UNIVERSITY OF
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A Comparative Study between the Neutralizing Capabilities of Fly Ash and Green Liquor Dregs with Acid Mine Drainage

By

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EXAMINER'S COPY

Preface

The candidate while based in the Discipline of Engineering, School of Chemical Engineering within the College of Agriculture, Engineering and Science, University of KwaZulu-Natal, Howard College Campus, South Africa completed the research contained in this dissertation. The research was financially supported by the Council for Scientific and Industrial Research (CSIR).

The work presented in this dissertation was performed at the University of KwaZulu-Natal from March 2017 to February 2018, and was supervised by Prof. B. B. Sithole, Mr. J. K. Johakimu and Mr. M. G. Ntunka. This dissertation is submitted as the full requirement for the degree of Master of Science in Engineering (Chemical). All the work presented in this dissertation is original, unless otherwise stated. It has not (in whole or in part) been previously submitted to any tertiary institute as part of a degree.

S. Ahmed

As supervisor of this candidate, I approve this dissertation for submission:

Prof. B. B. Sithole	Mr. J. K. Johakimu	Mr. M. G. Ntunka

Declaration: Plagiarism

I, Suhail Ahmed, declare that:

(i) the research reported in this dissertation, except where otherwise indicated or acknowledged, is my original work;

(ii) this dissertation has not been submitted in full or in part for any degree or examination to any other university;

(iii) this dissertation does not contain other persons' data, pictures, graphs or other information, unless specifically acknowledged as being sourced from other persons;

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(vi) this dissertation is primarily a collection of material, prepared by myself, published as journal articles or presented as a poster and oral presentations at conferences. In some cases, additional material has been included;

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Abstract

In South Africa, acid mine drainage (AMD) is a huge problem and arises when sulphide-bearing materials become exposed to oxygen and water. AMD formation is catalysed by mining and mineral extraction activities. The AMD produced seeps into water bodies and this renders the water highly toxic and harmful to humans, animals and vegetation due to its high acidity, high concentration of toxic heavy metals and sulphates. The combustion of coal is the primary method of power generation in South Africa. A by-product of this process is fly ash (FA). Approximately 20Mt of FA is produced in South Africa a year and only 5% of this is used in other applications. Green liquor dregs (GLD) are a by-product waste produced in the pulp and paper industry. They are produced in the Kraft pulping process and primarily comprised of a mixture of sodium and calcium carbonates. Both these waste products pose massive environmental and disposal problems.

GLD and FA are both highly alkaline; hence they can be used as neutralizing agents for the highly acidic AMD. The main aim of this project is to investigate the effectiveness of FA and GLDs in neutralizing AMD from coal mines. The effects of reaction time and neutralizing reagent (FA and GLD) concentration on the neutralization of AMD were studied. A 3^2 factorial design was employed for this research project. The reaction times used for the neutralization reaction were varied (1, 2 and 3 hours). The reagent concentrations used were also varied (0.4g/L, 1g/L and 2g/L). A total of 18 runs were conducted (9 for each reagent). The AMD was placed in beakers and electrical stirrers were used to ensure constant mixing. The reagent was added and the pH and electrical conductivity were measured after various reaction time intervals.

From using the preliminary 18 runs, an optimum FA and GLD reagent concentration was obtained, and a run was conducted for each reagent, to achieve a theoretical goal pH of 7. The results indicated that the optimum FA and GLD concentrations were 0.728g/L and 0.422g/L, respectively. Hence, GLD would be a better neutralizing reagent as less of it would be required to neutralize AMD, when compared to FA. It was also proven that time plays a very small effect on the neutralization reaction. Overall, the results conclude that GLD would be better than FA for neutralization of AMD. The deposition of heavy metals caused issues and a future research study may be conducted to reduce this problem.

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I would like to take this opportunity to express my sincere gratitude to the following individuals for their invaluable contributions to this project:

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Abbreviations

AMD	Acid Mine Drainage
ASTM	American Society for Testing and Materials
EC	Electrical Conductivity
EDX	Energy Dispersive X-ray Analysis/Spectroscopy
FA	Fly Ash
GLD	Green Liquor Dregs
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
LOI	Loss on Ignition
pH	Power of Hydrogen
SEM	Scanning Electron Microscopy
XRF	X-ray Fluorescence

Chapter 1 – Introduction

1.1. Background

Acid mine drainage is a massive problem in South Africa and it arises when a sulphide-bearing material becomes exposed to oxygenated water. The most common sulphide-bearing mineral that leads to this is pyrite, also known as "Fool's Gold". Pyrite is a constituent in many mineral deposits, including coal and gold mining deposits. It undergoes a two-stage oxidation process, in which a large amount of sulphuric acid is produced (McCarthy, 2011).

During normal weather conditions in South Africa, acid is produced. Since this is at a very slow rate, majority of the acid is removed via natural neutralization processes. However, it's during mining activities and mineral extraction that the rock is fragmented and this dramatically increases the surface area of exposed sulphur, thus increasing the rate of acid production. Certain rocks, especially those containing large amounts of calcite and dolomite, can neutralize the acid, however, this isn't the case for coal and gold mining deposits as the natural neutralizing process is overwhelmed and the large quantities of acidic water formed is released into the environment. This seeps into ground water and ultimately ends up in rivers and streams, rendering the water toxic at varying degrees. The highly acidic water becomes harmful to humans, animals and vegetation surrounding the areas affected (McCarthy, 2011).

In South Africa, combustion of coal is the primary method of power generation. The burning of the coal produces a large number of by-products and the major one is known as fly ash. The biggest power station in South Africa is Eskom and it's reported that burning of low-grade brown coal leaves behind fly ash residue which constitutes 25% of the raw material. Fly ash is generally collected using air controlling devices, such as bag filters and electrostatic precipitators, and dumped as a waste material in FA dams or heaps. Electricity generation in South Africa produces more than 20Mt/annum of fly ash, and only 5% of this is used in other applications. This presents a huge disposal problem for the FA in South Africa (Petrik, et al., 2003).

Green liquor dregs are a by-product waste produced in the pulp and paper industry. It is produced via the Kraft Process in which wood chips are treated with sodium hydroxide and sodium sulphide to release the cellulose required for paper-making. Green liquor dregs are a much firmer form of green liquor after the water is evaporated. The main constituent of GLD is calcite and even though it is reused and recycled, a large amount still remains and is disposed of as waste. This is another problem for South Africa as environmental and economic issues arise (Mäkitalo, et al., 2014).

1.2. Problem Statement

The disposal of FA and GLD poses environmental issues as they are generally disposed of in heaps and landfills. Maintenance costs rise as well to keep these heaps away from areas in which it may cause harm. AMD is another huge problem in South Africa as the effects are detrimental to ecosystems residing near the water bodies affected.

1.3. Motivation and Research Aims

Due to the large number of environmental problems that occur, because of AMD, this needs to be effectively neutralized and treated. FA and GLD was used as they are readily available. This may be due to the fact that they are waste products from the power, and pulp and paper industries respectfully. This study compared the neutralizing capabilities of FA and GLD with AMD.

The main aim of the project was to determine the better reagent between GLD and FA to use for AMD neutralization as well as the optimum dosage to achieve a neutral AMD state.

The objectives of the project include:

- Exploring the effect of reagent dosage on the neutralization process
- Exploring the effect of reaction time on the neutralization process
- Optimising the neutralization process by identifying the optimum reagent dosage
- Identifying the best neutralization reagent between FA and GLD
- Discussing the AMD, GLD and FA characteristics before and after the investigation

1.4. Thesis Statement

The FA and the GLD was obtained from pulp and paper mills in South Africa. These were added at varying dosages to the AMD, obtained from a coal mine. The time allowed for neutralization was also varied and the optimum reagent and reagent dosage was then obtained. Since GLD has similar neutralizing capabilities to limestone being used currently, the hypothesis for the investigation was that GLD will be a better neutralizing reagent than FA.

1.5. Research Contributions

This work made use of the fact that FA and GLD disposal is a huge problem in South Africa. By utilising their alkaline properties, they can be used to address the issue of AMD neutralization. This research contributes to the current knowledge of using FA and GLD as neutralizing reagents, however, now it is being used to treat AMD and this is potentially a new treatment method. By conducting this research, conclusions based on the amount of reagent required to neutralize AMD can be obtained. This work will therefore contribute to curbing the economic and environmental problems faced by the above-mentioned materials.

1.6. Outline of Dissertation Structure

Chapter 1 provides an introduction to the project. The background of the project is presented giving the reader an idea as to why AMD, FA and GLD are such huge problems. The main aims of this project as well as objectives that need to be met are explained. The reason for the dissertation is also explained to ensure that the reader understands why this investigation was carried out.

Chapter 2 is a contextual review of relevant literature that needs to be understood in order to fully understand this project. The main sections are AMD, FA and GLD and they are explained thoroughly, allowing the reader to fully understand the theory behind each raw material and why they were chosen for this research project.

Chapter 3 provides a description of the experimental apparatus as well as the materials used for the project. The usage of each piece of equipment is mentioned along with the geographical areas in South Africa that the raw materials were obtained from.

Chapter 4 elaborates on the experimental methods utilised during the conduction of the project. The research design is explained along with the methodology showing how the investigation was accomplished. An explanation of each analytical method used is also presented.

Chapter 5 presents the raw material analyses of the investigation. The elemental, chemical and physical properties are discussed. These properties were determined via a host of different analytical methods and presented for each raw material i.e. acid mine drainage, fly ash and green liquor dregs.

Chapters 6, 7 & 8 encompass the results and discussions of the findings from this study. The neutralizing capabilities of FA and GLD will be explained in chapter 5 and 6 respectively. Chapter 8 will show how the reagent concentration optimization was conducted along with the discussion of the best neutralizing reagent for AMD, between FA and GLD.

Chapter 9 provides an overall outline of the conclusions drawn up from this dissertation. Recommendations to improve the investigation will be made along with further work that can be possibly performed in this field of research.

Chapter 2 – Literature Review

2.1. Introduction

This chapter provides background information and fundamental concepts that are important in the understanding of this research project. Section 2.2 elaborates on the formation of AMD, its source as well as current treatment methods. Section 2.3 presents GLD, how it's produced as well as its neutralizing capabilities. Section 2.4 explains what FA is, how it can be classified as well as its neutralizing capability.

2.2. Acid Mine Drainage

Acid mine drainage (AMD) is the flow, or seepage, of polluted water from mining areas. Depending on the area, the water may contain toxic heavy metals or radioactive particles. This waste is detrimental to people's health, as well as plants and animals. AMD is produced by exposing the sulphide-bearing material to oxygen and water. This process occurs naturally, however mining promotes the rate at which AMD is formed due to the increase in the amount of sulphides exposed to oxygen and water (Akcil & Koldas, 2006).

Acidity is a measure of the hydrogen ion concentration and mineral acidity of a sample. At any given pH, the mineral acidity gives an idea of how the generation of hydrogen ions can occur upon precipitation of metal hydroxides in a solution. AMD consists of many metals and these remain in solution, even in a dissolved form when the pH is close to neutral. Hence, it is possible to obtain a neutral AMD sample with elevated acidity levels. Acidity is expressed as the mass $CaCO_3$ per unit volume (mg $CaCO_3$/L), using the following formula (Taylor, et al., 2005):

$$Acidity = 50\left\{10^{(3-pH)} + \frac{2[Mn]}{55} + \frac{3[Al]}{27} + \frac{3[Fe]}{56}\right\}$$

2.2.1. Formation of AMD

Properties of AMD include a low pH, high electrical conductivity, and a high concentration of toxic heavy metals such as iron, aluminium and manganese. Pyrite (FeS_2) is one of the most common sulphide materials which lead to acid mine drainage. It may also be known as "Fool's Gold" due to its metallic lustre and pale brass-yellow hue, making it resemble the mineral, gold.

Figure 2.1: Pyrite Rock Ore (Sandatlas, 2013)

The following reactions illustrate the formation of acid mine drainage from pyrite via contact with oxygen and water (Akcil & Koldas, 2006):

- The first important reaction is the oxidation of the sulphide material into dissolved iron, sulphate and hydrogen:

$$FeS_2 + 7/2O_2 + H_2O \rightarrow Fe^{2+} + 2SO_4^{2-} + 2H^+ \qquad (1)$$

- The dissolved Fe^{2+}, SO_4^{2-} and H^+ represent an increase in the dissolved solids and acidity of the water. If not neutralized, it may result in a decrease in pH. If the environment is sufficiently oxidising, much of the ferrous iron (Fe^{2+}) will oxidise to ferric iron (Fe^{3+}) as follows:

$$Fe^{2+} + 1/4O_2 + H^+ \rightarrow Fe^{3+} + 1/2H_2O \qquad (2)$$

- For pH values between 2.3 and 3.5, the ferric iron precipitates as iron hydroxide, leaving a small quantity of Fe^{3+} and simultaneously lowers the pH of the solution:

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_{3\,(solid)} + 3H^+ \qquad (3)$$

- Any Fe^{3+} from Eq. (2) that didn't precipitate in Eq. (3) is used to oxidise any additional pyrite as follows:

$$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+ \qquad (4)$$

- Finally the hydrogen and sulphate, in the presence of water, react to form sulphuric acid which contaminates ground water, thus producing AMD:

$$2H^+ + SO_4^{2-} \rightarrow H_2SO_4 \qquad (5)$$

Chemical, biological and physical factors are important when determining the rate of acid generation. The primary factors include (Akcil & Koldas, 2006):

- pH – the lower the pH, the stronger the acid is
- Temperature – the higher the temperature, the higher the rate of AMD formation
- Oxygen content of the gas phase (if saturation is less than 100%) – the higher the oxygen content, the higher the rate of sulphur oxidation, the higher the rate of AMD formation
- Degree of saturation in the water – the higher the degree of water saturation, the lower the oxygen diffusion, thus a lower rate of AMD generation
- Oxygen concentration in the water phase – a higher oxygen concentration in the water phase results in a higher oxidation rate of exposed sulphur, thus a higher rate of AMD formation
- Surface area of the exposed metal sulphide – the higher the exposed surface area of sulphide, the higher the rate of sulphuric acid generation
- Chemical activation energy – if the chemical activation energy required to initiate acid generation is low, then more acid can be produced easily; and
- Bacterial activity – a high amount of bacterial activity will decrease the rate of acid production, as it decreases the oxygen content in the water phase.

2.2.2. Sources of AMD

South Africa is richly blessed with an abundance of many minerals which are important to it and to other nations. Our country has one of the most sophisticated and developed mining industries in the world. The mining industry is the major contributor to AMD formation and can be classified into primary and secondary sources, as follows (Akcil & Koldas, 2006):

- <u>Primary Sources:</u>
    - Mine rock dumps
    - Tailings impoundment
    - Underground and open pit mine workings
    - Pumped/nature discharged underground water
    - Diffuse seeps from replaced overburden in rehabilitated areas
    - Construction rock used in roads, dams, etc.

- Secondary Sources:
    - Treatment sludge pounds
    - Rock cuts
    - Concentrated load-out
    - Stockpiles
    - Concentrated spills along roads
    - Emergency ponds

Figure 2.2 is an old abandoned metalliferous mine located in South Africa. Mining ceased in the late 1980s but a large amount of acidic-water is still being released from the underground workings to the surface environment. Pyrite is the main contributor to the water pollution caused. The pyrite is exposed to air and oxidises to form sulphuric acid, upon contact with water. Dark, reddish-brown water with a pH of lower than 2.5 is present on site (Akcil & Koldas, 2006).

Figure 2.2: AMD pool in South Africa (Akcil & Koldas, 2006).

2.2.3. Treatment Methods for AMD

AMD proves to be a huge environmental concern due to its low pH and heavy metal content. The high acidity and toxicity of water bodies make it impossible to be used as drinking water and it also poses a threat to plant and aquatic life. Treatment for AMD is therefore necessary, and there are two primary methods mainly used (Zipper, et al., 2011).

2.2.3.1. Passive Treatment of AMD:

The intention of passive treatment systems is mainly to improve the water quality of waters that pass through them. This form of treatment is cheaper and safer than its industrial alternative, however, it is not as effective as chemical treatment options. The main passive treatment options include: constructed wetlands, anoxic limestone drains and vertical flow systems. The option to be selected mainly depends on the AMD itself and factors, such as site conditions, flow rate of the stream and concentration of the contaminant elements (Zipper, et al., 2011).

- Constructed Wetlands:

There are two variations of the constructed wetlands used industrially, namely aerobic and anaerobic wetlands. The aerobic wetland is the simplest form of passive treatment, with its design characterised by a shallow, surface flow wetland, planted with vegetation such as *Typha*. Depending on the landscape conditions, the base of the wetland can be lined with a synthetic or clay barrier. This helps prevent treatment waters draining out the wetland base, or environmental waters moving into the system which may dilute the waters to be treated. This is shown in Figure 2.3. Aerobic wetlands are generally used for mildly acidic streams with a low flowrate. They are ineffective in treating highly contaminated waters. The basic mechanism of this wetland is to provide aeration, which allows precipitation of the dissolved heavy metals, upon oxidation. Having sufficient vegetation is important as this prevents 'channelized flow' which results in ineffective treatment. The dispersed flow increases the residence time of the contaminated waters within the wetland, thus increasing the amount of oxidation that occurs (Zipper, et al., 2011).

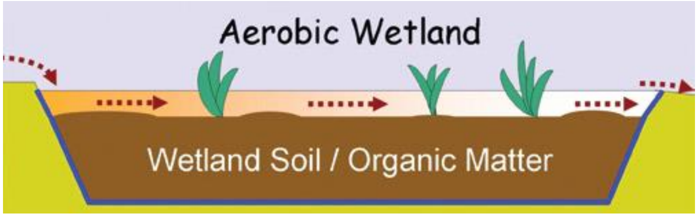

Figure 2.3: Cross-sectional view of an Aerobic Wetland (Zipper, et al., 2011)

Anaerobic wetlands are used when the stream to be treated is much more acidic in nature. The main difference between this wetland and an aerobic wetland is the reduced amount of oxygen required. Sulphate ions are responsible for a stream's acidity. Bacteria, present in the organic matter, reduce the sulphur content of stream waters, thus increasing its pH. The most common reaction that occurs is a reduction of sulphate ions and formation of hydrogen sulphide and bicarbonate, as follows (Zipper, et al., 2011):

$$SO_4^{2-} + 2CH_2O \rightarrow H_2S + 2HCO^{3-} \quad (6)$$

The above reaction can be detected as visible bubbles which emerge from the organic substrate, and the pungent odour of ‘rotten eggs’ which is common around H_2S gas. The bicarbonate that forms can be used to neutralize H^+ ions and by raising the pH, can acid-soluble metals be precipitated (Zipper, et al., 2011):

$$HCO^{3-} + H^+ \rightarrow H_2O + CO_2 \quad (7)$$

An alkaline layer may also be utilised to increase the pH of the stream. The most common neutralizing reagent used is limestone, as shown in Figure 2.4. This is settled below the organic matter layer. Diffusion occurs between the substrate and treatment waters (shown in as circular arrows) which generates alkalinity. The limestone used has a high calcium content, where $CaCO_3$ compromises of more than 90%. This is preferred for passive treatment as it’s more soluble, when compared to impure limestones or those that contain a larger proportion of total carbonates. The waters move through the organic substrate first, before making contact with the limestone layer. This allows bacteria in the organic material to remove oxygen from the waters, thus preventing ‘armouring’ of the limestone. ‘Armouring’ refers to iron being coated on the limestone surface, which reduces the surface reactivity of this layer. Due to the different layers, a large retention time is required to ensure the stream waters become effectively neutralized by the alkaline substrate (Zipper, et al., 2011).

