous ferric hydroxides and oxyhydroxides which have a large surface area that results in adsorption of $S0_4$ (Kumar et al., 2008). The oxidation of iron 2 in the presence of oxygen and which is maximized at pH 5 to 7 with the hydrolysis of the resulting Fe^{3+} cause the formation of amorphous ferric hydroxides, which adsorb more of the sulphate as well (Rose & Elliot, 2000). The formation of the amorphous $Al(OH)_3$ and incorporation of SO_4^{2-} as well as the formation of ettringite mineral phase contributed to the decrease of the SO_4. The leachates from column made of Eyethu AMD with Lethabo CFA shows a high sulphate removal compared to that from Eyethu AMD with Kendal CFA and it is explained by high concentration of CaO in Lethabo CFA than in Kendal CFA.

4.6 CHARACTERISATION OF SOLID RESIDUE PRODUCED AFTER TREATMENT PROCESS

This section gives the XRD and XRF results of the samples of solid residues produced at the end of the experiment from both Kendal and Lethabo column as pointed out in Chapter 3, Section 3.6.3 and Section 3.6.4. At the end of the experiment sample of solid residue was collected from top and bottom of the column and sent for XRD analysis to investigate if there was formation of new mineral phases that were responsible of Sulphate concentration reduction. The trend at the bottom represents fresh CFA, the middle was for the sample collected at the bottom and the one above was for sample collected on top of the column.

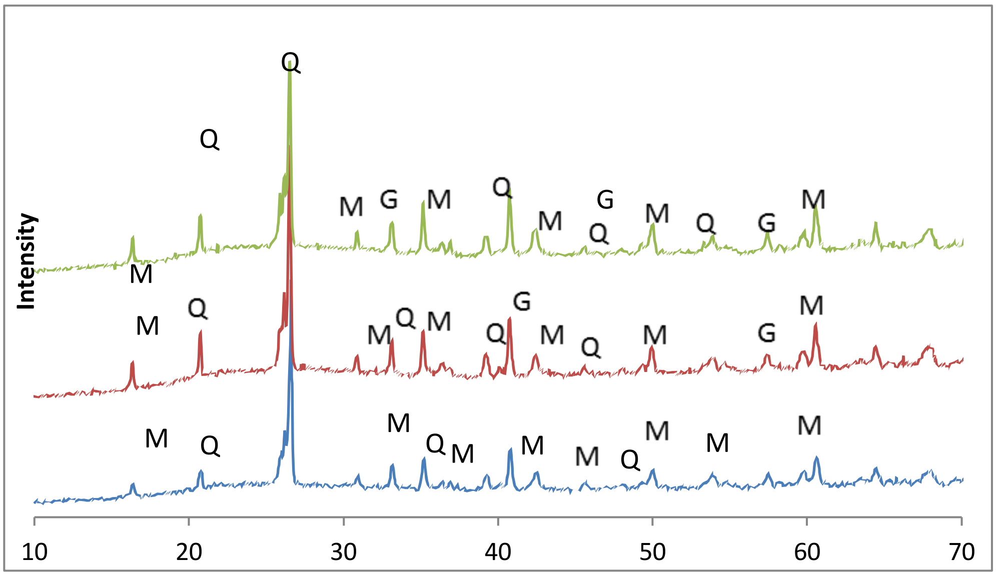

Figure 4. 14: XRD results of solid residue from Lethabo column

From the results shown in the figure 4.11 for solid residue from Lethabo column and figure 4.12 solid residues from Kendal column, it was observed that there were some formation of gypsum phases in the solid residue from both CFAs this confirming the decrease in concentration of sulphate in the treated water. The XRD results of the sample collected from the top and the bottom of the column did not present any difference.

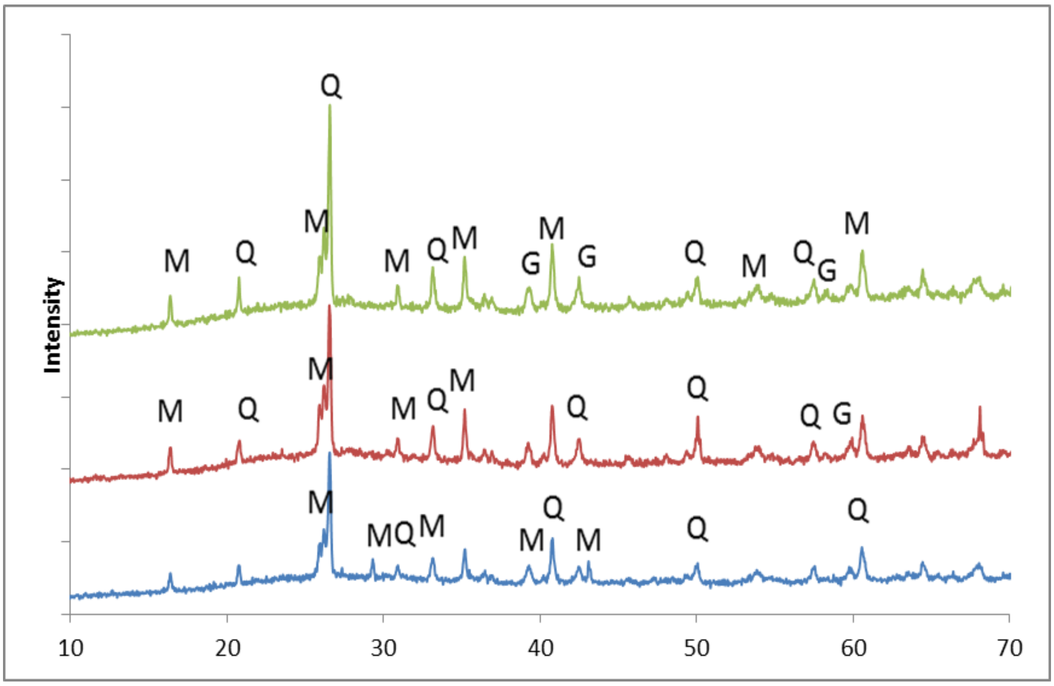

Figure 4. 15: XRD results of solid residue from Kendal column (n=3) G= Gypsum, M=mulite, Q= Quartz

From the XRD of the solid residue collected from Kendal column, it was observed that there was some appearance of gypsum peaks as new mineral phase formed.

The XRF results of the solid residue produced after treatment are presented in Table 4.6 for Kendal columns and Table 4.7 for Lethabo column. Three Solid residue samples were collected from the top and bottom of each column for analysis. The results given in the table are the average value and are given on dry basis.

Table 4. 6: XRF results of solid residue from Kendal columns (n=3)

Species	Major elements % W/W		
	Kendal CFA	SR Kend Top	SR Kend Btm
SiO_2	52.78 ± 0.21	**53.78 ± 0.21**	**52.76 ± 0.22**
Al_2O_3	29.17 ± 0.28	28.54 ± 0.28	29.56 ± 0.23
CaO	4.61 ± 0.09	**3.11 ± 0.09**	**4.42 ± 0.184**
Fe_2O_3	3.47 ± 0.03	5.28 ± 0.03	4.328 ± 0.07
TiO_2	1.59 ± 0.027	1.74 ± 0.027	1.66 ± 0.023
MgO	1.04 ± 0.182	2.05 ± 0.182	1.95 ± 0.182
BaO	0.12 ± 0.99	ND	ND
K_2O	0.77 ± 0.01	0.77 ± 0.01	0.73 ± 0.01
Na_2O	0.27 ± 0.006	0.19 ± 0.006	0.163 ± 0.006
MnO	0.3 ± 0.02	0.42 ± 0.02	0.38 ± 0.02
SO_3	0.19 ± 0.24	**0.697 ± 0.02**	**0.713 ± 0.08**
Cr_2O_3	0.03 ± 0.07	0.01 ± 0.008	0.009 ± 0.008
V_2O_5	0.02 ± 0.41	0.01 ± 0.41	0.02 ± 0.41
LOI	0.69 ± 0.53	4 ± 0.53	3.981 ± 0.53
Total	99.875	99.36	99,512

From XRF results, it was observed that the concentration of SO_3 increased in the solid residue compared to the initial value found in raw Kendal CFA. Furthermore the solid residue samples were collected from top and bottom of the column, the concentration of SO_3 in the top residues was high compared to the one from bottom, this was to explain that the bottom part of the column was more reactive than the bottom one, as the AMD was flowing from top to the bottom of the column. Moreover, CaO concentration decreased in solid residue this proving the dissolution of CaO during treatment. The XRF results of solid residue collected from Lethabo column is presented in Table 4.7 below.

Table 4. 7: XRF results of solid residue collected from Lethabo column (n=3)

Species	Major elements % W/W		
	Lethabo CFA	SR Lethabo Top	SR Lethabo Btm
SiO_2	52.78 ± 0.22	**58.47 ± 0.21**	57.173 ± 0.22
Al_2O_3	29.24 ± 0.23	28.39 ± 0.28	29.065 ± 0.23
CaO	**5.85 ± 0.184**	2.35 ± 0.09	3.22 ± 0.184
Fe_2O_3	4.11 ± 0.074	4.38 ± 0.03	3.48 ± 0.074
TiO_2	1.63 ± 0.023	1.70 ± 0.027	1.625 ± 0.023
MgO	1.55 ± 0.182	0.87 ± 0.182	0.957 ± 0.182
BaO	0.16 ± 0.99	ND	ND
K_2O	0.8 ± 0.01	0.78 ± 0.01	0.765 ± 0.01
Na_2O	0.54 ± 0.006	0.35 ± 0.006	0.172 ± 0.006
MnO	0.25 ± 0.02	0.029 ± 0.02	0.068 ± 0.02
SO_3	0.24 ± 0.01	**1.965 ± 0.074**	**1.865 ± 0.01**
Cr_2O_3	0.03 ± 0.008	0.015 ± 0.008	0.0098 ± 0.008
V_2O_5	0.02 ± 0.41	0.019 ± 0.41	0.0196 ± 0.41
LOI	3.24 ± 0.53	2.084 ± 0.53	1.8908 ± 0.53
Total	99.875	99.50	98.812

The XRF results given in Table 4.7 shows that the concentration of some oxides such as SiO_2, Al_2O_3, Fe_2O_3 had increases in the residue collected at the top of the column compared to the one in fresh Kendal fly ash, this is to prove that Si, Al and Fe have been removed from the AMD during treatment with both Lethabo and Kendal CFA to confirm the ICP-OES results given in Table 4.5. CaO concentration decreased, this demonstrates that it was dissolved during treatment process and it was observed in the treated water from both columns Lethabo and Kendal. BaO completely leached out of CFA as it was not observed in either of the solid residue sample. Same phenomenon was observed in the solid residue from Lethabo columns even though these samples were collected at the end of the experiment at the time when CFA was exhausted and could not handle AMD anymore. Furthermore, SO_3 concentration increased in the solid residue produced from Lethabo columns as well this proving the formation of gypsum.

4.7 COMPARAISON STUDY

The treatment of Eyethu AMD with both Kendal and Lethabo CFA shows that all these two CFAs have proven that they have the potential of neutralizing the AMD but with only few differences between them to highlight. During treatment with Lethabo CFA pH of the effluent water was raised to above 12 while with Kendal CFA the pH could not exceed 9 this making it difficult for some metals such as Mn, Mg and Na to be completely removed from mine water as this pH is below the pH of their minimum oxidation. The high concentration of CaO in Lethabo CFA compared to the one in Kendal CFA (Figure 4.2) is one of the reason to highlight for Ph difference in the leachates from these two columns. Table 4.8 and Table 4.9 given below showed the concentration of some metals in Eyethu AMD before and after treatment with Kendal and Lethabo CFA and the concentration range given by DWAF for irrigation and potable water.

Table 4. 8: Metals concentrations from Kendal column comparison with DWAF guidelines (n=3)

Metals	Initial conc mg/L	pH	Final conc mg/L	pH	DWAF
Fe	100.3	2.23	0.083	8.53	0-0.1)
Mn	32.84	2.23	10.23	8.76	(0-0.05)
Mg	112.3	2.23	30.02	8.75	(0-30)
Na	34.62	2.23	13.854	8.76	(0-100)
Al	120	2.23	0.018	7.93	(<0.005)
Ni	1.65	2.23	0.229	8.37	NA
Cu	0.05	2.23	0.0306	8.67	(0-1)
Zn	6.7	2.23	0.002	8.37	(0-3)
SO4	2680	2.23	700	8.76	(0-200)

From the Table 4.8 it could be seen that during treatment of Eyethu AMD with Kendal CFA some metals like Fe, Na, Cu and Zn had their concentration reduced to the accepted range value given by DWAF while on the other Mn, Mg, Al and Ni their final concentration could not meet the range given by DWAF for irrigation and portable water. This was explained by the fact that the highest pH of the recovered water could not meet the pH of minimum solubility of their respective oxide (Briton, 1956).