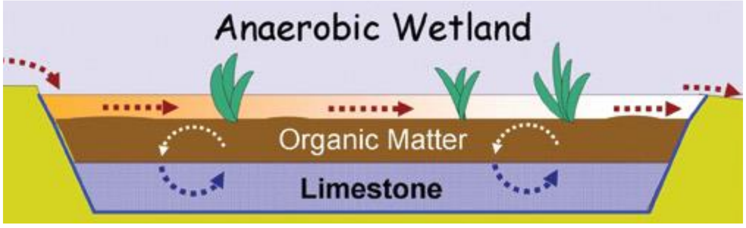

Figure 2.4: Cross-sectional view of an Anaerobic Wetland (Zipper, et al., 2011)

- <u>Anoxic Limestone Drain (ALD):</u>

ALDs (shown in Figure 2.5) are trenches that are filled with limestone, whereby acidic water flows straight through, and forms bicarbonate alkalinity via dissolution. These systems are generally capped with clay or compacted soil to prevent contact between oxygen and the AMD. The effluent that leaves the system is kept in a settling pond, which allows the pH to be adjusted naturally and metal to be precipitated. This method is generally used as a pre-treatment to the constructed wetland method, as this improves the water quality of the final discharge (Zipper, et al., 2011).

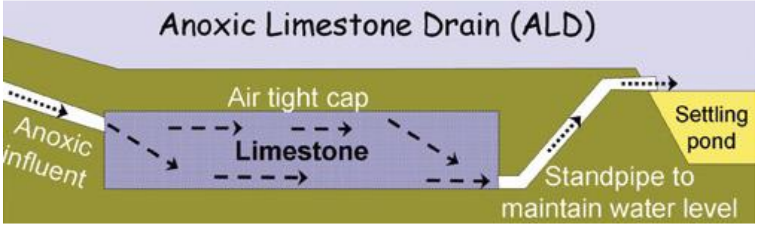

Figure 2.5: Cross-sectional view of an Anoxic Limestone Drain (Zipper, et al., 2011)

During normal operation, the ALD method of treating acidic waters is more cost-effective than wetland-based systems. However, they are not capable of treating all AMD waters. A high concentration of O_2, Al or Fe^{3+} in the stream waters, may cause the ALD to clog with metal hydroxides, once a pH of approximately 4.5 is reached. If the metal precipitation becomes significant, a 'floc' may form. A 'floc' is a gel, which is comprised of hydrolysed solid-phase metal precipitants. These clog the pores of the ALD and reduce the flow of water through the system, thus impairing its function. Once an ALD becomes non-functional, it will have to be replaced, repaired or abandoned (Zipper, et al., 2011).

- Vertical Flow Systems:

Vertical flow systems combine the anaerobic wetland and ALD treatment mechanisms to compensate for limitations that exist in the above-mentioned passive treatment methods. They may also be known as 'Successive Alkalinity Producing Systems' or 'SAPS'. The system utilises an anaerobic wetland, with the addition of a drainage system, which forces the AMD into direct contact with alkaline substrate. The three major system elements include an organic layer, an alkaline (limestone) layer and a drainage system – shown in Figure 2.6. As AMD waters flow downwards through the organic layer, numerous functions are performed: the dissolved oxygen within the AMD is removed by aerobic bacteria, and the sulphate-reducing bacteria generate alkalinity and sulphide metals. In the limestone layer, the high purity $CaCO_3$ is dissolved by the acidic, anoxic waters that move down the drainage system. This produces additional alkalinity. Finally, the effluent is discharged into a settling pond for neutralization and metal precipitation (Zipper, et al., 2011).

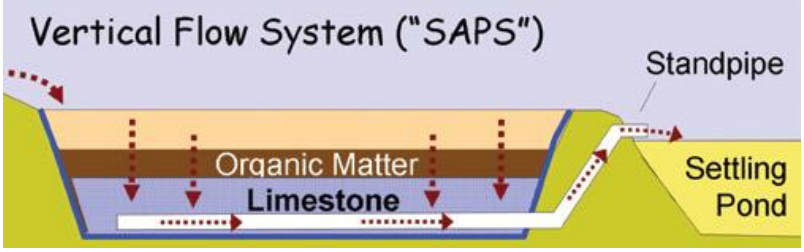

Figure 2.6: Cross-sectional view of a Vertical Flow System (Zipper, et al., 2011)

2.2.3.2. Active Treatment of AMD:

Active treatment of AMD refers to the use of chemical reagents in treating streams and requires constant maintenance. This form of remediation is the most commonly used in industry, as it is more effective than passive treatment methods. However, they do incur high capital and operational costs (Taylor, et al., 2005).

There are two main categories in which active treatment falls: (i) fixed plant and (ii) *in-situ*. The first category is a conventional active treatment plant which has a fixed location. The AMD is pumped to this plant. At the plant, the addition and mixing of reagents are accomplished in reactor tanks, the treatment sludge is collected and disposed, and the treated water is discharged. *In-situ* active treatment uses a portable land-based or water-based system to perform treatment at the location of the affected water body – a pit lake or stream. The infrastructure required is minor and the treatment costs are generally lower than that of fixed plants (Taylor, et al., 2005).

The main aim of active treatment methods is to control the pH of the desire water body, as well as, precipitate heavy metals, and this is commonly accomplished via the use of inorganic alkaline reagents. Selection of the most suitable reagent is based on a number of factors, which include the availability, volume to be treated, the cost, acidity, acidic loading and the performance of the reagent (Skousen, et al., 2000). The following chemicals are commonly used as reagents in active AMD treatment:

- Limestone ($CaCO_3$):

Limestone has been the reagent of choice for many decades as it raises the pH and precipitates metals in AMD efficiently. It is the safest and easiest to handle from the AMD treatment chemicals and has the lowest material cost. However, usage of limestone is limited due to its low solubility and its tendency to develop an ‘armour’ or external coating of $Fe(OH)_3$ when added to AMD. Limestone is preferred in cases where the pH is low and the metal concentration in the AMD is low as well. However, it isn’t very efficient when treating sludge bodies. The reason being that sludge isn’t very porous and this makes it difficult for limestone to react. Limestone is easy to use as the fine powder can just be dumped into the contaminated water bodies, or fed continuously (Skousen, et al., 2000).

- Soda Ash (Na_2CO_3):

Soda ash is used to treat AMD in remote areas where a low flow and low amounts of acidity and metals exist. The selection of soda ash is based on its convenience rather than its cost. It comes in the form of solid briquettes and is generally gravity fed into water with the use of barrels or bins. The amount of briquettes used depends on the flow of the stream and the quality of neutralization that is desired (Skousen, et al., 2000).

- Caustic Soda (NaOH):

Caustic soda is used in areas where electricity is unavailable, and in streams with a low flow and high acidity. It is the reagent of choice when the concentration of manganese (Mn) in the AMD is high. The system is gravity fed by dripping the liquid NaOH directly in the AMD. Caustic is very soluble in water and as it disperses rapidly, it raises the pH quickly. The caustic should be added at the surface of the water body as it is denser than water. Major drawbacks of using this reagent are the high costs and dangers associated with handling it (Skousen, et al., 2000).

- Ammonia (NH_3):

Ammonia is an extremely dangerous chemical that needs to be handled carefully. At ambient temperatures, it is a gas and upon compression, it can be stored as a liquid. Ammonia is very soluble in water and it reacts rapidly. It can easily raise the pH of a water body to 9.2 as it behaves as a strong base. In the case of AMD treatment, ammonia should be injected at the bottom of the water body as it is lighter than water. Using ammonia instead of caustic is more cost effective and a cost reduction of up to 70% can be achieved. Drawbacks from using ammonia as a reagent include hazards that may be associated with handling the chemical and possible nitrification, denitrification and acidification that may occur downstream (Skousen, et al., 2000).

2.3. Green Liquor Dregs

Green liquor dregs are an alkaline and inorganic waste with a low permeability and low hydraulic conductivity. The main constituent of green liquor dregs are calcite. They are produced via a recycling process in sulphate pulp and paper mills, known as the Kraft Process. Figure 2.7 presents a green liquor dregs sample. They are a sticky material and difficult to apply on mine deposits. The shear strength is insufficient for engineering applications; hence the mechanical properties need to be improved upon by combining it with other chemical compounds (Mäkitalo, et al., 2014). According to the work carried out by Pöykiö, et al. (2006), GLD has a pH of between 10.6 and 12.5. This indicates that they have a strong liming factor and can be effective neutralizing reagents.

Figure 2.7: Green Liquor Dregs (Mäkitalo, et al., 2014)

2.3.1. The Kraft Process

The Kraft process may also be known as Kraft pulping or the sulphate process. It is a process of converting raw wood into a wood pulp, constituting of almost pure cellulose fibres – which is the main component of paper. The Kraft process makes use of 'white liquor' (containing water, sodium hydroxide and sodium sulphide) at high temperatures to treat the wood chips. It is here where the waste green liquor dregs product is formed. The objective of the process is to break the bonds that link lignin, hemicellulose and cellulose. Recent advances in technology can be divided into chemical and mechanical processing techniques. The Kraft process is preferred as the paper produced is relatively strong, however, by-products from the process cause human and environmental problems (Patt, 2002).

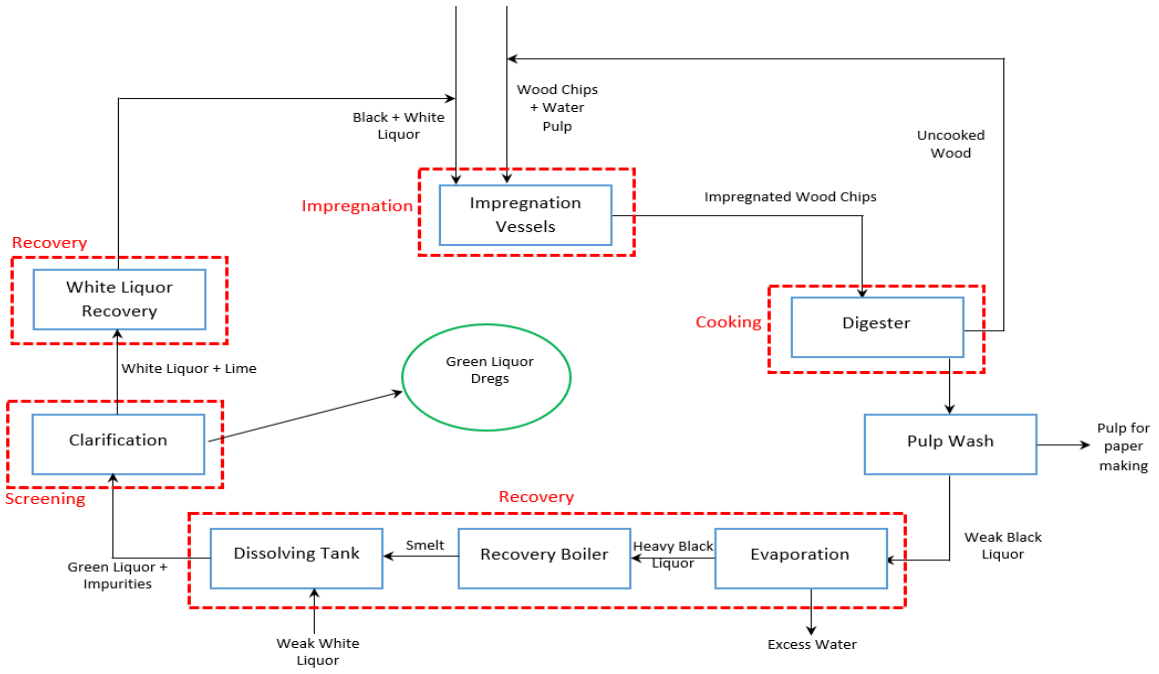

Figure 2.8: The Kraft Process

The process can be divided into 4 main sections, as shown in Figure 2.8:

- Impregnation:

  The average size of wood chips used is 12-25mm long and 2-10mm thick. The chips are wetted and heated to form a pulp mixture. The cavities within the wood chips are filled partly with liquid and air. The next step would be to saturate the chips with black and white liquor at a temperature below 100°C. Black liquor contains lignin fragments, carbohydrates from cellulose breakdown, sodium carbonate, sodium sulphate and other minute inorganic salts from the cooking process. The cooking liquor is made up of white liquor, water in chips, condensed steam and weak black liquor. In the impregnation step, the cooking liquor penetrates the channels within the wood chips and chemical reactions begin. The objective of this step is to obtain a homogenous cook before being sent to the digesters (Patt, 2002).

- Cooking:

  The cooking process occurs in large pressurised vessels known as digesters. They can operate in batch manner or in a continuous process. Digesters can process between 1000-3500 tons/day of wood pulp. In a continuous digester, materials are fed continuously and the pulping reaction needs to be complete before it leaves the reactor. Typically batch modes are selected and operate for several hours at temperatures between 170 and 176°C. It's under these conditions that the bonds between lignin, cellulose and hemicellulose break down into fragments. About 50 wt.% of the dry wood is collected and sent for washing. The remaining pulp is known as black liquor, because of its colour (Patt, 2002).

- Recovery:

  The black liquor usually contains about 15 wt.% solids and needs to be concentrated using a multiple effect evaporator. After the first step, it has a concentration of 20-30 wt.%. At this concentration, a rosin soap forms and rises to the surface of the liquor. It is skimmed off and can be further processed to form tall oil. The soap needs to be removed as this improves the evaporation of the liquor (Patt, 2002).

  The weak black liquor is evaporated to a concentration of 65-80 wt.% solids and this is known as the "heavy black liquor". This is burnt in a recovery boiler to recover the inorganic chemicals that may be reused in the pulping process. The reason the concentration of solids needs to be high as possible, is the fact that it increases the energy and chemical efficiency of the recovery recycle. However, a higher viscosity and precipitation of solids may cause fouling and plugging of equipment. The combustion reaction occurs with sodium sulphate being reduced to sodium sulphide upon contact with the organic carbon present in the mixture (Patt, 2002):

  $$Na_2SO_4 + 2C \rightarrow Na_2S + 2CO_2 \qquad (8)$$

  The molten salt from the recovery boiler is dissolved in process water and this is known as 'weak white liquor'. It is composed of all the liquors that can be used to wash lime mud and green liquor precipitates. A solution of sodium carbonate and sodium sulphide forms and this is known as 'green liquor'. In order to regenerate the white liquor used for the pulping process, calcium hydroxide is added and the equilibrium reaction is as follows (Patt, 2002):

  $$Na_2S + Na_2CO_3 + Ca(OH)_2 \leftrightarrow Na_2S + 2NaOH + CaCO_3 \qquad (9)$$

  The calcium carbonate is heated and recovered in a lime kiln, upon precipitation from the white liquor, to form calcium oxide (lime):

  $$CaCO_3 \rightarrow CaO + CO_2 \qquad (10)$$

The calcium oxide can react with water and regenerate calcium hydroxide which may be used in Eq. (9):

$$CaO + H_2O \rightarrow Ca(OH)_2 \tag{11}$$

The above reactions form a closed cycle loop with respect to sodium, sulphur and calcium. This is known as the recausticizing process whereby sodium hydroxide is regenerated from sodium carbonate (Patt, 2002).

- Screening:

  Screening of the pulp is used to separate the pulp from unwanted debris, such as knots and bundled fibres. This section consists of different sized sieves and centrifugal cleaning. The material removed from the pulp is known as the 'reject' and the pulp is known as the 'accept'. Sieves are generally setup in a multistage cascade to achieve maximum purity in the accept stream. The resulting pulp is then sent to be processed into strong, durable paper (Patt, 2002).

  After the smelt recovery stage comes the GLD separation stage. GLD clarifiers are used after the dissolving tanks to remove the GLD as a waste product. The GLD contains all the non-process elements (NPEs) and insoluble that may cause equipment operation problems if they aren't removed. Problems that may arise include scale forming on washers and plugging of process equipment. Metals that form part of the NPEs include barium, potassium, iron, copper, manganese, chromium, nickel and zinc. This section may also be known as the 'kidney' of the pulp mill as all these unwanted elements are removed and discarded as waste, in the form of GLD (Pöykiö, et al., 2006).

2.3.2. Neutralizing Capability of GLD

Currently, in industry, limestone is a popular chemical used to neutralize acidic process waters due to its high alkaline properties. Limestone is predominately made up of $CaCO_3$ and this is the reason it has such a high pH. A high amount of heavy metals is also present. The neutralization reaction of limestone allows for the precipitation of gypsum ($CaSO_4.2H_2O$). It's through this reaction that the sulphate content of the acidic process waters is reduced, thus increasing the pH of the water body. The following reaction occurs, releasing carbon dioxide (Geldenhuys, et al., 2001):

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4.2H_2O + CO_2 + H_2O \tag{12}$$

However, the utilisation of limestone is quite costly; hence alternatives need to be investigated. Green liquor dregs are a waste product formed in the pulp and paper industry. They possess a large amount of calcium carbonate, and this is why GLD can be used as an alternative to limestone. The high alkaline nature of GLD and the low cost of obtaining this waste product make it an attractive neutralizing reagent for the neutralization of acidic process waters (Geldenhuys, et al., 2001).

2.4. Fly Ash

Fly ash is a fine grey powder that is the main by-product generated during the combustion of coal or biomass in boilers at high temperatures which range between 1400°C and 1700°C. Fly ash accounts for approximately 75-80% of the total ash produced in power plants. Approximately 349Mt of coal ash was produced in the year 2000, worldwide. In South Africa, Eskom generates approximately 22.5 million tons of coal fly ash per annum (Nyale, et al., 2013).

In order to use FA, a number of factors play a role in determining its quality. They are as follows (Akbari, et al., 2015):

- LOI – is a measure of unburned coal in the sample. A high LOI results in a high carbon level, thus allowing an increase in air entrapment, ultimately reducing the strength of FA
- Fineness – is a measure of the size of the particles. The smaller the particles, the larger amount of exposed surface area, thus an increase in its reactivity
- Uniformity – refers to all particle sizes being the same. This factor helps in ensuring that the FA reactivity is equally distributed throughout the surface of the sample

2.4.1. Chemical Composition and Morphology

Fly ash (in Figure 2.9) is made of inorganic matter which is left behind after the coal burning processes, with a small amount of carbon that remains due to incomplete combustion. Fly ash is known as a ferro-alumino-silicate material, with common elements such as Si, Al, Fe, Mg, Ca, Na and K. Iron and magnesium, in large quantities, may decrease its neutralizing ability. There has been approximately 188 minerals or mineral groups identified in fly ash. Common minerals include quarts (SiO_2), hematite (Fe_2O_3), mullite ($Al_6Si_2O_{13}$) and magnetite (Fe_3O_4) (Akinyemi, et al., 2012). Several studies have been done over the years based on the morphology of fly ash. According to Ngu et al. (2007), fly ash comprises of fine spherical particles of alumino-silicate glass, with some being solid and others being hollow. The hollow spheres are known as ‘cenospheres’ and vary in size ranging between 45µm and 150µm. Fly ash particles have a smooth outer surface due to the presence of the alumino-silicate glass phase.

Figure 2.9: Fly Ash (Mäkitalo, et al., 2014)

2.4.2. Classification of FA

According to the American Society for Testing Materials (ASTM), there are two classes of fly ash that exist: Class C in which the total amount of SiO_2, Al_2O_3 and Fe_2O_3 lies between 50 and 70 wt.%, and Class F in which the tri-mineral content exceeds 70 wt.% . The main difference between the classes is the amount of calcium, alumina, silica and iron present in the ash. In addition, Class F contains a lower lime content in relation to class C. Class F fly ash is formed via combustion of anthracite or bituminous coal. It exhibits pozzolanic properties, where it hardens upon reacting with $Ca(OH)_2$ and water. Class C is formed via the combustion of lignites or sub-bituminous coals. It exhibits cementitious properties, where it hardens itself when contacted with water. The total calcium content in Class F doesn’t exceed 12 wt.%, whereas in Class C it exists within the range of 30 to 40 wt.%. Also, the combined sodium, potassium alkali quantity and sulphates are generally higher in Class C than Class F (Yao, et al., 2015)

2.4.3. Neutralizing Capability of FA

Utilising fly ash as an alternative neutralizing reagent has two main advantages: the maintenance costs of FA landfills is rapidly decreased and managing of the same landfills becomes much easier. However, using this method generates solid residues, during the neutralization reaction, that require disposal (Vadapalli, et al., 2008).