Table 4. 9: Metals concentrations from Lethabo column comparison with DWAF guidelines (n=3)

Metals	Initial conc mg/L	pH	Final conc mg/L	pH	DWAF
Fe	100.3	2.23	0.019	8.2	0-0.1)
Mn	32.84	2.23	0.008	9.12	(0-0.05)
Mg	112.3	2.23	9.584	12.41	(0-30)
Ca	219.6	2.23	1.581	12.34	(0-32)
Na	34.62	2.23	3.004	10.25	(0-100)
Al	120	2.23	0.014	6.2	(<0.005)
Ni	1.65	2.23	0.374	8.37	NA
Cu	0.05	2.23	ND	10.25	(0-1)
Zn	6.7	2.23	0.003	8.37	(0-3)
SO4	2680	2.23	328	12.56	(0-200)

For the case of Eyethu AMD with Lethabo CFA, highest Ph value obtained during treatment, which is 12.56, was the cause of the removal of most of heavy metals present in Eyethu AMD. Metals such as Fe, Mn, Mg, Ca, Al, Ni Cu and Zin had their concentration reduced to DWAF range for irrigation and potable water. Copper hydroxides precipitation from sulphate rich solutions typically results in the formation of bronchantite (Cu_4SO_4 (OH) $_6$) as shown in Equation 4.7 below and tenorite (CuO) Equation 4.8, as other phases like posnjakite [Cu_4SO_4 (OH) 6·H_2O] and spertiniite (Cu (OH)$_2$) are precursors to these more thermodynamically preferred minerals. This formation is caused by the precipitation of copper hydroxides in a sulphate rich solution such as AMD, hence the decrease of copper in the leachates (Pollard et al., 1992).

$Cu^{2+} + SO_4^{2-} + 6OH^- \rightarrow Cu\,(SO_4)(OH)_6$ ………………………………………………….Equation 4. 7

$CuSO_4 + 2OH \leftrightarrow CuO + SO_4^{2-} + H_2O$ ……………………………………………………...Equation 4. 8

Boron and Mo leached from the fly ash during this treatment. This leaching depended on the amount of CFA in the mixture. The observation was made where boron happens mostly as a surface oxide precipitate or is incorporated in the glassy matrix of FA (Hullet et al., 1880). the rate at which surface precipitates and glassy phases dissolve and also the adsorption on the precipitates that form as a result of the AMD: FA neutralization reaction control Boron concentration. Boron concentration decreased in the solution as a result of the adsorption of calcite. Some researchers have proven that boron concentration can decrease in alkaline leachates that are actively precipitating $CaCO_3$ similar to this study (Gitari et al., 2008).

Mn concentration decrease with an increase in pH, a substantial amount of Mn was removed in this experiment. Kuyucak (2006) states that the removal of manganese from AMD always requires a highly alkaline condition to produce manganese precipitates and this was the case while treating AMD with Kendal fly ash. The amount of zinc tented to decrease as the pH was rising and it was explained by the fact that zinc forms $ZnSO_4$ in sulphate rich environments. In addition, this $ZnSO_4$ was converted to hydrozincite at higher pH 6.66 (Park et al., 2013). The concentration of Nickel decreased as nickel ion precipitates to form nickel sulphate and this was observed during this treatment according to the equation below and this was thought to occur through Equation 4.9.

$Ni^{2+} + SO_4^{2-} \rightarrow NiSO_4$ …………………………………………………….....Equation 4. 9

Lethabo CFA effluent has a lower sulphate concentration to within the DWAF range while Kendal CFA effluent on the other hand has a high sulphate concentration above the DWAF range. This proves that for the case of this study Lethabo CFA has a higher neutralizing capacity of Eyethu AMD compared to Kendal CFA even though both are from Class F FA. For this study two parameters time and pH were monitored during the treatment process of Eyethu AMD with both Kendal and Lethabo CFA. Both CFAs had the ability to produce an alkaline solution within the first hour of contact of acid mine water with CFA.

Furthermore, recovered water from Lethabo columns had a pH greater than 12 which allowed many metals to be completely removed from treated water and some having their concentrations being reduced to within the range given by DWAF for irrigation and potable water Table 4.8 and this was not the case with recovered water from Kendal column.

4.8 ENGINEERING PARAMETERS

The engineering parameters section will present the results of some parameters such as flow rate of the effluent or treated water, the percent removal of metals as well as the rate at which the metals are removed from Eyethu AMD as highlighted in Chapter 3, Section 3.7.

4.8.1 Flow rate

Volumetric flow rate is the quantity of a fluid that passes through a given cross sectional area per unit time per unit time. The volumetric flow rate of the leachate was determined using Equation 10.

$$Volumetric\ flow\ rate = \frac{volumes\ of\ leachates\ (L)}{Times\ (s)} \ldots\ldots\ldots\text{..Equation 4. 10}$$

Results of the volumetric flow rate over time of the leachates from Kendal and Lethabo columns are presented in Figure below.

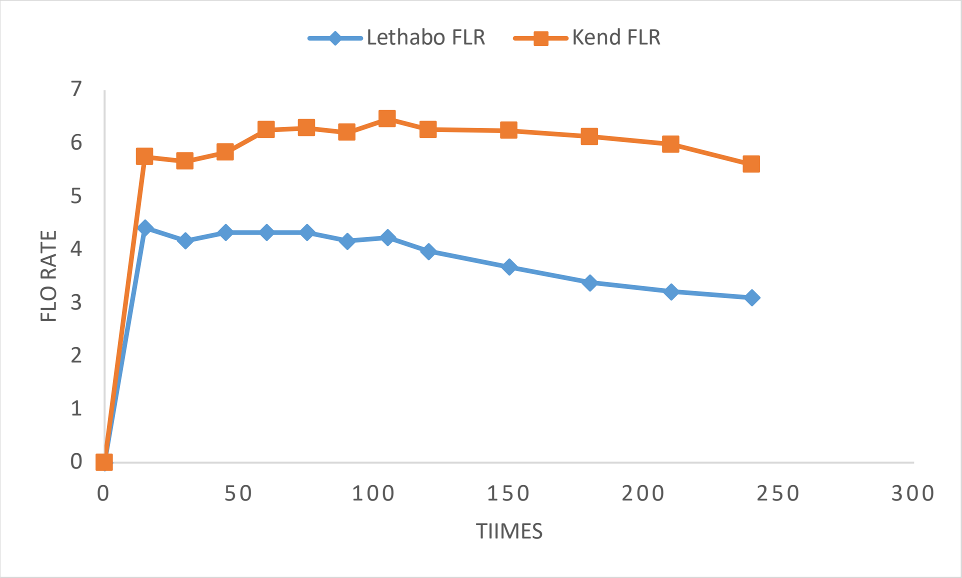

Figure 4. 16: Variation of flow rate over time of the leachate from Kendal and Lethabo CFA columns