FA is an excellent neutralizing agent due to the amount of calcium oxide (CaO) it contains. The free alkalinity, combined with its large surface area and small particle size make it ideal in neutralizing AMD. According to the work conducted by Petrik (2004), the co-disposal process of treating AMD with FA results in the effective removal of a high amount of sulphates and this, in turn, increases the pH of the AMD. Sulphate removal rates of over 90% were achieved. Iron and aluminium were also completely removed from the process waters, when a higher amount of FA was used.

2.8. Conclusion

The literature review has given sufficient background knowledge for the understanding of this project. Currently FA is a neutralizing reagent being utilized widely due to it being a waste product. Utilizing GLD as a substitute to limestone for AMD neutralization is a new method. This research conducted will bridge the gap in finding alternate neutralization reagents as well as compare the neutralizing capabilities of FA and GLD. The following chapter will describe the materials and equipment used for the investigation.

Chapter 3 – Equipment Description

3.1. Introduction

The aim of this chapter is to outline the mechanisms used to obtain experimental results. This served as an important factor in verifying the thesis statement. The description of the materials and equipment utilised during the experimental work will be presented.

3.2. Geographical Research Areas

Acid mine drainage, fly ash and green liquor dregs were obtained from three different locations in South Africa. These are shown in Table 3.1 below:

Table 3.1: Raw Material's Location

Material	Location
Acid Mine Drainage	Zaalklap Spruit Mine
Fly Ash	Ngodwana Sappi Mill
Green Liquor Dregs	Mondi Richards Bay

3.3. Materials Used

Different materials were used in this investigation and these are shown in Table 3.2 below, along with their respective purposes:

Table 3.2: Materials Used

Material	Purpose
Acid Mine Drainage	Material to be neutralized
Fly Ash	Neutralizing reagent
Green Liquor Dregs	Neutralizing reagent
Deionised Water	Cleaning of experimental apparatus

3.4. Equipment Used

Table 3.3 represents all the equipment that was utilised during the conduction of this research project:

Table 3.3: Equipment Used

Equipment	Purpose
Primary Analysis of Raw Materials	
XRF	Chemical composition measurement
SEM/EDX	Elemental composition measurement & micrography
ICP-OES	Elemental composition measurement

Secondary Analysis	
pH/EC meter	Determine pH and electrical conductivity
Neutralization Investigation	
Scale	Measurement of sample masses
Glass beaker	Measurement and container for the materials
Overhead stirrer	Stirs the AMD in the glass beakers
Buchner flask and funnel	Separation of solid precipitate and waste liquor
Oven	Provides heat for water evaporation

Figure 3.1 shows the experimental set-up. AMD was neutralized in all six beakers based on the runs shown in Section 4.2 of chapter 4. The overhead stirrers were kept at a constant speed and aid in the neutralization reactions. The apparatus was readily available at the CSIR and proper commissioning of the equipment was accomplished prior to carrying out the investigation.

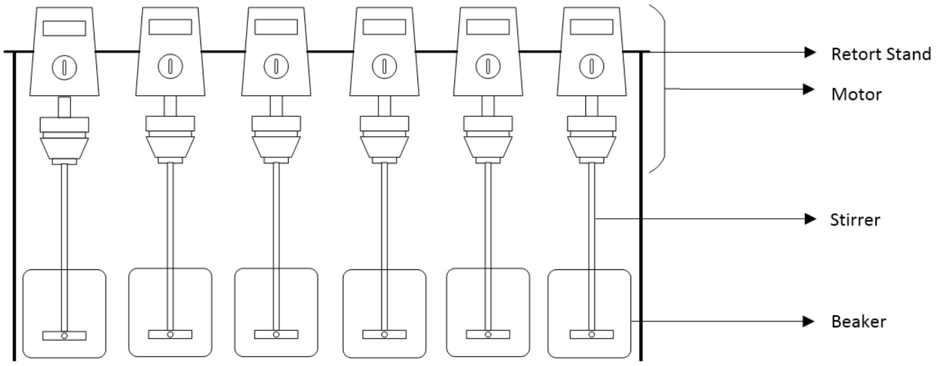

Figure 3.1: Experimental Set-up for AMD Neutralization

3.8. Conclusion

This chapter allowed the reader to understand the requirements needed to perform the investigation. Now chapter 4 can provide more detail as to how the investigation was performed, giving the actual procedures. The analytical methods used for analysis will also be described.

Chapter 4 – Experimental Methods

4.1. Introduction

The aim of this chapter is to delve deeper into the research design methodology and the procedure used to conduct the experimental work. The limitations of the project as well as the analytical methods used will be summarised accordingly.

4.2. Research Design

A statistical approach to the design method was selected for the project. Statistical methodology is preferred over 'One Variable At a Time' (OVAT) as it results in a more efficient investigation. The statistical method utilised for this project was the 3^2 factorial design. This method used two variables that were tested at three different levels. The two variables tested were the time allowed for the neutralization reaction to occur and the concentration of the neutralization reagent. The times that were used are 1, 2 and 3 hours (this basis allows for a slow/fast reaction to take place as prior to the experiment, reaction time was unknown), and the neutralization reagent concentrations used were 0.4g/L, 1g/L and 2g/L (these were selected to give a range from acidic to basic pH, thus allowing an optimum dosage to be obtained). This investigation tested both the neutralization ability of fly ash and green liquor dregs. Nine runs were conducted for each neutralizing reagent; hence a total of 18 runs were accomplished. Three set-ups for each run were employed. This is important as repeatability greatly improves the accuracy of the investigation. The following table represents the combinations used for each run:

Table 4.1: Experimental Run Combinations

Run	Reagent	A – Time (hrs)	B – Concentration (g/L)
1	FA	1	0.4
2	FA	2	0.4
3	FA	3	0.4
4	FA	1	1
5	FA	2	1
6	FA	3	1
7	FA	1	2
8	FA	2	2
9	FA	3	2
10	GLD	1	0.4
11	GLD	2	0.4
12	GLD	3	0.4
13	GLD	1	1
14	GLD	2	1
15	GLD	3	1

16	GLD	1	2
17	GLD	2	2
18	GLD	3	2

4.3. Methodology

The main part of this experimental investigation was to conduct the neutralization reactions of GLD with AMD as well as FA with AMD. Six stirring apparatus were available, hence two runs were accomplished simultaneously. Each run was conducted using three of the set-ups, as one is to be used as the standard and two are used for repeatability. The following will be summarised using the FA run for 3 hours and a neutralizing reagent concentration of 0.4g/L (Run 3). The same method is carried out for the other FA and GLD runs, by changing their respective times and reagent concentrations.

Three 1000mL glass beakers were washed and rinsed thoroughly with deionised water to remove any contaminants that may affect this investigation. The AMD was removed from the refrigerator and allowed to reach room temperature in a water bath. The beakers were filled with approximately 500mL of AMD, and placed below the stirring apparatus. The initial pH and electrical conductivity (EC) was then taken before the stirrers were switched on and set to 200rpm (This speed allowed sufficient stirring without splashing that may have affected results).

Pre-treatment of the FA and GLD was necessary prior to the experimental runs. Both GLD and FA were dried overnight in an oven at 110^0C and then crushed to a fine powder using a pastel and mortar afterwards to ensure fine, dry particles were obtained. The neutralizing reagent was weighed out and kept aside until it was ready to be added to the AMD. In this instance, a mass of 0.2g FA was used to allow for a reagent concentration of 0.4g/L in the 500mL AMD sample. The FA was then added to the first beaker and the time is started. After two minutes, the FA was added to the next beaker and after another two minutes, the process was repeated for the third beaker. This method allows for readings to be taken within the two minute difference and this ensures stirring occurred for the same duration, in all three set-ups.

For the first hour, readings were taken every 10 minutes. Afterwards, they were taken every 20 minutes for the remainder of the run. The procedure was as follows: the stirrer for the first beaker was switched off. The pH meter was inserted allowing the pH and EC to be determined and recorded. The pH meter was then removed and rinsed with deionised water. The stirrer was switched back on and the process was repeated for each beaker.

Upon completion of the run, the stirrer was switched off. The beaker sample was allowed to settle for an hour, thereafter, filtration using a Buchner flask was undertaken. The precipitate was collected and dried overnight in an oven. The waste liquor was sampled in vials. Both the precipitate and waste liquor were sent for analysis to determine the elements and compounds present within them.

4.4. Limitations

Even though the investigation was carried out as efficiently as possible, limitations may arise and these include:

- Time delay between readings – Even though a two minute time delay was employed to take readings, more than two minutes may have been used and this may affect consequent results in the runs carried out.
- pH meter – Due to the pH meter being used by other students, it may reduce its accuracy and this may affect results obtained. Hence, calibration was an important step in obtaining accurate results.
- Sharing of ovens – due to the limited amount of ovens in the laboratory, many students had to share the ovens. This may cause problems as different students require the oven at different times and different temperatures. Space also became a problem.

4.5. Analytical Methods

An important step in the research of this project was to analyse the raw materials and products formed. Analytical laboratory methods were used and the main ones are summarised as follows:

- pH Measurements:

  The pH of a component is a measure of the proton activity in an aqueous solution. It is important in determining whether a solution is acidic or alkaline. Hydrogen ions (H^+) are responsible for the pH of a component. A high concentration of hydrogen ions results in an acidic solution and a low concentration of hydrogen ions results in an alkaline solution. A pH meter is generally used and it consists of a measuring and reference electrode. The measuring electrode delivers a varying voltage and the reference electrode delivers a constant voltage to the meter. A potential is generated due to the free hydrogen ions in the solution. This potential then gives a pH reading. The pH of a solution is proportional to the potential obtained (Skoog, et al., 1998).

A Hanna H198195 Multi-parameter (pH/ORP/EC/Pressure/Temperature) meter was used to record the pH measurements. Calibration was important to ensure correct readings were obtained. Buffer solutions of 4.01 and 10.01 were used for the calibration. Thereafter, a quality control sample with a known pH of 7.01 was used to ensure the validity and accuracy of the pH meter.

- EC Measurements:

  Electrical conductivity (EC) is the measure of a sample's ability to conduct an electric current. The sensor comprises of two metal electrodes that are inserted into a solution. A constant voltage is applied across the electrodes and an electrical current flows through the solution. This current is proportional to the concentration of dissolved ions in the solution – the higher the amount of ions, the more conductive the solution is resulting in a higher electrical current. EC values are obtained at a reference temperature of 25°C as the electrical current flow in the solution is temperature dependent (Skoog, et al., 1998).

  A Hanna H198195 Multi-parameter (pH/ORP/EC/Pressure/Temperature) meter was used to record the EC measurements. The meter was calibrated using a standard solution of 1413µS. A quality control sample with a known EC of 1500µS was used to ensure accuracy and validity of the meter.

- ICP-OES:

  Inductively Coupled Plasma – Optical Emission Spectrometry (ICP-OES), is an analytical technique that is used to detect trace metals in a liquid sample. The sample is pumped into a nebulizer, where it is converted into a fine aerosol with argon gas. Fine droplets, which are 1-2% of the sample, are separated from the larger droplets using a spray chamber. This fine aerosol is sent to a plasma torch via a sample injector, thus ionizing the gas. A high-voltage spark results as a source of electrons and this forms a plasma discharge at a very high temperature (~10 000K). The plasma is generally vertically orientated, and used to generate photons of light by the excitation of ground state electrons to a higher energy level, within an atom. As the electrons 'fall' back to ground state, specific wavelengths are emitted and these are used to characterise different elements of interest (Skoog, et al., 1998).

The ICP-OES analysis was undertaken at the University of KwaZulu-Natal (Westville Campus) to determine the elements present in the liquid samples. Standard elemental samples of varying concentrations (in ppm) were prepared upon dilution and sent with the experimental samples. This was used to generate a calibration curve (between 1 and 1000ppm for each element) and the concentrations of each element could then be obtained. The unit was operated by a trained technician who ran it three times. An average reading was taken and this increased the accuracy of the results obtained.

- XRF:

  X-ray Fluorescence (XRF) analysis is a method that utilises a characteristic fluorescent X-ray that is generated when X-ray is irradiated on a substance. An electron within the inner shell is excited by an incident photon in the X-ray region. A de-excitation process then occurs and an electron moves from a higher energy level to fill the vacancy left by the excited electron. The energy difference between the two shells appears as an X-ray that’s emitted by the atom. An X-ray spectrum is then acquired and this reveals a large number of characteristic peaks. The energies of the peaks lead to identification of the elements present in a sample (qualitative analysis), and the intensity of the peaks provides the relevant elemental concentration (quantitative analysis) of each element in the sample. The irradiation is generally performed using radioisotope sources: however, X-ray tubes are more commonly used (Skoog, et al., 1998).

  The XRF analysis was undertaken at the University of Stellenbosch and used to determine the compounds within the solid samples. Approximately 0.35 – 0.7g of sample was required and this was crushed to a fine powder (particle size < 70µm). The analysis was conducted three times by a trained technician, and an average was taken for accurate results.

- SEM/EDX:

  The scanning electron microscope (SEM) uses a focused beam of high energy electrons on the surface of a solid sample, to generate a variety of signals. The SEM part of the unit is predominantly used to obtain microstructural imaging of the sample. Combination of SEM technology with Energy Dispersive X-ray (EDX) reveals more information on the sample. Upon the addition of energy, X-rays are generated from the collisions between incident electrons, from an electron beam, with electrons within the sample. The excited electrons move to a different energy state and this yields X-rays of a fixed wavelength. Characteristic X-rays are obtained and at different intensities, can different elements be classified. This technology is used to determine information about the chemical composition, external morphology, crystalline structure and orientation of the materials within the sample (Skoog, et al., 1998).

The SEM/EDX analysis was undertaken at the University of KwaZulu-Natal (Westville Campus) to determine the elemental components of the solid samples. A sample of at least 1g was used in the unit. The unit was operated by a trained technician who ran it three times. This increased the accuracy of the results obtained.

4.6. Conclusion

This chapter gave further detail into the experimental methods that were selected and how each part of the investigation was performed. Analytical methods along with project limitations were also presented. Now, the results from the investigation can be discussed within the next four chapters.

Chapter 5 – Results & Discussion: Raw Material Analyses

5.1. Introduction

The first, and one of the most important steps, is to characterize the raw materials utilized in this project by elemental and chemical analysis. This chapter summarises the constituents and physical properties of AMD, FA and GLD, obtained from the analytical experimental work. The classification of FA is presented as this is important in determining its properties.

5.2. Acid Mine Drainage

The AMD sample (Figure 5.1) is a colourless, odourless liquid. It was obtained from a coal mine; hence the elements present may differ from AMD collected from a gold mine. There are black particles present as the raw material had not been filtered after collection. Prior to analysis and experimental work, the sample is filtered to ensure the contaminants do not interfere with the results.

Figure 5.1: Acid Mine Drainage Sample

Analysis of the AMD was accomplished via ICP-OES analysis. Standard elemental solutions were prepared at varying concentrations and the composition of each element within the AMD sample is represented in Table 5.1:

Table 5.1: ICP Analysis of AMD

Element	Concentration (ppm)
Al	2.050
B	0.194
Ca	210.20
Co	0.147
Cr	0.020
Cu	3.120
Mn	499.20
Fe	70.23
S	772.23
Si	6.467
Sr	1.330
Zn	0.090

AMD contains heavy metals such as aluminium, cobalt, chromium, copper, iron and zinc, however, these are in small quantities. The main constituents of AMD are calcium, manganese and sulphur. Sulphur and manganese are responsible for the acidic nature of the AMD. The elements present are all hazardous to the environment, hence, they need to be reduced or eliminated.

Utilising the composition of AMD, the acidity can be calculated. The acidity was calculated as follows:

$$Acidity = 50\left\{10^{(3-pH)} + \frac{2[Mn]}{55} + \frac{3[Al]}{27} + \frac{3[Fe]}{56}\right\}$$

$$= 50\left\{10^{(3-4.10)} + \frac{2[499.2]}{55} + \frac{3[2.05]}{27} + \frac{3[70.23]}{56}\right\}$$

$$Acidity = 1111.11\,\frac{mgCaCO_3}{L}$$

The acidity is extremely high proving that a large quantity of hydrogen ions are present and will increase upon the dissolution and neutralization reactions that take place.

5.3. Fly Ash

Fly ash is mainly made up of fine grey particles. Due to moisture, some particles may be lumped together. Hence, drying of the FA was necessary before using it during the experimental runs. Figure 5.2 represents the FA sample used.

Figure 5.2: Fly Ash Sample

Figure 5.3 represents the signals that were obtained from the SEM analysis of FA. Each peak indicates a different chemical element at different electron beam intensities. The most significant peak occurs at approximately 1.6keV and with a displacement of 16cps/eV, and indicates that silicon is present in the FA sample.

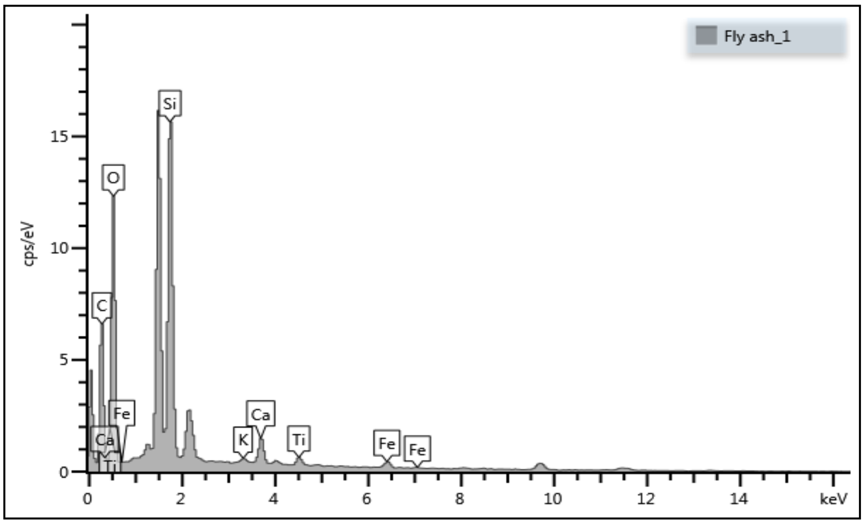

Figure 5.3: FA Peaks from SEM Analysis

Table 5.2 reveals the elemental composition of the FA sample. It can be seen that oxygen and silicon are the predominant elements present. Hence, the main constituent in the FA sample will be a compound that contains the above mentioned elements. According to literature, fly ash is mainly made up of silicon dioxide (SiO_2) (Fernández-Jiménez, et al., 2006). Heavy metals, such as titanium, iron and copper are also present in the FA sample, however, they are in low quantities.

Table 5.2: FA Elemental Composition

Element	Mass Weight Percentage (%)
O	59.92
Si	32.57
K	0.44
Ca	2.39
Ti	3.12
Fe	0.88
Cu	0.68
Total	100

XRF analysis was conducted to determine the chemical composition of the FA sample and this is represented in Table 5.3:

Table 5.3: FA Chemical Composition

Compound	Mass Weight Percentage (%)
Al_2O_3	28.73
CaO	6.72
Cr_2O_3	0.02
Fe_2O_3	3.78
K_2O	0.45
MgO	1.87
MnO	0.05
Na_2O	0.03
P_2O_5	0.42
SiO_2	50.84
TiO_2	1.64
LOI	4.72
Other	0.74
Total	100

ASTM C618 was used to classify the fly ash. The main criteria tested is the content of the tri-mineral (SiO_2, Al_2O_3 and Fe_2O_3) compounds in the sample. Since no Fe_2O_3 is present, the other two compounds will be used. The combined value is 79.57 wt.% and this exceeds 70 wt.%, hence, the criteria for Class F fly ash is accepted. The next criteria for Class F classification is the content of calcium. The calcium content in the fly ash sample is 2.39 wt.% and since this is less than 12 wt.%, this further classifies the sample as Class F.

Figure 5.4 is an image obtained from SEM analysis which shows what the FA sample looks like at microscopic level. It can be seen that the FA particles are spherical in shape and vary in size. The biggest particle size is approximately 10µm. This is quite small and resembles a powdery substance.

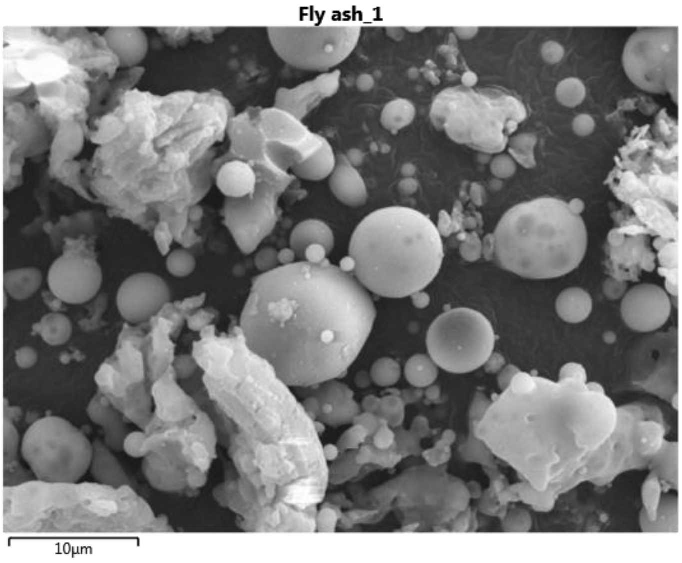

Figure 5.4: FA image from SEM Analysis

5.4. Green Liquor Dregs

Green liquor dregs are a dark green, sticky material. They are quite difficult to handle and measure. Figure 5.5 represents a wet GLD sample. Drying was extremely necessary as this makes it easier for use in this investigation. They were placed overnight in an oven at 110^0C.

Figure 5.5: Green Liquor Dregs Sample

Figure 5.6 represents the signals that were obtained from the scanning electron microscope. The most significant peak occurs at approximately 3.7keV and with a displacement of 8cps/eV, and indicates that calcium is present in the GLD sample.

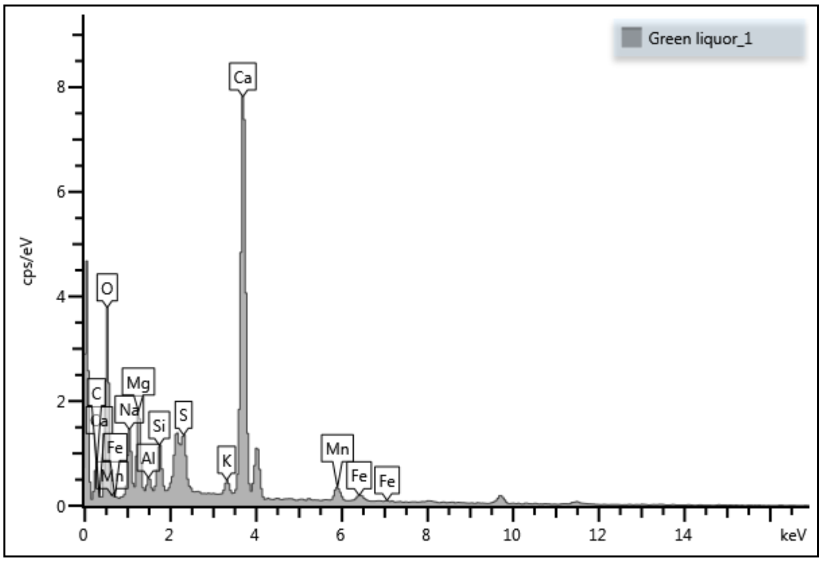

Figure 5.6: GLD Peaks from SEM Analysis

Table 5.4 reveals the elemental composition of the GLD sample. It can be seen that oxygen, calcium and carbon are the predominant elements present. This indicates that the GLD sample could be made up of majority $CaCO_3$ or CaO. This was expected and upon dissolution, the $Ca(OH)_2$ gives the GLD its alkaline nature. Heavy metals, such as magnesium, aluminium, manganese and iron are also present, but in small quantities.

Table 5.4: GLD Elemental Composition

Element	Mass Weight Percentage (%)
C	12.23
O	47.00
Na	4.47
Mg	4.22
Al	0.67
Si	1.84
S	2.16
K	0.86
Ca	23.93
Mn	1.88
Fe	0.74
Total	100

XRF Analysis was conducted to determine the chemical composition of the GLD sample and this is represented in Table 5.5:

Table 5.5: GLD Chemical Composition

Compound	Mass Weight Percentage (%)
Al_2O_3	0.81
CaO	36.42
Cr_2O_3	0.02
Fe_2O_3	0.67
K_2O	0.65
MgO	4.81
MnO	1.40
Na_2O	6.96
P_2O_5	0.41
SiO_2	2.38
TiO_2	0.02
LOI	38.29
Other	7.15
Total	100

From Table 5.5, it can be seen that the predominant species is CaO. This is what gives GLD its neutralizing capability. The LOI is also quite high which indicates a high amount of volatile compounds within the sample. This includes $CaCO_3$, which is another compound responsible for the neutralizing capability of GLD.

Figure 5.7 is an image obtained from SEM analysis which shows what the sample looks like at microscopic level. Colour is used to reveal exactly where each element is present. Since the image is predominantly green, it can be seen that calcium is present in large quantities within the sample.

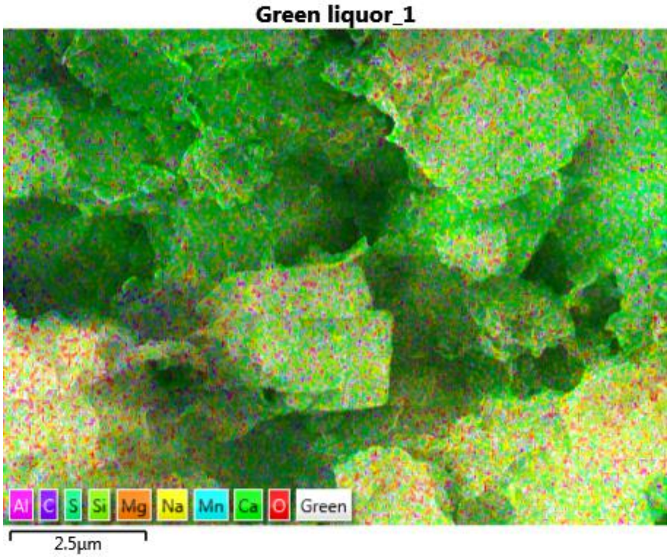

Figure 5.7: GLD image from SEM Analysis

5.5. Density and pH

The densities of FA and GLD was obtained using a simple displacement test, which is a standard method. A specified mass of each sample was used and placed in 10mL of deionized water. The volume of the sample was determined; thus the density was calculated. The density of AMD was obtained by pouring 10mL of it in a measuring cylinder, and its respective mass was measured. Hence, density can be obtained via division of the mass by its respective volume.

The pH of AMD was determined by inserting the pH meter into the sample. Due to FA and GLD being solid particles, they were placed in deionized water and only then, could the pH be obtained using the pH meter. For correct results, the pH meter was left in the respective sample for at least 5 minutes, or until the reading stabilized by staying constant. Table 5.6 represents the pH and density of the samples:

Table 5.6: Raw Material Properties

Material	Density (kg/m^3)	pH @ 21.6°C
Acid mine drainage	950.25	4.10
Green liquor dregs	1313.03	12.23
Fly ash	1986.40	11.71

It was expected that FA would have the highest density as it is solid particles, whereas the GLD is a paste and AMD is a liquid. AMD has a lower density when compared to water (1000kg/m^3), and this is why it forms a layer above the water body. The pH of AMD proves that it is quite acidic. The pH of GLD and FA shows that they are alkaline and this was expected.

5.6. Conclusions

The following conclusions were drawn up in this chapter:

- The AMD was obtained from a coal mine and is predominately made up of calcium, cadmium, magnesium, manganese (heavy metal), sulphur and low quantities of other heavy metals (aluminium, cobalt, chromium, copper, iron and zinc).
- The AMD has an acidity level of 1111.11 mg$CaCO_3$/L which is extremely high.
- The FA sample is mainly made up of silicon and oxygen, according to SEM analysis. It also contains small quantities of calcium, titanium, iron and copper.
- From XRF analysis, the tri-mineral (SiO_2, Al_2O_3 and Fe_2O_3) content of FA is obtained as 79.57 wt.%. A calcium content of 2.39 wt.% was also determined and this classifies the FA sample as Class F.
- According to SEM/EDX analysis, the GLD sample is predominantly made up of oxygen, calcium and carbon. It also contains sodium, magnesium, aluminium, silicon, sulphur, potassium and iron.
- From XRF analysis, CaO is the major compound within the sample. This is responsible for GLD’s alkaline nature.
- AMD has a low pH of 4.10, hence it is an acidic material.
- GLD and FA have a pH of 12.23 and 11.71 respectively. This indicates that they are alkaline substances.

Chapter 6 – Results & Discussion: Neutralizing Capabilities of Fly Ash

6.1. Introduction

This chapter discusses the results obtained from the investigation of acid mine drainage neutralization upon contact with different concentrations of fly ash and varying contact times. From Section 4.2, it can be seen that this chapter deals with runs 1 through 9. The following table summarises the combinations used for this part of the investigation:

Table 6.1: Experimental Run Combinations

Run	A – Time (hrs)	B – Concentration (g/L)
1	1	0.4
2	2	0.4
3	3	0.4
4	1	1
5	2	1
6	3	1
7	1	2
8	2	2
9	3	2

The pH and electrical conductivities will be presented along with the chemical analysis of the precipitate and waste liquor formed. A control as well as two duplicate tests were conducted. The average was taken and the results shown below. The full set of raw data is available in Appendix A.

6.2. pH and Reaction Time

The reaction time of each run plays an important role and this is exhibited in this section.

Table 6.2: pH at Time Intervals for FA/AMD Concentrations

Time (s)	0	60	120	180
pH – 0.4g/L	4.11	5.61	5.56	5.53
pH – 1g/L	4.10	8.17	8.00	7.95
pH – 2g/L	4.11	9.43	9.35	9.31

Table 6.2 represent the changes in the pH of the AMD at different periods of time with varying FA dosage concentration. It can be seen that all three dosage concentrations have a similar trend. The pH of the AMD increases sharply upon addition and then decreases gradually as the contact time increases. The reason being that an increase in time allows for solution stability to be achieved. It can be seen that the increments are relatively small, hence it can be confirmed that solution stability was reached.

6.3. Electrical Conductivity

This section represents the change in EC of the AMD solution as each run is conducted.

Figures 6.1, 6.2 and 6.3 depict the varying of electrical conductivity within the AMD solution during the investigation. Runs 1, 4 and 7 are shown in Figure 6.1, runs 2, 5 and 8 are shown in Figure 6.2 and runs 3, 6 and 9 are shown in Figure 6.6. The EC for each run varies sporadically, however, it generally decreases from the start of the run to the end of the run. EC is dependent on the ions within the solution. Metal ions precipitated from the liquid, thus decreasing the EC. Points at which an outlier lies above the trend (Figure 6.1, at 20 minutes for a concentration of 1g/L) and below the trend (Figure 6.2, at 40 minutes for a concentration of 0.4g/L) are due to insufficient times allowed EC stability to be reached.

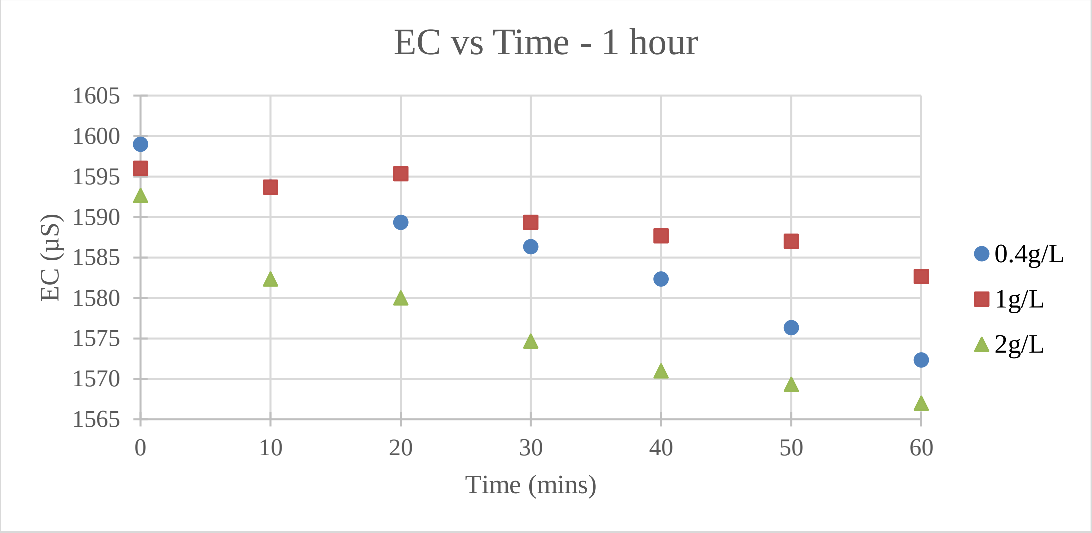

Figure 6.1: EC vs Time at varying FA/AMD Concentrations for 1 hour

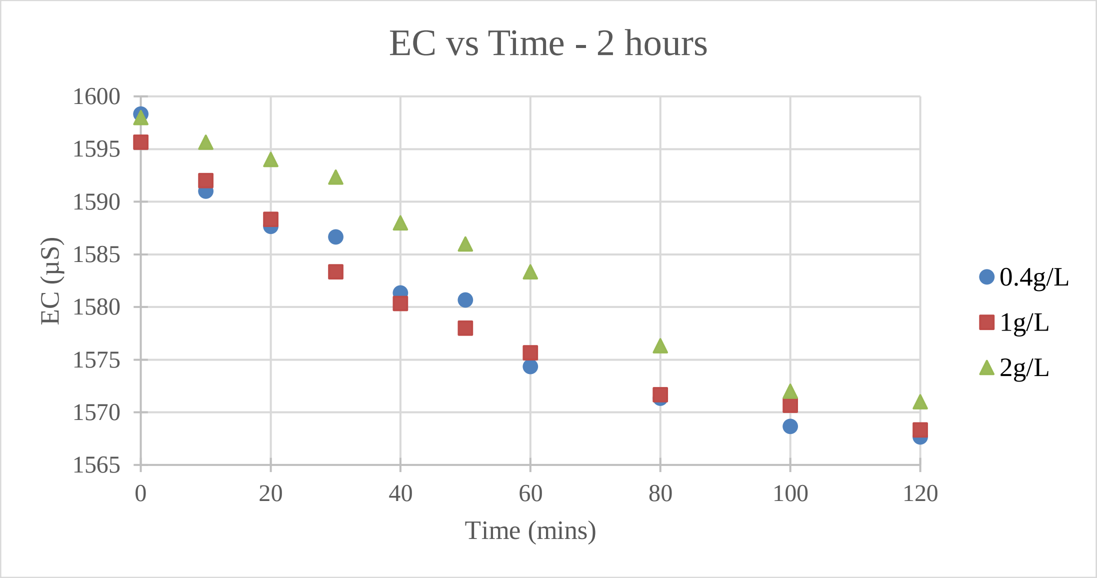

Figure 6.2: EC vs Time at varying FA/AMD Concentrations for 2 hours

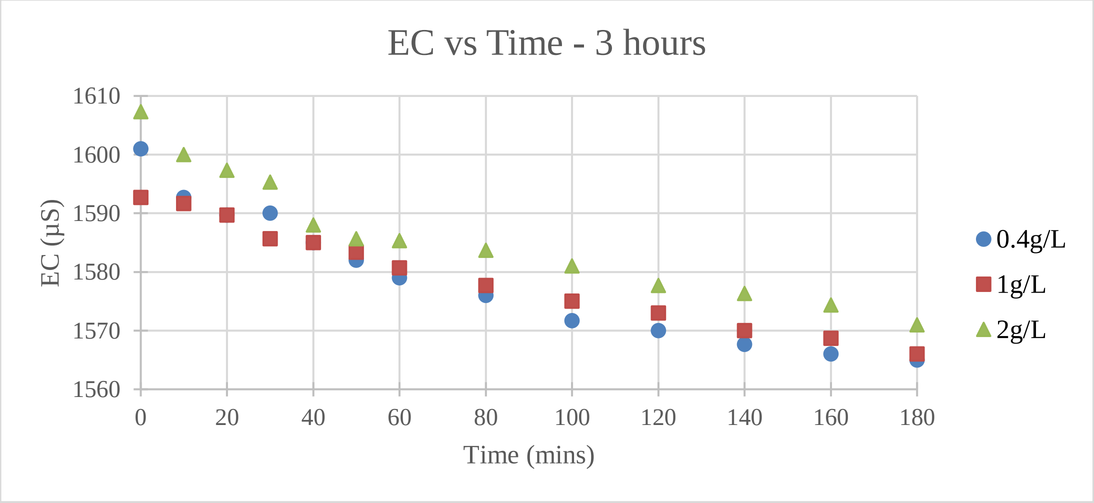

Figure 6.3: EC vs Time at varying FA/AMD Concentrations for 3 hours

6.4. pH and Reagent Dosage

The aim of this section is to compare the effect of the FA dosage on the pH of the AMD as the run proceeds. In order to compare the effects of reagent dosage on the neutralization of AMD, the reaction time needed to be kept constant. These are shown in Figures 6.4, 6.5 and 6.6.

Figure 6.4 represents the results of the 1 hour runs (Runs 1, 4 and 7). The initial pH of AMD was approximately 4.11. The pH increased quite significantly in the first 20 minutes, upon addition of the FA and reached a maximum. Thereafter, it decreased slowly and eventually stabilised by staying at a constant pH. For a reagent dosage of 2g/L, a final pH of 9,43 was obtained. For the 1g/L reagent dosage, a pH of 8.17 was obtained. Both these lean towards the alkalinity side of the pH scale and were expected. When a reagent dosage concentration of 0.4g/L was used, a pH of 5.61 was achieved. This leans towards the acidic side of the pH scale.

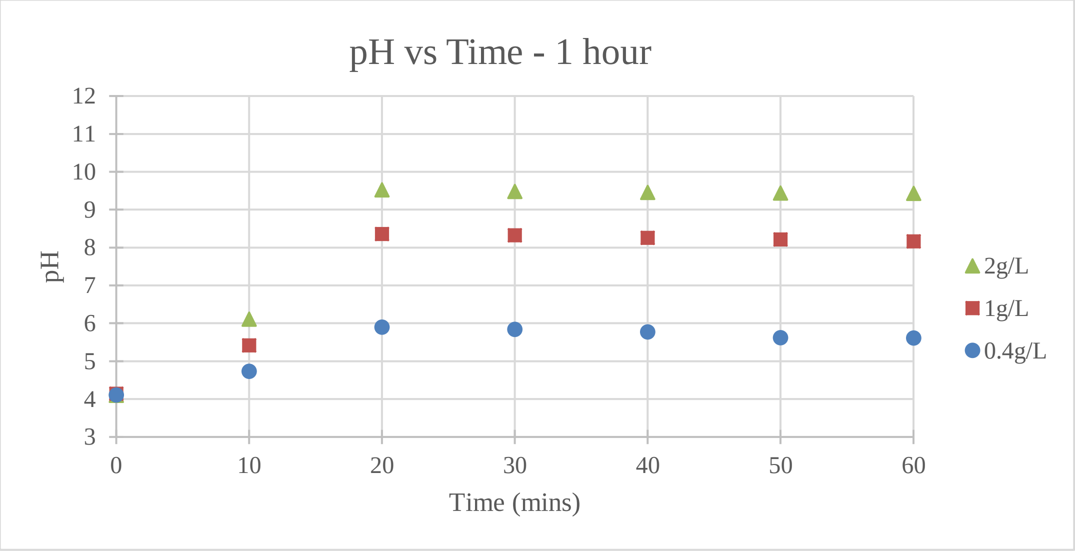

Figure 6.4: pH vs Time at varying FA/AMD Concentrations for 1 hour

Figure 6.5 represents the results of the 2 hour runs (Runs 2, 5 and 8). The initial pH of AMD was approximately 4.10. Upon addition of the FA, the pH increased rapidly and reached a maximum at approximately 20 minutes. Then it decreased gradually and eventually started to even out. Stabilisation of the pH was obtained and it continued to stay at this level for the remaining minutes of the run. For a reagent dosage of 2g/L, a final pH of 9,35 was obtained. For the 1g/L reagent dosage, a pH of 8.00 was obtained. Both of these show the AMD is now alkaline. When a reagent dosage concentration of 0.4g/L was used, a pH of 5.56 was achieved. This shows the AMD is still acidic, however, it isn’t that strong anymore.