From the trend Figure 4.16 it can be seen that, leachates from the columns of Kendal CFA with Eyethu AMD has a high flow rate than those from Lethabo CFA columns. The volumetric flow rate was observed to decrease with time and this explained by the formation of secondary minerals that was obstructing the AMD to run through easily. The volumetric flow rate from leachates of Lethabo columns was increasing with time until after 100 minutes, the flow rate suddenly starts decreasing as shown in the figure 4.13. This was observed in the leachates from Lethabo columns as well. Furthermore, final volumetric flow rate of leachates from Kendal column was so high comparing to the one from Lethabo columns and this was explained by the particle size of these CFAs.

4.8.2 Percentage removal

Percentage removal which is defined as the percent of the amount of metals that is being removed from the solution during the treatment. It will be clearly demonstrated in this section. It is calculated based on the composition and concentration of Eyethu AMD before treatment and during the treatment at specific time by using the Equation 11.

$$\% \text{ removal} = \left(\frac{\text{conc of ionic species in raw sol.} - \text{conc.of ionic species at a given time}}{\text{conc.of ionic species in raw sol.}}\right) * 10 \ldots\ldots\text{Equation 4. 11}$$

Figure 4.14 and 4.15 presents trends of % removal of heavy metals form Eyethu AMS during the neutralization process using Lethabo and Kendal CFA respectively.

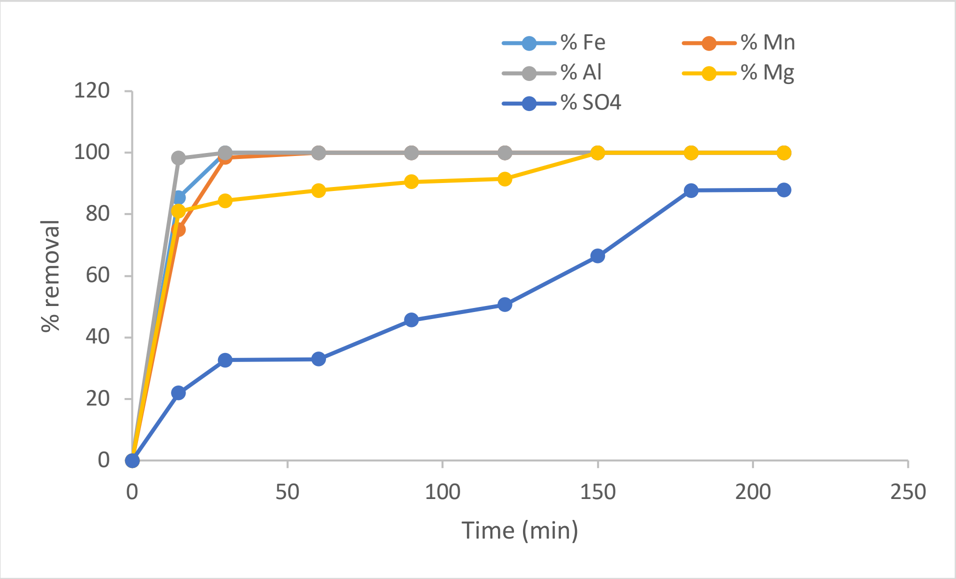

Figure 4. 17: Percentage removal of some metals from Lethabo leachate

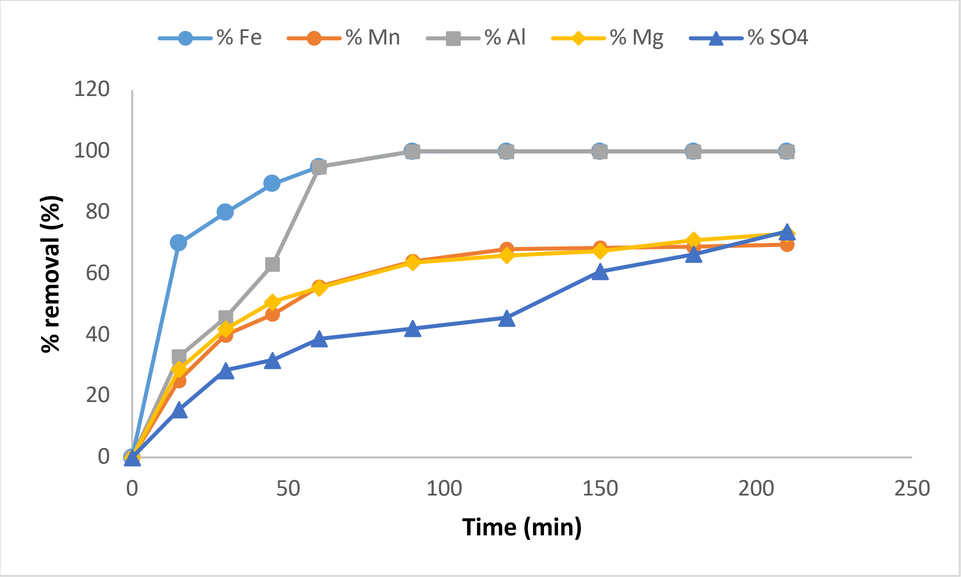

Figure 4. 18: Percentage removal of some metals from Kendal leachate

From the percentage removal it was seen that, in the effluent from Lethabo column Fe, Al, Mn and Mg were presenting high percentage removal 100% and for some close to 100% as explained in the section 4.3.1.2.1. However, heavy metals from effluent from Kendal column did not reach 100% removal for the reasons elaborated in the section 4.3.1.2.2. Moreover, sulphate concentration in both effluents did not get 100% removal.

4.8.3 Rate of removal

The rate of removal is the degree at which an element or its concentration is removed per unit time. On this study, the rate of removal of some selected elements was calculated using Equation 4.12 below. Additionally, rate o removal was calculated by considering the concentration of some metals at a specific time during the treatment.

$$Rate\ of\ removal = \frac{concentration\ of\ elements\ (mol/L)}{Time\ (s)} \ldots\ldots\ldots\ldots\ldots\ldots\text{Equation 4. 12}$$

Figures 4.19 presents rate of removal of Fe, Mg, Mn and Al at different time during treatment of Eyethu AMD with Lethabo CFA. Data was taken on triplicate.