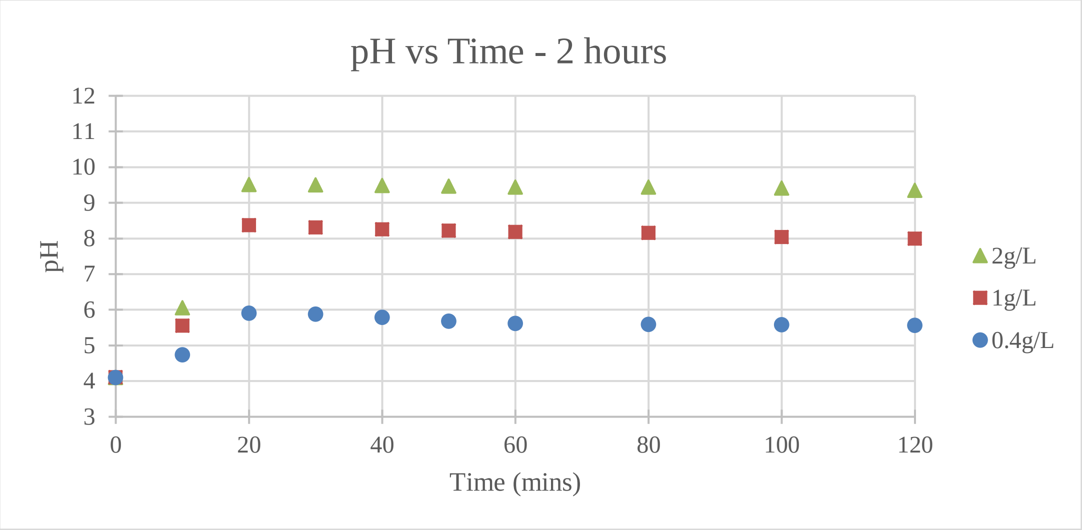

Figure 6.5: pH vs Time at varying FA/AMD Concentrations for 2 hours

Figure 6.6 represents the results of the 3 hour runs (Runs 3, 6 and 9). The initial pH of AMD was approximately 4.12 at room temperature The pH increased drastically in the first 20 minutes, upon addition of the FA, thereafter, it reached a maximum. The pH then decreased slowly and eventually stabilised by staying at a constant pH. For a reagent dosage of 2g/L, a final pH of 9,31 was obtained. For the 1g/L reagent dosage, a pH of 7.95 was obtained. Both these represent an alkaline AMD sample. When a reagent dosage concentration of 0.4g/L was used, a pH of 5.53 was achieved. The AMD is still acidic.

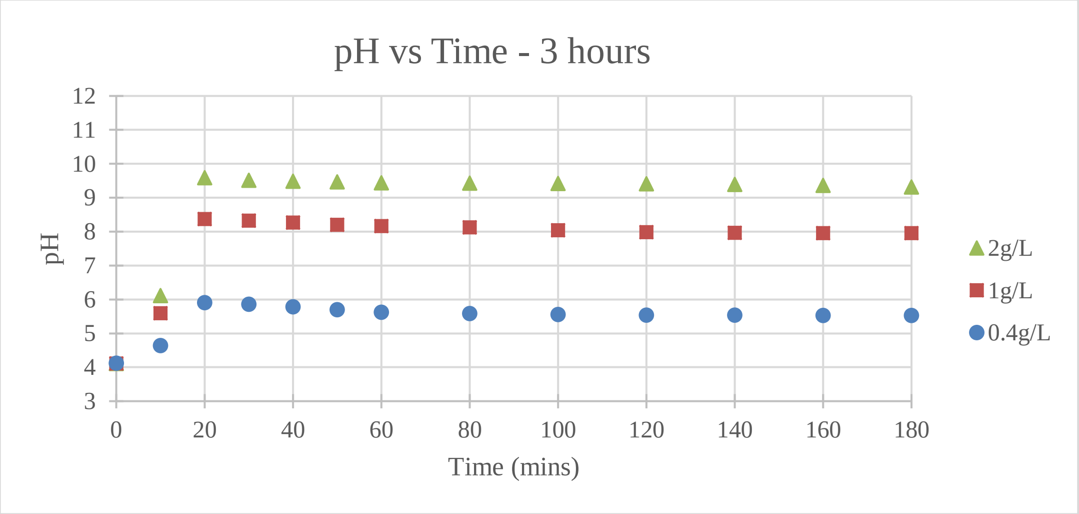

Figure 6.6: pH vs Time at varying FA/AMD Concentrations for 3 hours

Figures 6.4, 6.5 and 6.6 all exhibited similar behaviour. Upon addition of the FA, they increased exponentially within the first 30 minutes. This is an indication of a fast reaction. Once the maximum pH was reached, the pH gradually decreased as the reaction reached completion, within the first hour, allowing for solution stability to occur and the pH to stay constant. An increase in reaction time did affect the final pH, however, this change is quite small. As the dosage concentration increased, the pH increased as well. This was expected (Surender, 2009). An optimum reagent dosage concentration which yields a neutral waste liquor (pH of 7) may lie between 0.4g/L and 1g/L.

6.5. Precipitate and Waste Liquor Analysis

Analysis of the precipitate and waste liquor formed during the investigation is important as this gives a representation of the reactions that were carried out and the change in elemental compositions.

Table 6.3 shows the change in the elements within the waste liquor:

Table 6.3: ICP Analysis of FA Runs

Element	**Concentration (ppm)**									
	AMD	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**	**Run 6**	**Run 7**	**Run 8**	**Run 9**
Al	2.050	0.084	0.071	0.056	0.036	0.022	0.005	0.106	0.084	0.059
B	0.194	0.104	0.096	0.091	0.086	0.056	0.038	0.077	0.024	0.014
Ca	210.20	219.60	217.54	216.71	225.00	223.80	221.10	229.81	226.26	223.12
Co	0.147	0.143	0.139	0.132	0.140	0.130	0.122	0.138	0.129	0.119
Cr	0.020	0.018	0.015	0.011	0.015	0.012	0.009	0.012	0.009	0.007
Cu	3.120	0.019	0.015	0.012	0.030	0.025	0.021	0.010	0.008	0.007
Mn	499.20	495.23	489.25	479.12	477.80	465.23	442.65	339.70	321.63	315.26
Fe	70.23	65.23	61.27	58.72	40.12	35.62	33.47	35.23	31.17	29.24
S	772.23	512.88	502.31	490.54	453.12	421.89	409.32	387.26	366.11	350.54
Si	6.467	5.860	5.812	5.787	6.277	5.570	5.564	5.187	5.107	5.098
Sr	1.330	1.161	1.158	1.148	1.229	1.204	1.196	1.414	1.277	1.271
Zn	0.090	0.072	0.063	0.057	0.040	0.032	0.029	0.011	0.008	0.004

Comparing runs 1, 4 and 7 show that with an increase in FA dosage, the amount of calcium in the solution increases. The amount of sulphur also decreased significantly. The concentration of manganese decreased as well and all these played a part in increasing the pH of the solution. Comparing runs 1, 2 and 3 show that with an increase in reaction time, the elemental concentration of all the elements analysed decreases. This was expected until the reaction reached solution stability and elemental compositions remained constant.

Table 6.4 represents the XRF analysis of the solid precipitate that formed:

Table 6.4: XRF Analysis of FA Runs

Compound	**Mass Weight Percentage (%)**									
	FA	**Run 1**	**Run 2**	**Run 3**	**Run 4**	**Run 5**	**Run 6**	**Run 7**	**Run 8**	**Run 9**
Al_2O_3	28.73	26.21	28.83	27.97	23.87	27.58	28.40	29.33	28.89	28.12
CaO	6.72	6.06	5.31	5.65	5.76	5.66	5.28	4.49	4.68	4.72
Cr_2O_3	0.02	<0.01	<0.01	<0.01	<0.01	<0.01	1.95	<0.01	0.01	<0.01
Fe_2O_3	3.78	3.35	3.47	4.25	3.84	3.71	3.23	3.18	3.14	4.18
K_2O	0.45	0.50	0.46	0.45	0.41	0.42	0.43	0.45	0.45	0.46
MgO	1.87	2.81	2.17	2.28	2.15	2.10	2.02	1.85	1.66	1.38
MnO	0.05	0.17	0.15	0.11	0.15	0.13	0.11	0.10	0.13	0.09
Na_2O	0.03	<0.01	<0.01	<0.01	0.07	0.06	0.04	0.05	0.04	<0.01
P_2O_5	0.42	0.45	0.40	0.39	0.44	0.41	0.39	0.37	0.37	0.41
SiO_2	50.84	47.00	49.99	49.03	49.96	49.70	49.36	50.86	51.62	49.43
TiO_2	1.64	1.58	1.50	1.66	1.63	1.62	1.62	1.65	1.63	1.71
LOI	4.72	9.76	6.82	6.39	8.01	7.23	5.69	6.45	6.75	7.76
Other	0.74	2.13	0.91	1.81	3.71	1.38	1.48	1.23	0.63	1.73
Total	100	100	100	100	100	100	100	100	100	100

Upon comparison of runs 1, 4 and 7, it can be seen that an increase in FA dosage results in a decrease in the precipitates CaO concentration. This was expected as the amount of calcium did increase in their respective waste liquors (Surender, 2009). CaO is a fairly strong base so it reacts with acid to form water and a calcium salt ($CaCl_2$). By comparing reaction time, using runs 7, 8 and 9, it can be seen that it had a very small effect on the change in compounds within the precipitate. This proves the other compounds did not take part in the neutralization reaction.

6.6. Conclusions

The following conclusions were made from this chapter:

- The final pH obtained at different time intervals (1, 2 and 3 hours) decreased by small values when the dosage concentration was kept constant.
- Electrical conductivity measurements for each run changed gradually, however a trend is observed between the initial and final EC - it generally decreases due to ions precipitating from the solution.
- Upon addition of the FA neutralizing reagent, the pH increased rapidly within the first 20 minutes, reached a peak then slowly decreased until it levelled off. This trend was observed in all 9 runs, resulting in solution stability.

- An increase in reaction time (3 hours) results in a lower pH. However, this change is small when compared to a reaction time of 1 hour, as the pH after 20 minutes begins to stabilise.
- An increase in reagent dosage results in an increase of the waste liquor’s final pH. An optimum dosage can be found between an FA dosage concentration of 0.4g/L and 1g/L.
- An increase in FA dosage increased the amount of calcium present and decreased the amount of sulphur in the waste liquor – resulting in an increase in pH.
- Reaction time played a minor role in decreasing the elemental and compound concentrations within the waste liquor and precipitate.
- The change in the precipitate compounds didn’t change much as majority of the neutralization reaction products remained in the waste liquor.

Chapter 7 – Results & Discussion: Neutralizing Capabilities of Green Liquor Dregs

7.1. Introduction

The focus of this chapter is to present the results obtained from the investigation of acid mine drainage neutralization with varying contact times and different dosage concentrations of green liquor dregs. With regards to Section 4.2, it can be seen that this chapter deals with runs 10 through 18. Table 7.1 summarises the different combinations used for this part of the investigation:

Table 7.1: Experimental Run Combinations

Run	A – Time (hrs)	B – Concentration (g/L)
10	1	0.4
11	2	0.4
12	3	0.4
13	1	1
14	2	1
15	3	1
16	1	2
17	2	2
18	3	2

The pH and electrical conductivities are presented below, along with the chemical analysis of the precipitate and waste liquor formed. Two repeatability tests were conducted along with the control run. The average was taken and the results have been graphically presented below. The full set of raw data is available in Appendix A.

7.2. pH and Reaction Time

This section exhibits the effect of reaction time on the pH of each run.

Table 7.2: pH at Time Intervals for GLD/AMD Concentrations

Time (s)	0	60	120	180
pH – 0.4g/L	4.11	7.11	6.99	6.93
pH – 1g/L	4.10	8.79	8.49	8.35
pH – 2g/L	4.11	9.38	9.09	8.92

Table 7.2 represents the changes in the pH of the AMD at different periods of time as the dosage concentrations of GLD change. A similar trend is observed with all three dosage concentrations. As the time allowed for contact between GLD and AMD increases, the final pH obtained decreases slightly, after the sharp increase upon addition of the reagent. It can be concluded that the longer the reaction is allowed to proceed, the lower the final pH of the AMD comes to be. However, the change is quite small, and almost insignificant.

7.3. Electrical Conductivity

The EC of the AMD is an important factor and is shown in this section.

Figures 7.1, 7.2 and 7.3 depict the varying of electrical conductivity within the AMD solution during the investigation. Runs 10, 13 and 16 are shown in Figure 7.1, runs 11, 14 and 17 are shown in Figure 7.2 and runs 12, 15 and 18 are shown in Figure 7.3. The runs in which a GLD dosage concentration of 2g/L was used, showed the largest EC increase. This may be due to the amount of heavy metals present in GLD which increase the EC in the solution. This may pose another problem however they can be used via electrolysis methods if need be. The EC increases vastly within the first 10 minutes, then begins to level off with small increases until completion of the run. The reason the solution EC increases is due to the increase in metal ions within the solution as a result of the neutralization reaction that takes place. Reaction time doesn’t affect the EC significantly for the 0.4g/L and 1g/L runs. For the 2g/L run, the EC does increase with time. The reason may be that the heavy metal content is continuously increasing.

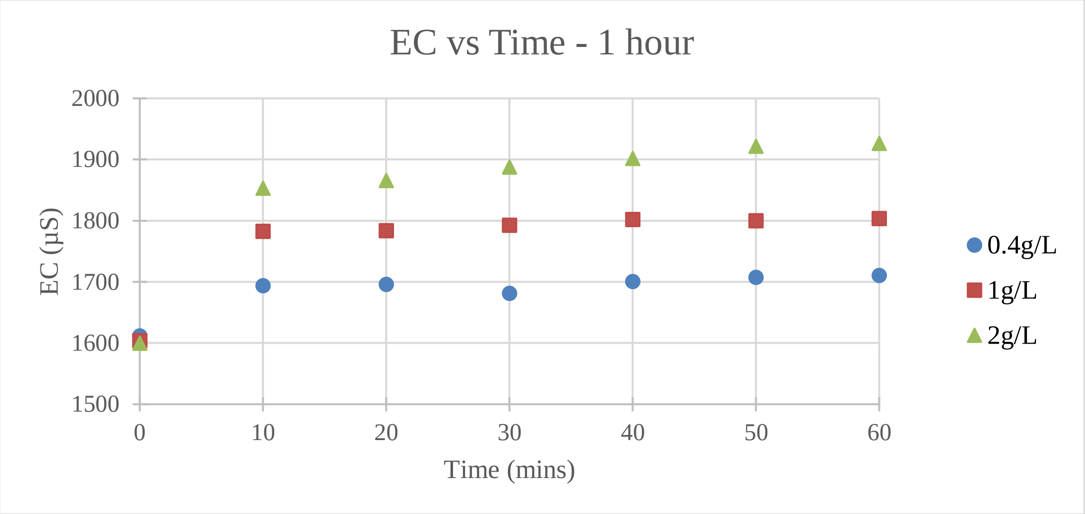

Figure 7.1: EC vs Time at varying GLD/AMD Concentrations for 1 hour

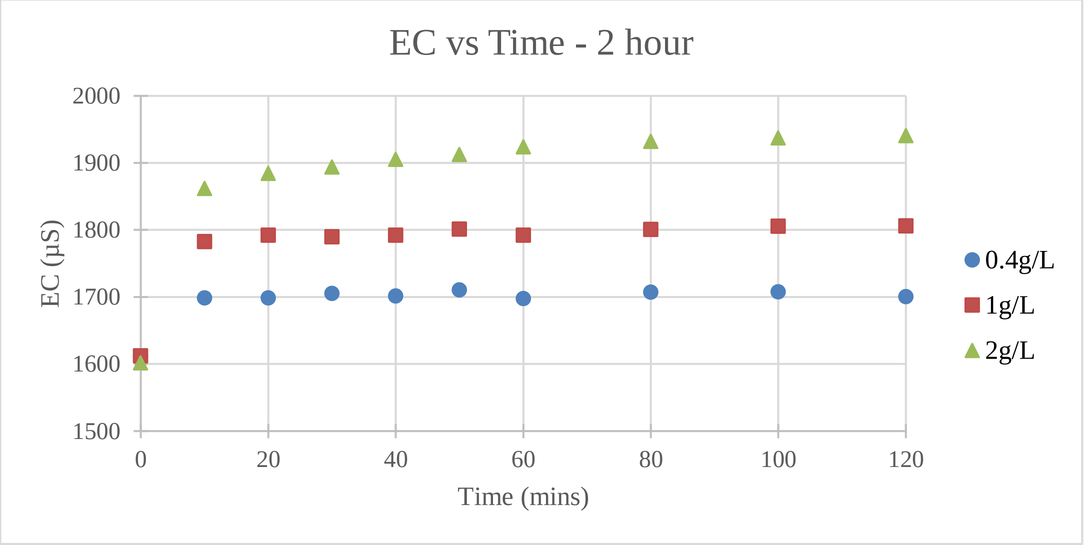

Figure 7.2: EC vs Time at varying GLD/AMD Concentrations for 2 hours

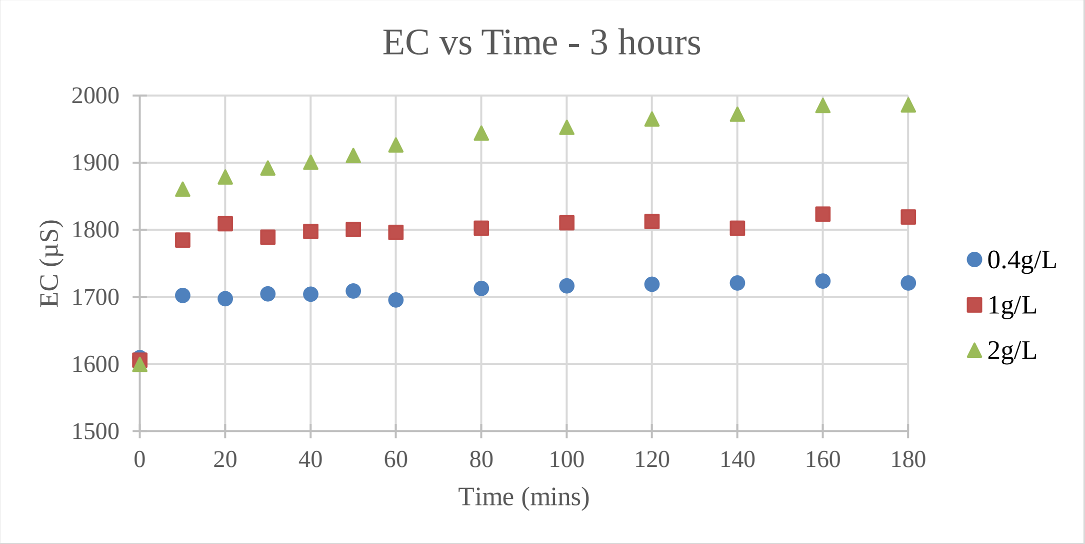

Figure 7.3: EC vs Time at varying GLD/AMD Concentrations for 3 hours

7.4. pH and Reagent Dosage

In order to compare the effects of GLD dosage on the neutralization of AMD, the reaction time needed to be kept constant. These are shown in Figures 7.4, 7.5 and 7.6.

Figure 7.4 represents the results of the 1 hour runs (Runs 10, 13 and 16). The initial pH of AMD was approximately 4.10. It can be seen that the pH increased substantially within the first 10 minutes, and reached a maximum. Thereafter, it decreased slowly and eventually stabilised at a constant pH. For a reagent dosage of 2g/L, a final pH of 9,38 was obtained. For the 1g/L reagent dosage, a pH of 8.79 was obtained. Both these dosages result in an alkaline AMD being obtained. When a reagent dosage concentration of 0.4g/L was used, a pH of 7.11 was achieved. This is slightly above a neutral pH of 7 and the dosage can be changed slightly to obtain neutrality.

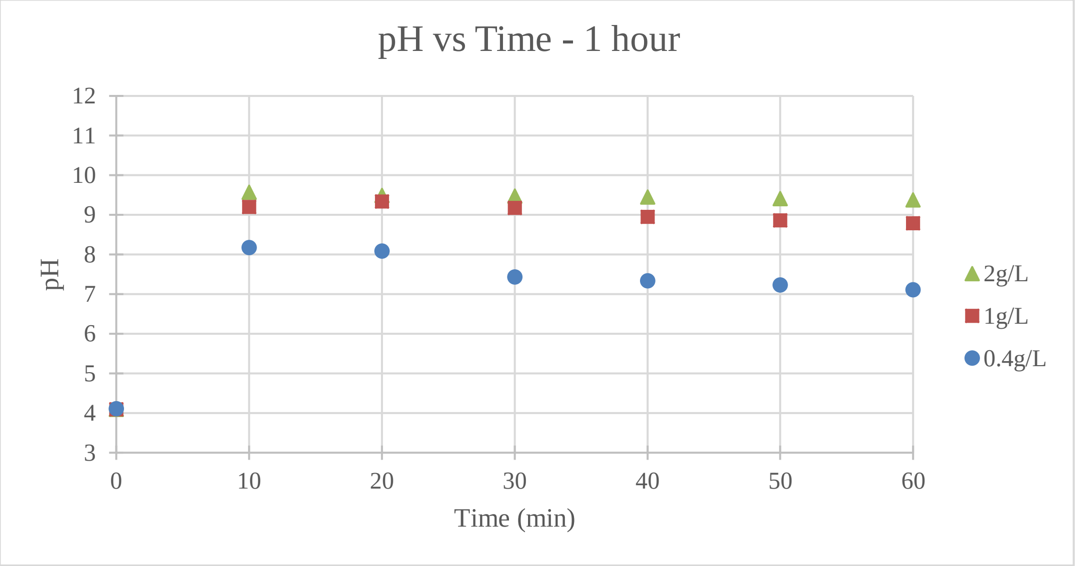

Figure 7.4: pH vs Time at varying GLD/AMD Concentrations for 1 hour

Figure 7.5 represents the results of the 2 hour runs (Runs 11, 14 and 17). The initial pH of AMD was approximately 4.11. Upon addition of the GLD, the pH increased significantly within the first 10 minutes and reached its maximum. Thereafter, the pH slowly decreased and stabilised by reaching a constant pH. For a reagent dosage of 2g/L, a final pH of 9,09 was obtained. For the 1g/L reagent dosage, a pH of 8.49 was obtained. This shows with an increased GLD dosage, the pH also increases and lies within the alkaline side of the pH scale. When a reagent dosage concentration of 0.4g/L was used, a pH of 6.99 was achieved. This is extremely close to neutrality, hence the optimum dosage should be quite close to this value.

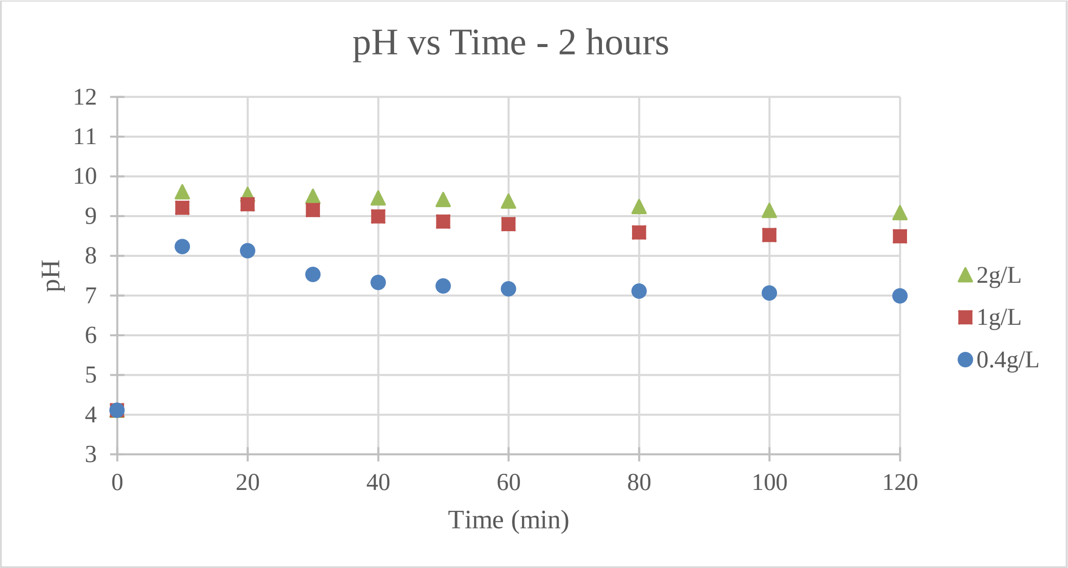

Figure 7.5: pH vs Time at varying GLD/AMD Concentrations for 2 hours

Figure 7.6 represents the results of the 3 hour runs (Runs 12, 15 and 18). An initial AMD pH of approximately 4.11 was noted. The pH increased substantially, upon addition of the GLD within the first 10 minutes once again. A maximum was reached and this result is consistent with the other shorter timed runs in this section. The pH then continued to decrease and reached a constant pH after 80 minutes. For a reagent dosage of 2g/L, a final pH of 8.92 was obtained. For the 1g/L reagent dosage, a pH of 8.35 was obtained. Both these values obtained show the AMD is quite alkaline. When a reagent dosage concentration of 0.4g/L was used, a pH of 6.93 was achieved. This is below neutrality and shows that time did not play a big effect on the final pH obtained as the change is quite small.

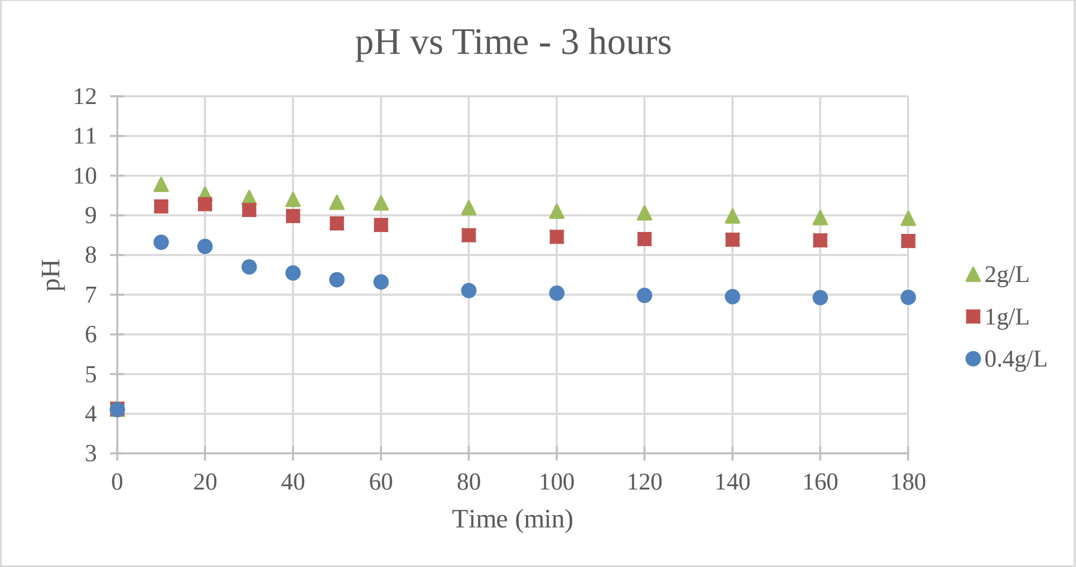

Figure 7.6: pH vs Time at varying GLD/AMD Concentrations for 3 hours

Figures 7.4, 7.5 and 7.6 all exhibit similar behaviour and this was expected. Within the first 10 minutes of adding the GLD, they increased exponentially. The main reason being how fast the reaction occurs. Once the maximum pH was reached, the pH gradually decreased as the reaction reached completion and stability of the solution occurred. It can be seen that the reaction reached completion around 60 minutes. An increase in reaction time did affect the final pH, however this change was minuscule. With an increased GLD dosage, an increase in the final pH was obtained. This was expected as more of an alkaline substance increases a solution's pH. With reference to run 11, a pH of 6.99 was obtained and neutrality was almost reached within the 2 hours. This value can be improved in the 3 hour set reaction time and an optimum dosage should lie between a GLD/AMD concentration of 0.4g/L and 1g/L.

7.5. Precipitate and Waste Liquor Analysis

This section represents the results obtained from the analysis of the precipitate and waste liquor formed during the investigation. This displays the change in the elemental compositions due to the reactions that occurred.

Table 7.3 shows the change in the elements within the waste liquor:

Table 7.3: ICP Analysis of GLD Runs

Element	**Concentration (ppm)**									
	AMD	**Run 10**	**Run 11**	**Run 12**	**Run 13**	**Run 14**	**Run 15**	**Run 16**	**Run 17**	**Run 18**
Al	2.050	0.078	0.052	0.041	0.055	0.047	0.034	0.047	0.035	0.021
B	0.194	0.154	0.148	0.139	0.095	0.087	0.081	0.089	0.082	0.075
Ca	210.20	214.20	212.19	211.65	186.90	185.21	184.10	125.90	124.10	122.50
Co	0.147	0.141	0.138	0.134	0.139	0.132	0.126	0.135	0.129	0.121
Cr	0.020	0.019	0.014	0.011	0.018	0.014	0.012	0.018	0.015	0.012
Cu	3.120	0.032	0.029	0.025	0.021	0.017	0.011	0.015	0.011	0.008
Mn	499.20	329.71	327.50	326.12	265.60	264.40	262.95	107.21	105.10	104.23
Fe	70.23	44.16	41.14	38.78	35.74	31.19	26.14	25.62	19.98	15.11
S	772.23	439.78	429.12	415.56	327.31	320.43	315.77	215.66	209.13	204.45
Si	6.467	4.567	4.278	4.164	3.905	3.782	3.619	3.837	3.615	3.562
Sr	1.330	1.321	1.089	1.073	1.305	1.037	1.028	1.162	0.848	0.832
Zn	0.090	0.084	0.072	0.062	0.078	0.061	0.052	0.062	0.054	0.046

Comparing runs 10, 13 and 16 show that with an increase in GLD dosage, the amount of calcium in the waste liquor decreases. The concentration of sulphur and manganese also decreased. A combination of these increased the pH of the final solution. Comparing time, using runs 16, 17 and 18, the elemental composition decreases but not substantially.

Table 7.4 represents the XRF analysis of the solid precipitate that formed:

Table 7.4: XRF Analysis of GLD Runs

Compound	**Mass Weight Percentage (%)**									
	GLD	**Run 10**	**Run 11**	**Run 12**	**Run 13**	**Run 14**	**Run 15**	**Run 16**	**Run 17**	**Run 18**
Al_2O_3	0.81	1.29	1.07	1.45	1.56	1.18	1.05	1.57	1.14	1.75
CaO	36.42	42.33	43.44	41.67	38.79	43.29	45.01	43.44	44.78	41.74
Cr_2O_3	0.02	<0.01	<0.01	<0.01	0.26	0.05	0.02	<0.01	0.01	<0.01
Fe_2O_3	0.67	0.94	0.75	2.54	1.68	1.92	1.06	1.78	1.00	2.43
K_2O	0.65	0.04	0.06	0.01	0.38	0.07	0.06	0.06	0.04	0.10
MgO	4.81	5.14	5.40	5.79	8.77	5.61	5.41	5.69	5.14	5.82
MnO	1.40	2.19	1.96	1.77	1.94	1.93	1.77	2.24	1.90	1.92
Na_2O	6.96	0.22	0.18	<0.01	<0.01	<0.01	0.17	0.30	0.21	0.19
P_2O_5	0.41	0.48	0.50	0.50	0.93	0.51	0.48	0.51	0.45	0.55
SiO_2	2.38	3.24	2.60	2.10	2.50	2.27	2.74	3.35	2.93	2.95
TiO_2	0.02	0.28	0.14	0.37	1.40	0.22	0.09	0.19	0.08	0.36
LOI	38.29	37.26	37.90	39.02	40.00	37.85	37.76	38.13	36.51	37.45
Other	7.15	6.58	6.01	4.77	1.79	5.10	4.38	2.74	5.80	4.74
Total	100	100	100	100	100	100	100	100	100	100

Upon comparison of runs 10, 13 and 16, it can be seen that an increase in GLD dosage results in an increase in the CaO precipitate. Na_2O decreases as it dissociates and enters the waste liquor. Both these result in an increase in the pH of the AMD waste liquor. The heavy metals leached into the waste liquor may also increase the EC and this can limit the GLD's neutralizing capability. Time does not affect the compounds concentration substantially.

7.6. Conclusions

The following conclusions were made from this chapter:

- The final pH obtained at different reaction time intervals (1, 2 and 3 hours) decreased gradually when the dosage concentration was kept constant, however it's quite insignificant.
- Electrical conductivity measurements for each run increased substantially within the first 10 minutes due to the increase in metal ions in solution. Thereafter, they slowly increased until reaching a final EC.
- Upon addition of the GLD neutralizing reagent, an increase in pH was observed within the first 10 minutes. A peak was then reached, thereafter it slowly decreased until stabilisation occurred as the pH levelled off. This trend was observed in all 9 runs.

- An increase in reaction time (3 hours) results in a lower pH, however the change is menescule. The reaction reaches completion around 60 minutes as after this, a stable pH is obtained at each time interval.
- An increase in GLD dosage results in an increase of the waste liquor’s final pH. An optimum dosage can be found between a dosage concentration of 0.4g/L and 1g/L.
- The concentration of calcium increased and, sulphur and manganese in the waste liquor decreased, thus increasing the solution pH.
- The amount of CaO in the precipitate increases with an increasing GLD dosage.
- Heavy metals leached into the AMD and increased its EC. Electrolysis can be used to reduce this problem.
- Time had a very low effect on the change in elements and compounds in both the waste liquor and precipitate.

Chapter 8 – Results & Discussion: Optimization and Comparison of Neutralizing Reagents

8.1. Introduction

The aim of this chapter is to compare the neutralizing capabilities of fly ash and green liquor dregs on acid mine drainage. An optimization study will also be presented in which the optimized reagent dosage will be calculated. The optimized runs were conducted and the results presented. Analysis was also undertaken to present the elemental and chemical compositions of the precipitate and waste liquor. The most viable reagent was then selected.

8.2. Optimization Study

An optimization study was conducted in order to determine the optimum reagent dosages that result in a neutral AMD sample (pH of 7) being obtained. The 3 hour runs were used as the reactions were completed effectively, and the final pH values were plotted. A "line of best fit" was drawn and the equation obtained was used to determine the optimum reagent dosage that results in the AMD liquor achieving a pH of 7 upon completion of the 3 hour run. The run was conducted using the optimized dosage and the 3 hour time window (to negate the solution not stabilising) and the corresponding results are presented below.

8.2.1. Fly Ash Optimization

The FA optimization curve is presented in Figure 8.1. The "line of best fit" obtained was parabolic and had a correlation coefficient of 1, with a domain between 0.4 and 2g/L. Using this equation, a FA/AMD concentration of 0.728g/L was determined. Since the tests were conducted using 500mL AMD samples, the FA dosage that gives the required concentration is 0.364g.

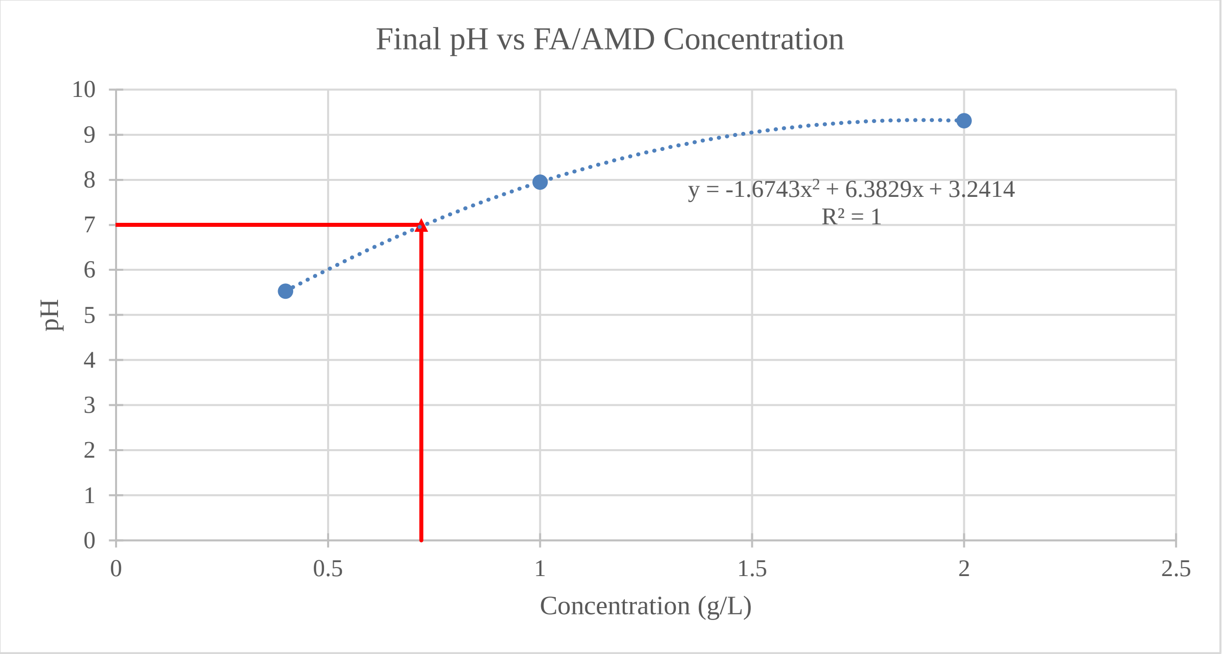

Figure 8.1: FA Optimization Curve

Using the calculated FA dosage, a final run was conducted for 3 hours to determine the final pH and electrical conductivity of the AMD.