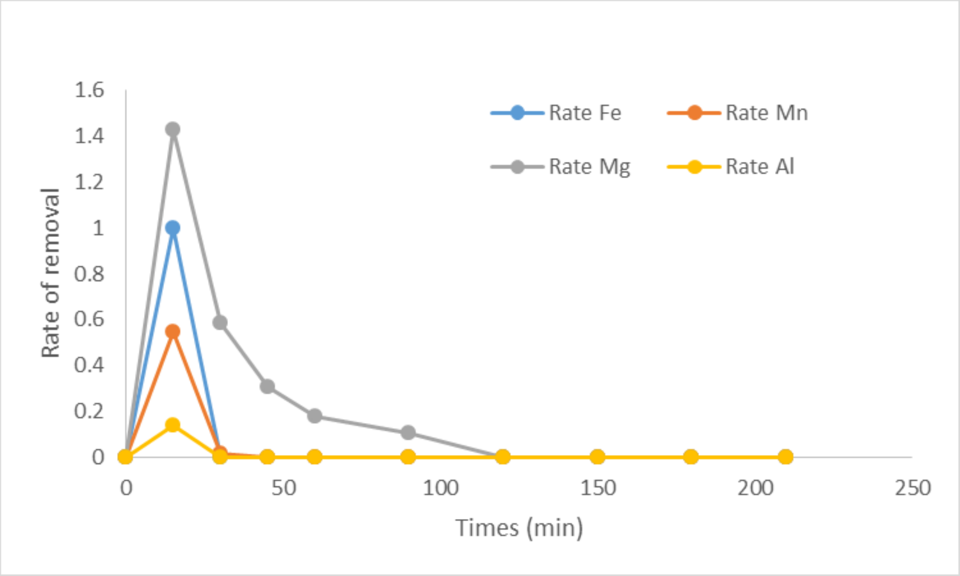

Figure 4. 19: rate of removal of some metals during treatment of Eyethu AMD with Lethabo CFA (n=3)

From the rate of removal trend, it was seen that Fe, Mn, Mg and Al their percentage of removal was decreasing with reaction time as within the first 15 minutes it has a high value and started to decrease with time this is explained by the increase of pH. After 30 minutes, it was observed that Al, Fe and Mn were completely removed from the AMD.

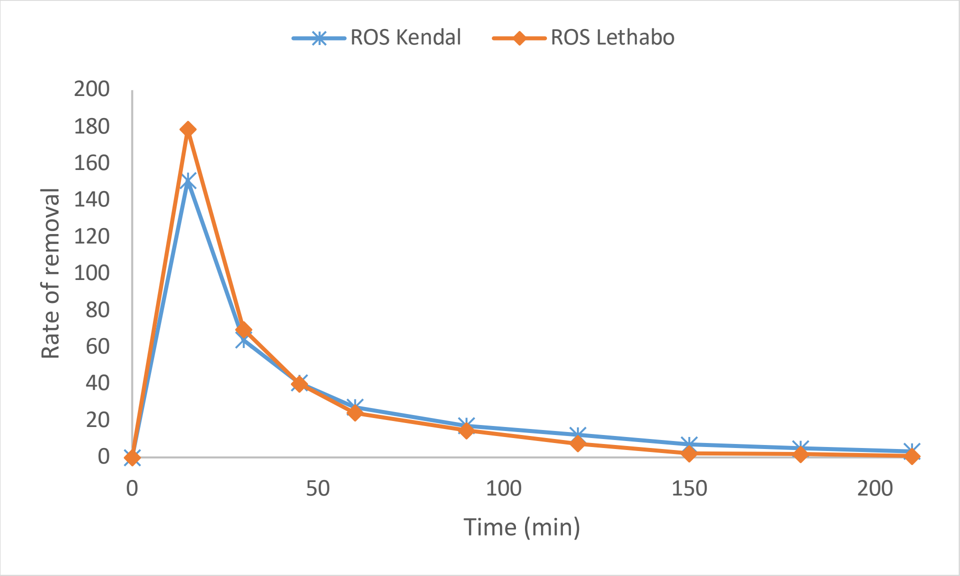

Figure 4. 20: Rate of removal of sulphate in leachate from Kendal and Lethabo columns

The rate at which sulphate was removed from the solution was decreasing with time. This is due to the formation of gypsum and the sulphate concentrations were decreased from the solution and being accumulated in the gypsum.

4.9 MASS BALANCE

This section presents the mass balance calculations around Kendal and Lethabo columns as highlighted in Chapter 3, Section 3.5.9. In this section, the % of water recovery and the moisture content of the solid residue will be determined.

4.9.1 Mass balance around Lethabo columns

The mass balance calculations were conducted following the general equation and assumptions below:

$$Accumulation = input - output + generation - consumption \ldots \ldots \text{Equation 4. 13}$$

Assumptions:

- The balanced quantity is total, generation = 0 and consumption = 0; input = output
- The bulk density (ρ)of AMD is used in the calculation.
- The system is at steady state, accumulation = 0.

The bulk density of AMD was used in this study,

$$\rho_{\text{AMD}} = \frac{\boldsymbol{Kg}}{\boldsymbol{m^3}} \ldots\ldots\ldots\ldots\text{Equation 4. 14}$$

$$\text{V}_{\text{AMD}} = 275\ \text{L} = 0.275\ \text{m}^3$$

$$\rho = \frac{m}{\text{v}} \rightarrow \text{m}_{AMD} = \rho \times \text{v} = 945 \times 0.275 = 259.88\ \text{kg}$$

The mass balance will be measured in the form of mass flow rates rather than molar flow rates due to the fact that mass can be practically measured compared to moles. By doing so, it is convenient to express concentrations in terms of mass fractions which are determined correspondingly to mole fractions:

$$Xa = \frac{m_a}{m_T} \ldots\ldots\ldots\ldots\ldots\text{Equation 4. 15}$$

From the equation above:

X_a: the mass fraction of component A

m_a: the mass of component A (kg)

m_t: represent the total mass of all components that enters the system from the same stream.