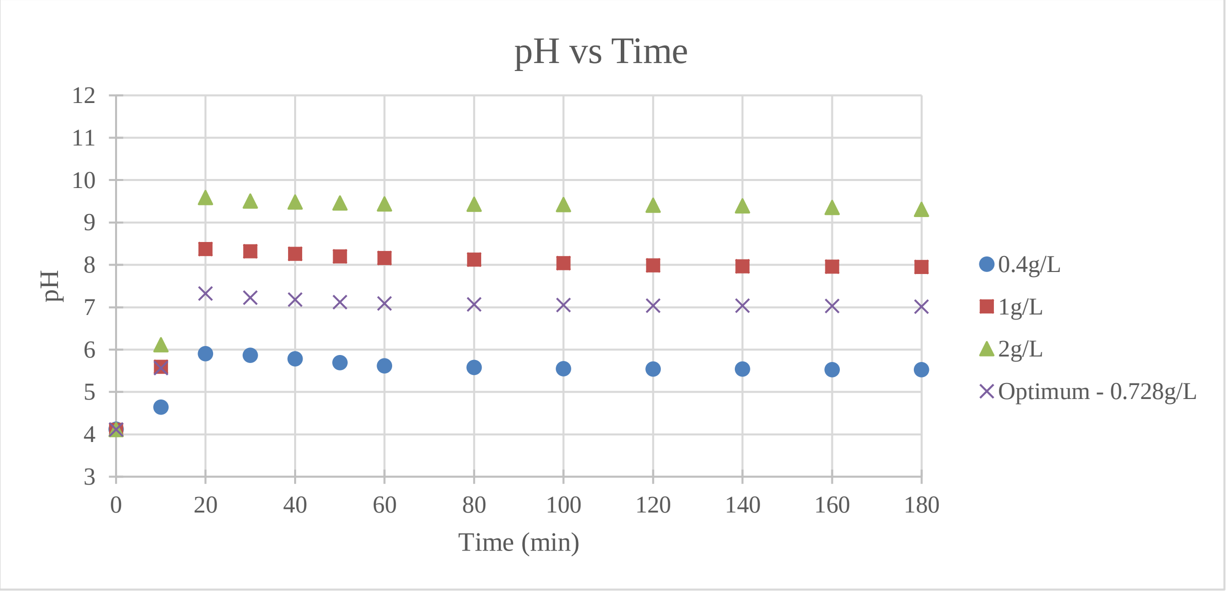

Figure 8.2: pH vs Time for the FA Runs – 3 hours

Figure 8.2 presents the optimized FA run along with the previous FA runs for ease of comparison. The final pH obtained using the FA dosage of 0.728g was 7.01. Using the theoretical value of 7, an error of 0.14% is established. This is quite low and can be accepted.

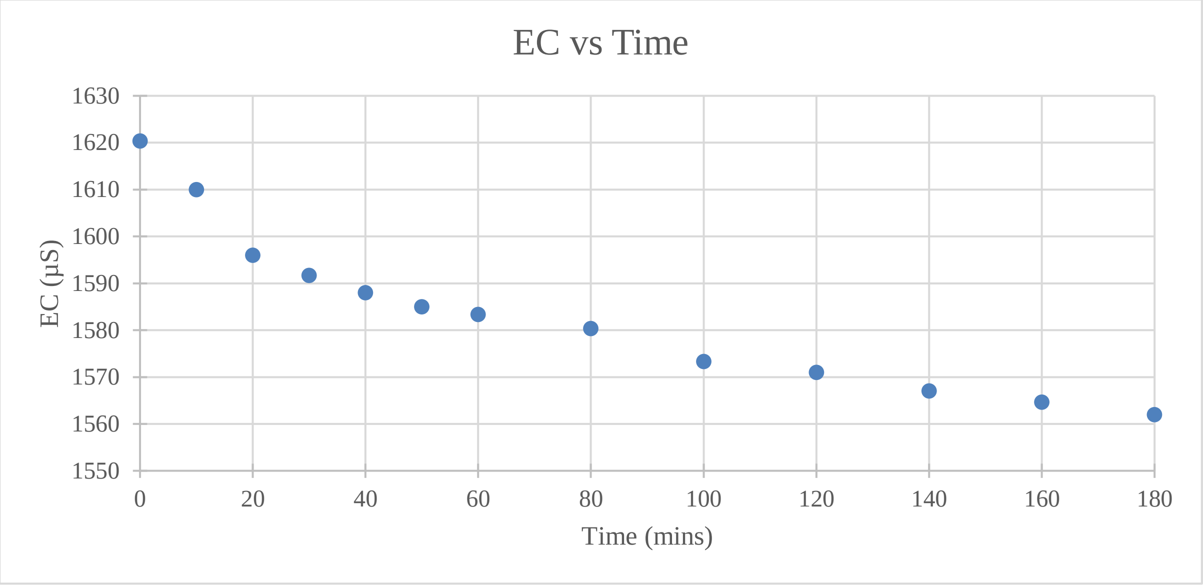

Figure 8.3: EC vs Time for the FA Optimized Run

The EC during the optimized run is shown in Figure 8.3. The initial EC was 1620µS and it gradually decreased to a final value of 1562µS at the end of the 3 hour run.

Table 8.1 presents the change in the elements within the waste liquor:

Table 8.1: ICP Analysis of Optimized FA Run

Element	Concentration (ppm)	
	AMD	**Run 19**
Al	2.050	0.061
B	0.194	0.095
Ca	210.20	214.23
Co	0.147	0.135
Cr	0.020	0.013
Cu	3.120	0.012
Mn	499.20	482.62
Fe	70.23	61.23
S	772.23	415.25
Si	6.467	5.812
Sr	1.330	1.154
Zn	0.090	0.061

The most significant change in the AMD solution is the change in sulphur from 772.23ppm to 415.25ppm. This is directly responsible for the increase in pH until neutrality was reached. The other compounds present did vary but to a very low extent.

Table 8.2 represents the XRF analysis of the solid precipitate that formed:

Table 8.2: XRF Analysis of Optimized FA Run

Compound	Mass Weight Percentage (%)	
	FA	**Run 19**
Al_2O_3	28.73	29.77
CaO	6.72	4.42
Cr_2O_3	0.02	0.02
Fe_2O_3	3.78	2.98
K_2O	0.45	0.49
MgO	1.87	1.79
MnO	0.05	0.08
Na_2O	0.03	0.05
P_2O_5	0.42	0.38
SiO_2	50.84	51.10
TiO_2	1.64	1.66
LOI	4.72	6.04
Other	0.74	1.23
Total	100	100

The amount of Al_2O_3 and SiO_2 in the precipitate increased, along with the amount of CaO decreasing. However, these weren't substantial and showed very low interaction between the components as they didn't participate in the reaction.

8.2.2. Green Liquor Dregs Optimization

The GLD optimization curve is presented in Figure 8.4. The "line of best fit" obtained was parabolic and had a correlation coefficient of 1, with a domain between 0.4 and 2g/L. Using this equation, a GLD/AMD concentration of 0.422g/L was determined. The tests were conducted using 500mL AMD samples, hence the GLD dosage that gives the required concentration is 0.211g.

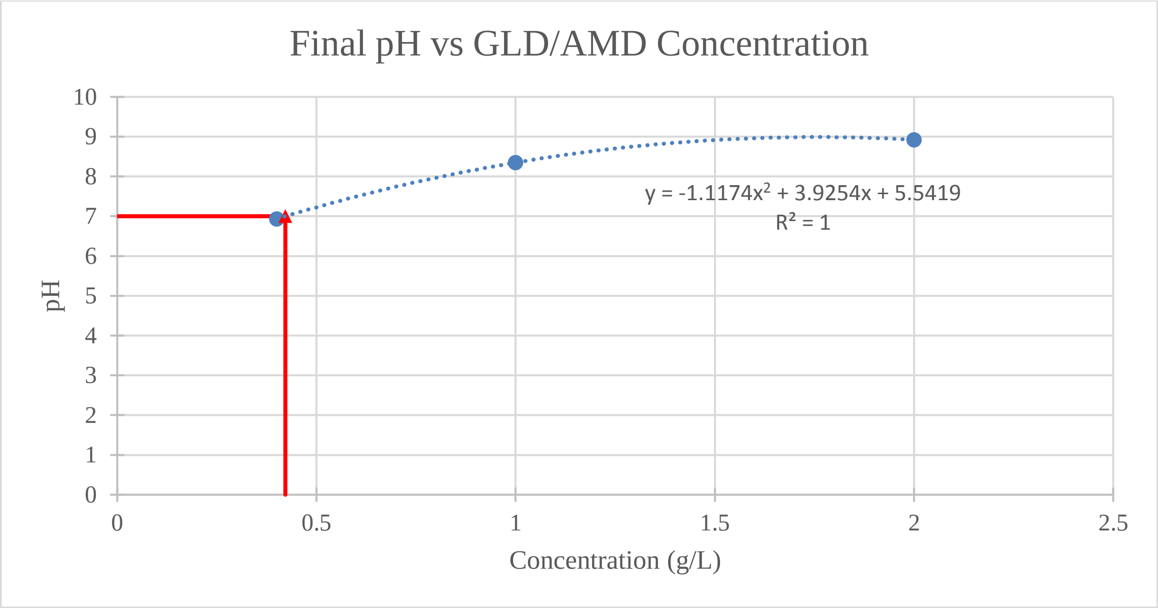

Figure 8.4: GLD Optimization Curve

Using the calculated GLD dosage, a final run was conducted for 3 hours to determine the final pH and electrical conductivity of the AMD.

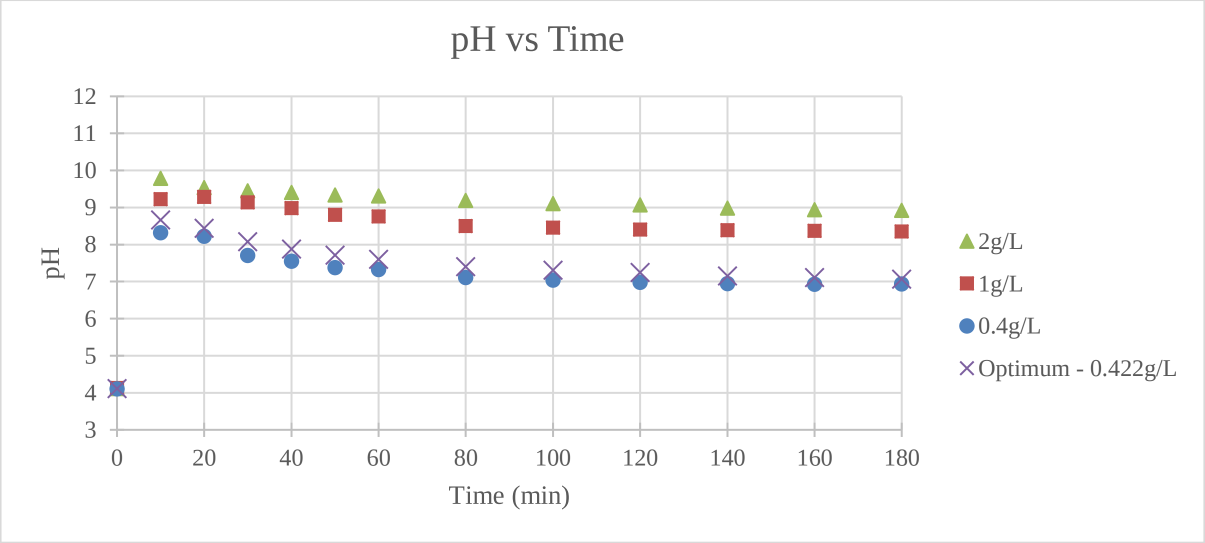

Figure 8.5: pH vs Time for the GLD Runs – 3 hours

Figure 8.5 presents the optimized GLD run along with the previous GLD runs so they can be easily compared. The final pH obtained using the FA dosage of 0.422g was 7.06. An experimental error of 0.86% was obtained, using a theoretical value of 7. This is low and can be accepted.

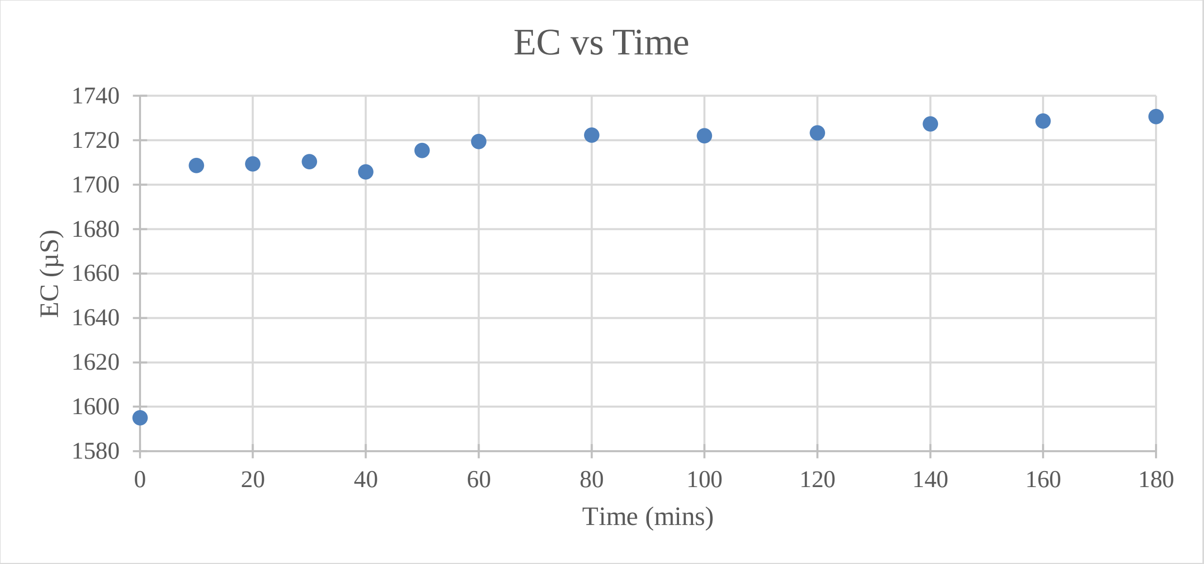

Figure 8.6: EC vs Time for the GLD Optimized Run

The EC during the optimized run is shown in Figure 8.6. The initial EC was 1595µS and it gradually increased to a final value of 1731µS at the end of the 3 hour run. Minor discrepancies in its behaviour occur at 20 and 40 minutes. This may be due to a human timing error during the reading of the results.

The behaviour of pH and EC with the change in time is similar to that of the preliminary runs. This was expected and the results obtained for this were conclusive.

Table 8.3 presents the change in the elements within the waste liquor:

Table 8.3: ICP Analysis of Optimized GLD Run

Element	Concentration (ppm)	
	AMD	**Run 20**
Al	2.050	0.152
B	0.194	0.088
Ca	210.20	201.30
Co	0.147	0.140
Cr	0.020	0.013
Cu	3.120	0.029
Mn	499.20	375.10
Fe	70.23	44.17
S	772.23	411.13
Si	6.467	5.452
Sr	1.330	1.129
Zn	0.090	0.081

The most significant change is the change in the concentration of sulphur from 772.23ppm to 411.13ppm. This allowed the reaction to occur and neutralization to be obtained. The other compounds did change and weren't very significant, apart from the change in manganese which was quite large.

Table 8.4 represents the XRF analysis of the solid precipitate that formed:

Table 8.4: XRF Analysis of Optimized GLD Run

Compound	Mass Weight Percentage (%)	
	GLD	Run 20
Al_2O_3	0.81	3.97
CaO	36.42	39.32
Cr_2O_3	0.02	<0.01
Fe_2O_3	0.67	2.21
K_2O	0.65	0.16
MgO	4.81	5.74
MnO	1.40	2.02
Na_2O	6.96	0.45
P_2O_5	0.41	0.53
SiO_2	2.38	6.90
TiO_2	0.02	0.39
LOI	38.29	37.83
Other	7.15	0.48
Total	100	100

The compounds within the precipitate varied but very slightly to the original GLD composition. This was expected as majority of the compounds do not participate in the neutralization reaction. The amount of CaO increased slightly but it was mainly dissociated in the solution thus increasing the AMD's pH.

8.3. Comparison between FA and GLD Neutralization

The aim of this study was to determine the best neutralizing agent between FA and GLD. Using the optimization part of the investigation, presented in this chapter, it can be concluded that GLD is the best neutralizing reagent. The reason being that a lower amount of GLD is required to neutralize the AMD when compared to FA. The reaction time is also much faster with GLD, however, it does take longer to stabilise. The change in sulphur concentration upon neutralization is almost the same, hence it cannot be used for effective comparison. The heavy metals leached into the waste liquor is higher for GLD when compared to FA. This may pose problems as further processing (electrolysis) will be required to reduce these heavy metals downstream. This may be much costlier downstream, however, the aim of the project was to determine the best neutralizing capability reagent. Therefore, for effective neutralization of AMD in industry, GLD should definitely be used.

8.4. Conclusions

The following conclusions can be drawn up from this chapter:

- Both FA and GLD optimizations yielded a parabolic “line of best fit”.
- The optimized FA reagent dosage concentration is 0.728g/L. This yielded a final pH of 7.01 which gives an experimental error of 0.14%.
- The EC gradually decreased which is similar to the behaviour of the preliminary FA runs.
- The final optimized FA dosage resulted in an AMD sulphur concentration decrease from 772.23ppm to 415.25ppm.
- The optimized GLD reagent dosage concentration is 0.422g/L. This yielded a final pH of 7.06 which gives an experimental error of 0.86%.
- The EC gradually increased which is similar to the behaviour of the preliminary GLD runs.
- The final optimized GLD dosage resulted in an AMD sulphur concentration decrease from 772.23ppm to 411.13ppm.
- Utilisation of GLD results in heavy metal deposition after AMD neutralization and this may cause issues. Electrolysis will need to be practiced to reduce this.
- The better neutralizing reagent is GLD as a lower dose is required, when compared to FA.

Chapter 9 – Conclusions & Recommendations

9.1. Summary of Research Findings

The following conclusions can thus be made upon completion of the investigation:

- AMD was obtained from a coal mine and is predominately made up of calcium, cadmium, magnesium, manganese, sulphur and low quantities of heavy metals (aluminium, cobalt, chromium, copper, iron and zinc). The acidity of AMD was 1111.11 mg.$CaCO_3$/L which is extremely high and may result in a large amount of hydrogen ions forming.
- The FA sample is made up of silicon and oxygen, according to SEM/EDX analysis. It also contains small quantities of calcium, titanium, iron and copper. Upon XRF analysis, it was concluded that the FA is classified as Class F.
- According to SEM/EDX analysis, the GLD sample is predominantly made up of oxygen, calcium and carbon. It also contains sodium, magnesium, aluminium, silicon, sulphur, potassium and iron. From XRF analysis, CaO is the major compound within the sample. This is responsible for GLD's alkaline nature.
- AMD has a low pH of 4.10, hence it is an acidic material. GLD and FA have a pH of 12.23 and 11.71 respectively. This indicates that they are alkaline substances.
- The final pH obtained at different time intervals (1, 2 and 3 hours) decreased gradually when the dosage concentration of FA and GLD was kept constant. The trend is non-linear.
- Electrical conductivity measurements for each FA run changed gradually, however a trend is observed between the initial and final EC - it generally decreases due to the solution precipitating ions.
- Upon addition of the FA neutralizing reagent, the pH increased rapidly within the first 20 minutes, reached a peak then slowly decreased. This trend was observed in all 9 FA runs.
- An increase in reaction time (3 hours) results in a lower pH for the FA runs. However, this change is small when compared to a reaction time of 1 hour, as the pH after 20 minutes begins to stabilise.
- An increase in reagent dosage results in an increase in the waste liquor's final pH.
- An increase in FA dosage increased the amount of calcium present and decreased the amount of sulphur in the waste liquor – resulting in an increase in pH.

- Reaction time played a minor role in decreasing the elemental and compound concentrations within the waste liquor and precipitate.
- EC measurements for each GLD run increased substantially within the first 10 minutes. Thereafter, they slowly increased until reaching a final EC.
- Upon addition of the GLD neutralizing reagent, an increase in pH was observed within the first 10 minutes. A peak was then reached, thereafter it slowly decreased until stabilisation occurred. This trend was observed in all 9 GLD runs.
- An increase in reaction time (3 hours) results in a lower pH for the GLD runs, however it's small. The reaction reaches completion around 60 minutes as after this, a stable pH is obtained at each time interval.
- The concentrations of sulphur and manganese in the waste liquor decreased, thus increasing the waste liquor's pH.
- Both FA and GLD optimizations yielded a parabolic "line of best fit".
- The optimized FA reagent dosage concentration is 0.728g/L. This yielded a final pH of 7.01 which gives an experimental area of 0.14%.
- The optimized GLD reagent dosage concentration is 0.422g/L. This yielded a final pH of 7.06 which gives an experimental area of 0.86%.
- The final optimized FA dosage resulted in an AMD sulphur concentration decrease from 772.23ppm to 415.25ppm. The final optimized GLD dosage resulted in an AMD sulphur concentration decrease from 772.23ppm to 411.13ppm.
- Using GLD results in a higher amount of heavy metal deposition, when compared to FA and this may cause serious downstream issues.
- The better neutralizing reagent is GLD as a lower dose is required and the initial reaction time is much faster, when compared to FA. However, it takes longer to stabilise. Deposition of heavy metals does occur, however this can be reduced via electrolysis methods.

9.2. Recommendations

The following recommendations can be made to improve the investigation:

- A wider range of FA and GLD dosages should be used in order to get a better "line of best fit", thus determining a more accurate optimum dosage concentration.
- The run times should be increased in order to obtain a better behaviour estimate at which the neutralization reaction undergoes.

- Other neutralizing agents such as magnesium oxide, sodium hydroxide or limestone should be investigated and compared with fly ash and green liquor dregs.
- A method should be designed to reduce the amount of heavy metals that form after the neutralization reaction has completed, e.g Electrolysis.

9.3. Future Research Suggestions

- The development of a geopolymer that can be used to line AMD ponds and allow neutralization to occur as the liquid passes through it.
- Reduction/removal of heavy metals that may form on a geopolymer that can be used for neutralization of AMD.
- The financial benefit of using GLD as a neutralizing agent by replacing its limestone predecessor.
- The removal of heavy metals that generally precipitate after the neutralization reaction.
- Scale up neutralization investigation using actual AMD water bodies and GLD.

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Appendix A – Raw Data

During the conduction of the experimental runs, raw data was recorded. This data was then analysed and a summary was presented within the report. This Appendix represents all the raw data that was recorded.

Table A1 represents the FA run for 1 hour with a dosage concentration of 0.4g/L:

Table A1: Run 1 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.10	1598	4.13	1600	4.11	1599	4.11	1599
	10	4.77	1590	4.75	1595	4.70	1596	4.74	1594
	20	5.89	1588	5.90	1590	5.91	1590	5.90	1589
	30	5.82	1589	5.86	1586	5.84	1584	5.84	1586
	40	5.76	1579	5.80	1585	5.77	1583	5.78	1582
	50	5.64	1575	5.55	1578	5.69	1576	5.63	1576
	60	5.60	1570	5.61	1573	5.63	1574	5.61	1572
2	80								
	100								
	120								
3	140								
	160								
	180								

Table A2 represents the FA run for 2 hours with a dosage concentration of 0.4g/L:

Table A2: Run 2 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.10	1598	4.11	1598	4.10	1599	4.10	1598
	10	4.74	1590	4.70	1592	4.77	1591	4.74	1591
	20	5.92	1588	5.90	1588	5.89	1587	5.90	1588
	30	5.89	1586	5.88	1586	5.85	1588	5.87	1587
	40	5.80	1582	5.80	1580	5.77	1582	5.79	1581
	50	5.66	1579	5.70	1583	5.68	1580	5.68	1581
	60	5.61	1575	5.64	1572	5.60	1576	5.62	1574
2	80	5.59	1572	5.61	1570	5.58	1572	5.59	1571
	100	5.57	1569	5.59	1567	5.59	1570	5.58	1569
	120	5.55	1566	5.57	1568	5.56	1569	5.56	1568
3	140								
	160								
	180								

Table A3 represents the FA run for 3 hours with a dosage concentration of 0.4g/L:

Table A3: Run 3 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.11	1603	4.11	1600	4.13	1600	4.12	1601
	10	4.62	1591	4.64	1595	4.66	1592	4.64	1593
	20	5.90	1589	5.89	1590	5.92	1590	5.90	1590
	30	5.87	1587	5.86	1591	5.85	1592	5.86	1590
	40	5.80	1584	5.77	1585	5.76	1586	5.78	1585
	50	5.69	1580	5.71	1582	5.68	1584	5.69	1582
	60	5.60	1576	5.63	1580	5.62	1581	5.62	1579
2	80	5.55	1573	5.59	1576	5.59	1579	5.58	1576
	100	5.54	1570	5.56	1572	5.55	1573	5.55	1572
	120	5.53	1569	5.55	1571	5.53	1570	5.54	1570
3	140	5.53	1568	5.54	1566	5.54	1569	5.54	1568
	160	5.51	1565	5.54	1566	5.53	1567	5.53	1566
	180	5.52	1564	5.53	1565	5.53	1566	5.53	1565

Table A4 represents the FA run for 1 hour with a dosage concentration of 1g/L:

Table A4: Run 4 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.15	1597	4.14	1596	4.15	1595	4.15	1596
	10	5.43	1594	5.40	1595	5.44	1592	5.42	1594
	20	8.38	1592	8.36	1593	8.35	1601	8.36	1595
	30	8.32	1589	8.33	1588	8.33	1591	8.33	1589
	40	8.25	1587	8.27	1586	8.27	1590	8.26	1588
	50	8.21	1585	8.22	1587	8.23	1589	8.22	1587
	60	8.17	1582	8.19	1583	8.15	1583	8.17	1583
2	80								
	100								
	120								
3	140								
	160								
	180								

Table A5 represents the FA run for 2 hours with a dosage concentration of 1g/L:

Table A5: Run 5 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.12	1596	4.09	1594	4.11	1597	4.11	1596
	10	5.55	1593	5.57	1591	5.54	1592	5.55	1592
	20	8.37	1589	8.39	1587	8.35	1589	8.37	1588
	30	8.31	1582	8.32	1583	8.30	1585	8.31	1583
	40	8.27	1579	8.25	1580	8.26	1582	8.26	1580
	50	8.22	1577	8.21	1578	8.22	1579	8.22	1578
	60	8.17	1574	8.20	1576	8.19	1577	8.19	1576
2	80	8.15	1571	8.17	1573	8.16	1571	8.16	1572
	100	8.01	1569	8.04	1570	8.06	1573	8.04	1571
	120	7.96	1568	8.01	1567	8.03	1570	8.00	1568
3	140								
	160								
	180								

Table A6 represents the FA run for 3 hours with a dosage concentration of 1g/L:

Table A6: Run 6 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.10	1595	4.10	1590	4.11	1593	4.10	1593
	10	5.58	1590	5.60	1592	5.59	1593	5.59	1592
	20	8.36	1588	8.38	1590	8.37	1591	8.37	1590
	30	8.30	1587	8.32	1585	8.33	1585	8.32	1586
	40	8.26	1585	8.27	1585	8.25	1585	8.26	1585
	50	8.20	1582	8.21	1583	8.19	1585	8.20	1583
	60	8.15	1579	8.17	1581	8.17	1582	8.16	1581
2	80	8.12	1576	8.11	1579	8.13	1578	8.12	1578
	100	8.03	1574	8.05	1575	8.03	1576	8.04	1575
	120	7.98	1572	8.00	1573	7.97	1574	7.98	1573
3	140	7.96	1569	7.97	1570	7.96	1571	7.96	1570
	160	7.95	1567	7.96	1569	7.95	1570	7.95	1569
	180	7.94	1564	7.95	1566	7.96	1568	7.95	1566

Table A7 represents the FA run for 1 hour with a dosage concentration of 2g/L:

Table A7: Run 7 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.10	1593	4.12	1592	4.10	1593	4.11	1593
	10	6.11	1584	6.13	1581	6.09	1582	6.11	1582
	20	9.53	1581	9.55	1579	9.50	1580	9.53	1580
	30	9.50	1578	9.49	1575	9.47	1571	9.49	1575
	40	9.47	1574	9.46	1571	9.44	1568	9.46	1571
	50	9.46	1571	9.44	1569	9.42	1568	9.44	1569
	60	9.45	1570	9.43	1567	9.42	1564	9.43	1567
2	80								
	100								
	120								
3	140								
	160								
	180								

Table A8 represents the FA run for 2 hours with a dosage concentration of 2g/L:

Table A8: Run 8 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.09	1600	4.11	1599	4.09	1595	4.10	1598
	10	6.05	1595	6.07	1594	6.06	1598	6.06	1596
	20	9.52	1596	9.53	1592	9.50	1594	9.52	1594
	30	9.50	1594	9.49	1592	9.51	1591	9.50	1592
	40	9.49	1587	9.48	1588	9.49	1589	9.49	1588
	50	9.45	1586	9.46	1587	9.48	1585	9.46	1586
	60	9.43	1579	9.44	1583	9.46	1588	9.44	1583
2	80	9.42	1579	9.44	1578	9.45	1572	9.44	1576
	100	9.40	1573	9.43	1570	9.42	1573	9.42	1572
	120	9.36	1569	9.36	1571	9.34	1573	9.35	1571
3	140								
	160								
	180								

Table A9 represents the FA run for 3 hours with a dosage concentration of 2g/L:

Table A9: Run 9 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.11	1609	4.12	1607	4.10	1606	4.11	1607
	10	6.11	1598	6.13	1600	6.09	1602	6.11	1600
	20	9.57	1596	9.59	1598	9.61	1598	9.59	1597
	30	9.51	1595	9.52	1595	9.49	1596	9.51	1595
	40	9.48	1589	9.49	1587	9.47	1588	9.48	1588
	50	9.46	1585	9.47	1586	9.45	1586	9.46	1586
	60	9.43	1583	9.44	1588	9.44	1585	9.44	1585
2	80	9.42	1581	9.43	1586	9.43	1584	9.43	1584
	100	9.42	1579	9.42	1583	9.42	1581	9.42	1581
	120	9.40	1577	9.42	1579	9.40	1577	9.41	1578
3	140	9.38	1576	9.40	1577	9.39	1576	9.39	1576
	160	9.35	1574	9.36	1575	9.36	1574	9.36	1574
	180	9.32	1572	9.30	1570	9.31	1571	9.31	1571

Table A10 represents the GLD run for 1 hour with a dosage concentration of 0.4g/L:

Table A10: Run 10 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.12	1612	4.12	1613	4.11	1610	4.12	1612
	10	8.17	1697	8.19	1689	8.17	1695	8.18	1694
	20	8.09	1700	8.12	1695	8.07	1692	8.09	1696
	30	7.40	1679	7.49	1680	7.42	1685	7.44	1681
	40	7.32	1698	7.36	1699	7.33	1705	7.34	1701
	50	7.26	1703	7.25	1710	7.20	1709	7.24	1707
	60	7.12	1706	7.10	1715	7.11	1711	7.11	1711
2	80								
	100								
	120								
3	140								
	160								
	180								

Table A11 represents the GLD run for 2 hours with a dosage concentration of 0.4g/L:

Table A11: Run 11 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.13	1607	4.09	1612	4.12	1615	4.11	1611
	10	8.22	1702	8.25	1695	8.23	1698	8.23	1698
	20	8.12	1699	8.14	1702	8.11	1695	8.12	1699
	30	7.50	1706	7.55	1710	7.54	1700	7.53	1705
	40	7.33	1702	7.36	1703	7.30	1699	7.33	1701
	50	7.21	1709	7.26	1710	7.25	1712	7.24	1710
	60	7.14	1698	7.17	1701	7.19	1694	7.17	1698
2	80	7.09	1710	7.12	1705	7.13	1707	7.11	1707
	100	7.05	1705	7.04	1712	7.09	1706	7.06	1708
	120	6.99	1701	7.00	1695	6.97	1705	6.99	1700
3	140								
	160								
	180								

Table A12 represents the GLD run for 3 hours with a dosage concentration of 0.4g/L:

Table A12: Run 12 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.09	1605	4.11	1609	4.11	1615	4.10	1610
	10	8.30	1699	8.34	1702	8.32	1705	8.32	1702
	20	8.24	1697	8.20	1695	8.22	1700	8.22	1697
	30	7.69	1704	7.70	1700	7.72	1710	7.70	1705
	40	7.52	1706	7.54	1702	7.59	1704	7.55	1704
	50	7.38	1705	7.35	1710	7.40	1711	7.38	1709
	60	7.32	1693	7.31	1698	7.34	1695	7.32	1695
2	80	7.10	1713	7.12	1710	7.10	1715	7.11	1713
	100	7.04	1716	7.06	1715	7.02	1719	7.04	1717
	120	6.97	1719	7.01	1722	6.96	1715	6.98	1719
3	140	6.95	1718	6.96	1725	6.93	1720	6.95	1721
	160	6.93	1720	6.95	1729	6.90	1722	6.93	1724
	180	6.94	1715	6.96	1722	6.90	1726	6.93	1721

Table A13 represents the GLD run for 1 hour with a dosage concentration of 1g/L:

Table A13: Run 13 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.08	1604	4.11	1606	4.09	1602	4.09	1604
	10	9.19	1779	9.21	1784	9.20	1785	9.20	1783
	20	9.35	1785	9.33	1786	9.35	1780	9.34	1784
	30	9.18	1795	9.20	1790	9.16	1792	9.18	1792
	40	8.95	1801	8.99	1805	8.92	1800	8.95	1802
	50	8.86	1799	8.90	1802	8.84	1798	8.87	1800
	60	8.77	1805	8.82	1798	8.79	1807	8.79	1803
2	80								
	100								
	120								
3	140								
	160								
	180								

Table A14 represents the GLD run for 2 hours with a dosage concentration of 1g/L:

Table A14: Run 14 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.11	1612	4.09	1615	4.12	1610	4.11	1612
	10	9.20	1780	9.23	1782	9.19	1785	9.21	1782
	20	9.31	1790	9.29	1795	9.28	1792	9.29	1792
	30	9.15	1787	9.18	1790	9.13	1792	9.15	1790
	40	8.98	1795	9.01	1792	8.97	1790	8.99	1792
	50	8.84	1797	8.89	1801	8.86	1805	8.86	1801
	60	8.78	1790	8.81	1795	8.79	1792	8.79	1792
2	80	8.59	1797	8.60	1805	8.58	1800	8.59	1801
	100	8.52	1805	8.55	1810	8.50	1801	8.52	1805
	120	8.50	1810	8.49	1809	8.47	1799	8.49	1806
3	140								
	160								
	180								

Table A15 represents the GLD run for 3 hours with a dosage concentration of 1g/L:

Table A15: Run 15 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.15	1601	4.11	1611	4.12	1605	4.13	1606
	10	9.25	1789	9.20	1780	9.23	1785	9.23	1785
	20	9.28	1811	9.26	1805	9.30	1811	9.28	1809
	30	9.12	1787	9.15	1790	9.14	1790	9.14	1789
	40	8.95	1798	8.99	1800	9.01	1795	8.98	1798
	50	8.78	1797	8.80	1805	8.82	1800	8.80	1801
	60	8.73	1791	8.75	1795	8.78	1802	8.75	1796
2	80	8.49	1797	8.50	1801	8.51	1810	8.50	1803
	100	8.46	1818	8.46	1805	8.45	1809	8.46	1811
	120	8.40	1809	8.42	1812	8.39	1816	8.40	1812
3	140	8.39	1803	8.38	1799	8.38	1805	8.38	1802
	160	8.36	1827	8.37	1825	8.37	1819	8.37	1824
	180	8.34	1822	8.36	1819	8.35	1817	8.35	1819

Table A16 represents the GLD run for 1 hour with a dosage concentration of 2g/L:

Table A16: Run 16 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.08	1599	4.09	1601	4.11	1599	4.09	1600
	10	9.55	1852	9.56	1858	9.60	1850	9.57	1853
	20	9.47	1864	9.48	1869	9.54	1865	9.50	1866
	30	9.46	1888	9.47	1890	9.49	1885	9.47	1888
	40	9.45	1901	9.46	1899	9.44	1905	9.45	1902
	50	9.42	1922	9.42	1924	9.40	1919	9.41	1922
	60	9.37	1928	9.38	1926	9.38	1925	9.38	1926
2	80								
	100								
	120								
3	140								
	160								
	180								

Table A17 represents the GLD run for 2 hours with a dosage concentration of 2g/L:

Table A17: Run 17 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.09	1606	4.12	1600	4.12	1599	4.11	1602
	10	9.60	1860	9.65	1864	9.59	1862	9.61	1862
	20	9.55	1880	9.57	1885	9.51	1887	9.54	1884
	30	9.51	1891	9.50	1895	9.48	1896	9.50	1894
	40	9.46	1902	9.47	1908	9.45	1905	9.46	1905
	50	9.40	1910	9.44	1915	9.42	1912	9.42	1912
	60	9.35	1925	9.39	1926	9.39	1920	9.38	1924
2	80	9.21	1930	9.25	1931	9.27	1935	9.24	1932
	100	9.12	1935	9.16	1936	9.14	1940	9.14	1937
	120	9.08	1936	9.10	1940	9.09	1945	9.09	1940
3	140								
	160								
	180								

Table A18 represents the GLD run for 3 hours with a dosage concentration of 2g/L

Table A18: Run 18 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.13	1599	4.11	1601	4.10	1598	4.11	1599
	10	9.70	1856	9.81	1866	9.84	1860	9.78	1861
	20	9.54	1875	9.52	1880	9.55	1881	9.54	1879
	30	9.47	1890	9.45	1895	9.43	1892	9.45	1892
	40	9.42	1901	9.40	1903	9.39	1899	9.40	1901
	50	9.35	1910	9.33	1911	9.32	1912	9.33	1911
	60	9.33	1928	9.31	1925	9.30	1926	9.31	1926
2	80	9.19	1942	9.20	1945	9.18	1946	9.19	1944
	100	9.11	1953	9.12	1956	9.09	1950	9.11	1953
	120	9.06	1970	9.07	1960	9.07	1965	9.07	1965
3	140	8.95	1972	8.96	1975	9.03	1970	8.98	1972
	160	8.92	1982	8.94	1989	8.96	1985	8.94	1985
	180	8.91	1984	8.92	1986	8.94	1988	8.92	1986

Table A19 represents the optimized FA run for 3 hours with a dosage concentration of 0.728g/L:

Table A19: Run 19 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.11	1620	4.12	1622	4.11	1619	4.11	1620
	10	5.54	1609	5.60	1611	5.55	1610	5.56	1610
	20	7.29	1595	7.33	1597	7.35	1596	7.32	1596
	30	7.19	1592	7.22	1593	7.25	1590	7.22	1592
	40	7.16	1587	7.17	1590	7.20	1587	7.18	1588
	50	7.11	1585	7.10	1586	7.15	1584	7.12	1585
	60	7.09	1584	7.07	1584	7.11	1582	7.09	1583
2	80	7.07	1580	7.04	1582	7.09	1579	7.07	1580
	100	7.06	1576	7.05	1572	7.03	1572	7.05	1573
	120	7.04	1572	7.03	1571	7.04	1570	7.04	1571
3	140	7.05	1569	7.03	1567	7.03	1565	7.04	1567
	160	7.03	1566	7.02	1564	7.02	1564	7.02	1565
	180	7.02	1564	6.99	1560	7.02	1562	7.01	1562

Table A20 represents the optimized GLD run for 3 hours with a dosage concentration of 0.422g/L:

Table A20: Run 20 Raw Data

Time		A		B		C		Average	
hours	min	pH	EC	pH	EC	pH	EC	pH	EC
1	0	4.13	1595	4.10	1590	4.11	1600	4.11	1595
	10	8.65	1711	8.70	1705	8.63	1710	8.66	1709
	20	8.40	1713	8.51	1710	8.40	1705	8.44	1709
	30	8.08	1705	8.05	1715	8.10	1711	8.08	1710
	40	7.85	1707	7.89	1700	7.88	1710	7.87	1706
	50	7.71	1711	7.72	1720	7.71	1715	7.71	1715
	60	7.55	1711	7.65	1725	7.61	1722	7.60	1719
2	80	7.33	1725	7.45	1720	7.41	1722	7.40	1722
	100	7.26	1721	7.31	1725	7.36	1720	7.31	1722
	120	7.20	1724	7.29	1725	7.24	1721	7.24	1723
3	140	7.13	1726	7.15	1727	7.17	1729	7.15	1727
	160	7.10	1727	7.09	1728	7.12	1731	7.10	1729
	180	7.06	1727	7.05	1730	7.07	1735	7.06	1731