The mass fraction of all components entering the system was calculated as follows:

The mass of coal fly and AMD that were used to make the slurry were 1.44 Kg and 4.064 Kg respectively, with a total mass of 5.50 Kg, and the total overall mass of the AMD that was used during the time of the experiment was 543.4 Kg (bed volume times time). The fraction of each components for each stream is calculated as follows:

$$X_{\mathrm{CFA}} = \frac{m_{\mathrm{CFA}}}{m_t} = \frac{1.44}{5.50} = 0.26$$

$$X_{\mathrm{AMDs}} = \frac{m_{\mathrm{AMDs}}}{m_t} = \frac{4.064}{5.50} = 0.74$$

$$X_{\mathrm{AMD}} = \frac{m_{\mathrm{AMD}}}{m_t} = \frac{259.88}{259.88} = 1$$

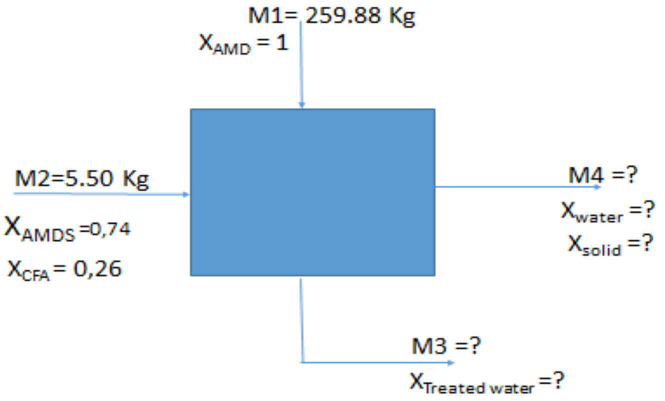

Figure 4. 21: Mass balance block flow diagram around the Kendal column.

M_1: the mass of AMD fed to the process (kg)
M_2: the total mass of CFA and AMD made the slurry the filter cake (Kg)
M_3: the mass of water recovered from the process (kg)
M_4: the mass of slurry recovered from the process (kg)
X: the mass fraction of a component

From Figure 4.21, it can be seen that the unknowns are M_3, M_4, $X_{\mathrm{Water\ recovery}}$, and components for the residue (X_{solid}, and X_{water}). The experiment was carried out within 21 days and at the end of the experiment the volume and mass of water recovered was determined experimentally and amounted to 249 L (236.23 Kg). The percentage of water recovery was calculated as follows:

$$\%\ \text{of water recovery} = \left[\left(\frac{\mathrm{M}_{\text{water recovery}}}{\mathrm{M}_{\mathrm{AMD}}}\right) \times 100\right] = \left[\left(\frac{236.23}{259.88}\right) \times 100\right] = 90.9\% \ldots\ldots \text{Equation 4. 16}$$

Besides treatment of AMD, water recovery was among the objectives pursued in this study. Recovering a considerable amount of water at the end of the process was the target, 249 L of AMD was used in this process for treatment, at the end of the experiment, and 249 L was recovered representing 90.9 % of the AMD that was fed to the process. The assumptions made from the general material balance equation were that inputs equals to outputs. This should be applied to all the components involved in the AMD treatment process. According to the law of conservation of mass which states that mass can neither be created nor destroyed (Felder, 1986). The 9.1 % of the remaining water was retained in the slurry and can be determined to finally have 236.5 Kg of water exiting the process.

The slurry is made of moist solid materials that separated from clear water after settling and decanting of water. In addition to solids, sludge contains a high percentage of water. At the end of the experiment 29.15 kg of thick slurry was recovered, the amount of water and solid in the slurry was determined, using the method of moisture content set out in Chapter 3, Section 3.5.9.

4.9.1.1 Moisture content determination

Table below gives the weights of dry and wet samples from Lethabo columns. Samples were collected following the method detailed in Chapter 3, Section 3.5.9.

Table 4. 10: Moisture content determination sample

Type of samples	Mass (g)		
	Sample 1	Sample 2	Sample 3
Wet weight samples	21	20	20.4
Dry weight samples	4	3.5	4

The moisture content of the sample was calculated using the following Equation 4.17:

$$\%W = \left(\frac{A-B}{A}\right) \times 100 \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots.. \text{Equation 4. 17}$$

Where,

%W: Percentage by mass of moisture in the sample,

A : Weight of wet sample in grams

B : Weight of dry sample in grams as well

The moisture content of the slurry was determined as follows:

Sample 1

$$\%W = \left(\frac{A-B}{A}\right) \times 100 = \frac{21-3}{21} \times 100 = 85.7\ \%$$

Sample 2

$$\%W = \left(\frac{A-B}{A}\right) \times 100 = \frac{20-3.5}{20} \times 100 = 82.5\ \%$$

Samples 3

$$\%W = \left(\frac{A-B}{A}\right) \times 100 = \frac{20.4-3}{20.4} \times 100 = 85.3\ \%$$

$$\text{Average \% moiture content} = \frac{85.7+82.5+85.3}{3} = 84.5\ \%$$

The moisture content in the slurry was found to be 84.5% from the column made of Eyethu AMD with Kendal CFA recovered at the end of the experiment. The amount of water in the slurry was calculated as follows: Average moisture content multiplied by the mass of slurry as shown in Equation 4.18:

$$\text{Amount of water in slurry} = \text{average moisture content of slurry} \times \text{mass of slurry} \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \ldots \text{Equation 4. 18}$$

$$\text{Amount of water in slurry} = 0.845 \times 29.15 = 24.6\ \text{kg}$$

After treatment process, water recovered in the slurry was found to be 24.6 kg representing 8.9% of water that was retained in the columns; which means a significant amount of water could still be recovered if the process could be improved by adding a dewatering unit operation to the system so that a dry solid can be back filled or reused for other purposes, and the water can be recycled into the process overall 90.9 % or an equivalent of 236.23 kg of water was recovered as main product; the remaining 9.1 % of water is equivalent to 23.65 kg of water that was retained in the slurry. From the results obtained, it could be said that most of the water was recovered.

The slurry is a combination of water and solid material. In this study, the amount of settled solids and water in the slurry recovered were found to be 15.27 kg and 24.6 kg, respectively. The following material balance equation was used to determine the amount of dry solids in the slurry:

$$\text{Mass of slurry} = \text{mass of water in the slurry} + \text{mass of solid in the slurry} \ldots \ldots \text{Equation 4. 19}$$

$$29.15 = 24.6 + \text{mass of solid in the sludge}$$

Mass of solids in the slurry = 4.55 Kg

The amount of solids fed in form of slurry to the AMD treatment process was 5.50 kg (CFA with AMD) and 4.55 kg of solid was recovered.

The following Figure 4.22 is the overall material balance block flow diagram of the column where all the flow rates of all the streams entering and leaving the column are determined

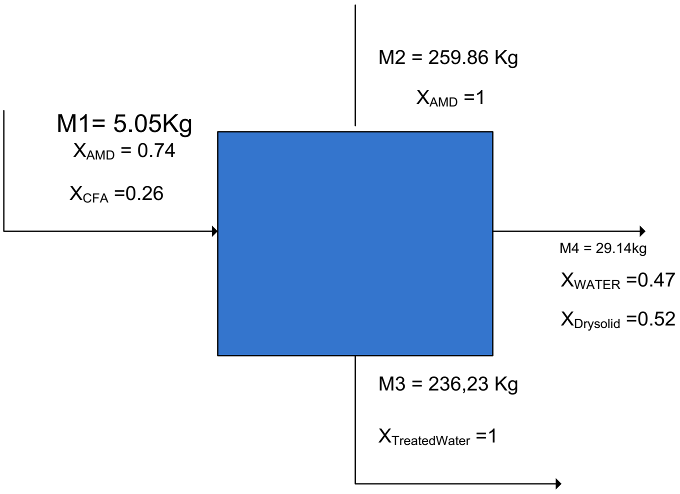

Figure 4. 22: Block flow diagram of the overall mass balance

The amount of materials fed into the AMD treatment process was found to be almost equal to that produced in terms of masses of solids and liquids. The water produced from Kendal column could not meet the standard for irrigation according to DWAF as shown in Table 4.9.

4.9.2 Mass balance around Kendal coulumns

$$\mathrm{V_{AMD}} = 300\ \mathrm{L} = 0.3\ \mathrm{m^3}$$

$$\rho = \frac{m}{\mathrm{v}} \rightarrow \mathrm{m}_{AMD} = \rho \times \mathrm{v} = 945 \times 0.3 = 283.5\ \mathrm{kg}$$

The mass of coal fly ash and AMD that makes the slurry were 1.28 Kg and 3.123 Kg respectively, forming their total mass of 4.501 Kg, and the total mass of the AMD that was used during the experiment was 283.5 Kg this is the bed volumes times time. The mass fraction of each component in streams is presented below:

$$\mathrm{X_{CFA}} = \frac{1.28}{4.501} = 0.28$$

$$\mathrm{X_{AMDs}} = \frac{3.123}{4.501} = 0.72$$

$$\mathrm{X_{AMD}} = \frac{\mathrm{m_{AMD}}}{\mathrm{m_t}} = \frac{283.5}{283.5} = 1$$

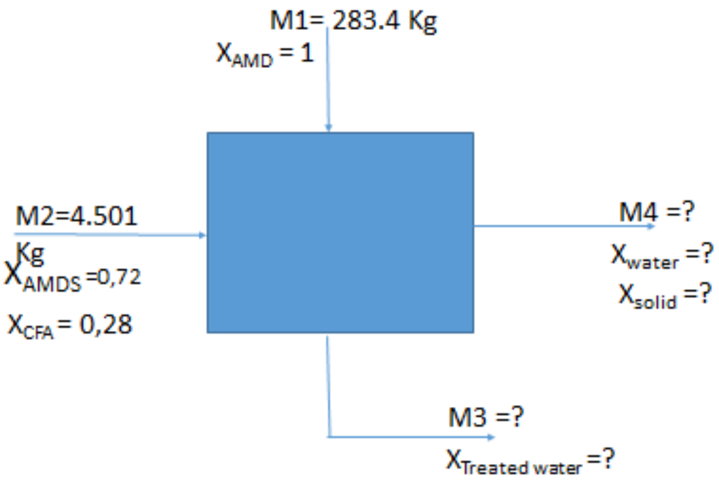

Figure 4. 23: Kendal column mass balance Block flow diagram

From the block flow diagram, it can be seen that the unknowns are M_3, M_4, $X_{\text{Water recovery}}$, and components for the residue (X_{solid}, and X_{water}). The experiment was performed as in the same way as in Section 4.9.1. The experiment the volume and mass of water recovered was determined experimentally at the end and amounted to 275 L (259.9 Kg). The percentage of water recovery was calculated as follows:

$$\text{\% of water recovery} = \left[\left(\frac{\mathrm{M_{water\ recovery}}}{\mathrm{M_{AMD}}}\right) \times 100\right] = \left[\left(\frac{250}{300}\right) \times 100\right] = 83.33\ \%$$

The water recovered experimentally from Lethabo column was 250 L out of 300 L that was fed into the process that represents 83.33% of the water. Thus 16.67% of the remaining water was retained in the slurry. The mass of slurry at the end of the experiment was found to be 28.09 kg. The mass of water and dry solid that made up the slurry was calculated through determining the moisture content.

4.9.2.1 Moisture content determination

Three slurry solid residue samples have been collected as described in Chapter 3, Section 3.5.9. The samples were weighted, dried and cooled. The cooled samples were weighed again, and their masses recorded as dry weight of sample as shown in Table 4.7 below.

Table 4. 11: Moisture content calculation for Kendal column

Type of samples	Mass (g)		
	Sample 1	Sample 2	Sample 3
Wet weight samples	30	35	27
Dry weight samples	6	5.4	4.2

The moisture content of the solid residue sample was calculated using the Equations as shown above:

$$\%\mathrm{W} = \left(\frac{\mathrm{A} - \mathrm{B}}{A}\right) \times 100$$

Sample 1

$$\%\mathrm{W} = \frac{30 - 6}{30} \times 100 = 80\ \%$$

Sample 2

$$\%\mathrm{W} = \frac{35 - 5.4}{35} \times 100 = 84.6\ \%$$

Samples 3

$$\%\mathrm{W} = \frac{27 - 4.2}{27} \times 100 = 84.4\ \%$$

$$\text{Average \% moiture content} = \frac{80 + 84.6 + 84.4}{3} = 83\ \%$$

80.67 % was found to be the average moisture content in the slurry from the column made of Eyethu AMD with Kendal CFA recovered at the end of the experiment.

$$\text{Amount of water in slurry} = 0.83 \times 28.09 = 23.31\ \text{kg}$$

With the amount of water in the slurry being known, the mass of dry solid in the slurry was determined following Equation 4.18, and the dry mass was 4.52 kg.

The mass fraction of water and dry solid in the slurry was determined following Equation 4.19 and was found to be 0.17 and 0.83 respectively.

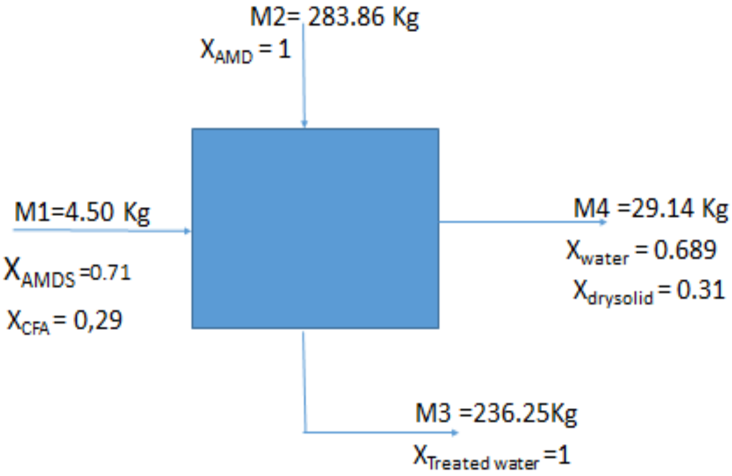

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Figure 4. 24: Overall block flow diagram around Kendal column

From the mass balance calculation, it was shown that Kendal and Lethabo CFA can treat Eyethu AMD and recover most of the water at the end of the process and they both produced water that met the standard for irrigation according to DWAF guideline (Table 4.9). Treatment with Lethabo CFA shows a high recovery percentage of water 90.1% compared to treatment with Kendal CFA 83.33% and this was explained by the difference in particle size and CaO content of these two fly ashes.

CHAPTER FIVE

5 CONCLUSION AND RECOMMENDATION

This study was conducted in order to determine the neutralisation capacity of Kendal and Lethabo CFA while treating Eyethu AMD. After treatment, it was seen that Kendal and Lethabo CFA could both neutralise the mine water by reducing sulphate concentration and removing metals from the water. Results have proved that during treatment with Lethabo CFA sulphate concentration was reduced up to 91% and 53% for Kendal CFA. Some metals like Mg, Al, Mn and Fe have been removed to within the DWAF limits for irrigation. Treatment of AMD using CFA in a column leaching system is not a new way of treating AMD. However, it is a modified method that was used in this study, to treat AMD in a continuous process which helped to determine how many bed-volumes of AMD can be treated by a certain amount of CFA. It was shown in Chapter 4, Section 4.3.1 and Section 4.4.1, that 1280g of Kendal CFA could treat up to 13 bed volumes of Eyethu AMD, while on the other hand to 1440g of Lethabo CFA was enough to neutralise 15 bed volumes of Eyethu AMD. This made this study so important in terms of precision of the amount of CFA that could be used to neutralise a certain volume of the acid water. Moreover, understanding and monitoring the flow rate through the columns of fly ash from Kendal and Lethabo was among the objectives of this research. From the study it was shown that volumetric flow rate was showing some variations with time, it was decreasing with time and this observed from both Kendal and Lethabo columns this brought to attention the fact that the dissolution of some oxides was affecting the flow of acid water through the columns.

After treatment the solid residue sample produced was sent for XRD and XRF analysis and from the XRD results it was seen that there was the formation of some new other minerals phases such as gypsum which played a major part in the reduction of sulphate concentration. Furthermore, XRF results displayed changes in % by weight of some major oxides such as SiO_2, Al_2O_3, SO_3 and Fe_2O_3 showing that the hydrolysis and the dissolution of the oxides such as CaO contributed to the neutralisation of Eyethu AMD by raising the pH of the effluent water produced. The neutralisation process was a function of contact time. Time was a vital parameter to consider during the treatment of AMD with CFA as the degree of neutralisation achieved depends on the time. From the first minutes of contact of AMD with CFA, the pH was raised from 2.23 to 12 for leachates from Lethabo columns and 8.75 for leachate from Kendal CFA, but the pH was rising until after 10 days of non-stop running, it started to decrease due to the fact that the CaO CFA started to be exhausted. The volumetric flow rates of the effluent from both columns were decreasing with time as well. For the leachate from Lethabo CFA the volumetric flow rate of 4.83 mL/min 5.83 mL/minutes was recorded after the first 30 minutes of treatment and at the end of the experiment the last flow rate recorded were 3.9 mL/minutes for leachate from Lethabo CFA and 5.10 mL/minutes for the leachates from Kendal CFA. During treatment with both Kendal and Lethabo CFA, some metals contained in the AMD were completely removed and the concentrations of other metals were reduced to within the guidelines given by DWAF for irrigation. Fe and Al was removed at pH 4-7, while other metals like Mn and Mg were removed at pH 9 and 11 respectively for leachates from Lethabo columns, Mn and Mg concentration was reduced in the leachates from Kendal coal fly ash. Moreover, elements such as K, Na, Ti, V, and Cu, As, Se, B, Ba, Pb and Si leached out of CFA during the neutralisation process of AMD with CFA but levels were below the allowed DWAF limits for potable water. The ABA test was conducted in this study using a sample of Kendal or Lethabo CFA to determine the quality or post mining water that can be formed. From the results given in Chapter 4, Section 4.2.4, it was seen that both Kendal and Lethabo CFA are from non-acid generating rock as their NNP and NPR were 23.56, 30.14; 26.1, 46.87 respectively and they are both from rock type III which proves that they cannot generate acid mine water.

The advantage of using CFA to treat mine water in a column system compared to the use of chemical is that, this system is cheaper because it is using a waste material to treat another waste, CFA is found close to coal mines producing polluted mine water. Furthermore, the treated water generated from this system can be used back in coal combustion plant and used for cooling the system. This system has a high % recovery of water of 90.1% and 68.8% recovery percent of water from Lethabo and Kendal columns respectively.

Recommendation

It has been proven that CFAs used in this study can treat Eyethu AMD by reducing sulphate concentration to a value that is accepted by DWAF, remove many metals from mine water, and reduce others to the concentration range given by DAWF. There is always a probability of some trace elements for instance Cr, B and Sr to leach into treated water. In order to obtain a high quality or potable water a recommendation is to use some catalyst such as zeolite to further treat this water to a level which is acceptable for portable water standard. Furthermore, other types of AMD should be tested to find out about the efficiency of work and see if Kendal and Lethabo CFA can still be able to reduce as much as possible sulphate concentration from other acid mine waters and remove a significant amount of metals as well. Furthermore, this study were conducted on a labaoraty level, for industrial uses or to upscale this process, it will require the addition of some equipment such as pump that will facilitate the running of acid water from reservoir to columns.

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