BENEFICIATION OF KRAFT PULP MILLWASTE: USING GREEN LIQUOR DREGS IN TREATMENT OF ACID MINE DRAINAGE AS A NEW DISPOSAL SOLUTION IN SOUTH AFRICA

By

Keolebogile Revelation Sebogodi

Submitted in fulfilment of the academic requirements for the degree of Doctor of Philosophy in Chemical Engineering, at the School of Engineering, College of Agriculture, Engineering, and Science, University of KwaZulu-Natal

Durban, South Africa

Supervisor: Prof. Bishop Bruce Sithole

Co-Supervisor: Mr Jonas Kalebe Johakimu

PREFACE

The research contained in this doctoral degree thesis is my original work, and its contents have not been submitted in any form to another University for a degree, and except where the work of others is acknowledged in the text. The research work described the thesis was carried out at the University of KwaZulu-Natal in the Discipline of Chemical Engineering, School of Engineering, of the College of Agriculture, Engineering and Science, Howard College Campus, South Africa, and was supervised by Prof. Bruce B. Sithole and Mr Jonas. K Johakimu.

07 August 2020

Signed: Prof. B. Sithole (Supervisor) Date

07 August 2020

Signed: Mr J.K Johakimu (Co-supervisor) Date

DECLARATION 1: PLAGIARISM

I, Keolebogile Revelation Sebogodi, hereby declare that:

(i) This thesis, except where otherwise indicated, is my original work.

(ii) The contents of this research have not been submitted in any form to another university for any degree or examination.

(iii) This thesis does not contain another person's data, pictures, graphs or other information unless explicitly acknowledged as being sourced from other persons.

(iv) This thesis does not contain another person's writing unless explicitly acknowledged as being sourced from other researchers. Where other written sources have been quoted, then:

a) Their words have been re-written, but the general information attributed to them has been referenced;

b) Where their exact words have been used, their writing has been placed inside quotation marks and referenced.

(v) This thesis does not contain text, graphics or tables copied and pasted from the internet unless explicitly acknowledged and the source being detailed in the thesis and the References section.

07 August 2020

______________________________ ____________________

Signed: Keolebogile R. Sebogodi Date

DECLARATION 2: PUBLICATIONS

The author wrote the listed publications of this thesis, whose primary responsibilities were to design and conduct the laboratory experiments, data analysis and reporting of the results.

List of Publications:

1. Keolebogile R. Sebogodi, Jonas K. Johakimu, and B. Bruce Sithole (2020) "Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa". Published in the *Journal of Cleaner Production*. DOI: 10.1016/j.jclepro.2019.118979.

2. Keolebogile R. Sebogodi, Jonas K. Johakimu, and B. Bruce Sithole. "A Review of Technologies Used in Handling the Acid Mine Drainage Challenge: Perspectives on Using Green Liquor Dregs as a Sustainable Option for Treatment of Acid Mine Drainage". Manuscript accepted for publication in the *Journal of Solid Waste Technology and Management* and will be available in the February 2021 issue).

3. Keolebogile R. Sebogodi, Jonas K. Johakimu, and B. Bruce Sithole. Co-disposal of acid mine drainage and green liquor dregs: Optimisation of pH and electrical conductivity of acid mine drainage as a result of neutralisation with green liquor dregs." Manuscript submitted to the *Journal of Cleaner Production*.

ABSTRACT

Globally, water scarcity, depletion of non-renewable natural resources, handling and management of industrial wastes are not only significant environmental and economic burdens but also impact human and environmental health. In South Africa, the mining industry is essential to the country and a significant contributor to the GDP of the country. Two major ones are gold and coal mining. Unfortunately, the industries generate large amounts of acid mine drainage (AMD) that originate from the mining activities. The AMD is formed when the 3% pyrite mineral found in the mine effluent dams and voids of gold and coal mines is oxidised upon exposure to water and oxygen resulting in the formation of sulphuric acid which dissolves and leaches surrounding rock and soil matter thus introducing toxic metals into the aquatic waters and biota thus negatively impacting human, animal, and environmental health. Currently, this acidic discharge is neutralised by the use of alkaline reagents such as CaO, $Ca(OH)_2$, NaOH, and $CaCO_3$. However, these chemicals are expensive or are not sustainably resourced in the case of the widely used calcium carbonate.

Possible landfilled, industrial, carbonic wastes such as the green liquor dregs (GLDs), from Kraft pulp mills, could be used as sustainable alternatives for the $CaCO_3$ and its derivatives in pre-treating AMD. These wastes streams are produced at the rate of 7-15 kg/ton of dry pulp. In South Africa, this translates to ~100 000 tons of GLDs that are produced and landfilled annually. However, this is an environmentally challenging and not cost-effective practice. Thus, this study entailed characterising GLDs produced in South Africa, evaluating them for the potential of neutralisation of AMD, and optimising the neutralisation process variables. This is the first time that this type of study has been conducted in South Africa. Furthermore, the neutralisation of the coalfields AMD with GLDs has not yet reported in the literature and this is the first time the optimisation of AMD treatment by GLDs is being studied.

The study entailed statistically designed experiments that employed a Box-Behnken Design and Response Surface Methodology to optimise the variables involved in the neutralisation process. The results indicate that although characteristics of GLDs from different mills differ they all are effective in neutralisation of AMD from gold or coal mines and their neutralisation potential is similar to that of calcium carbonate. Nevertheless, the SEM/EDX, ICP-AES/ICP-MS, XRF, and XRD analysis on the sludge that emanated from either of the neutralisation processes showed that the neutralisation of AMD using GLDs is effective and enables precipitation, co-precipitation, or adsorption of the different metals from the AMD. The pH of AMD could be raised to optimum pH process value and reduce the acidity at a low dosage, thus offering a competitive advantage over commercial $CaCO_3$. Thus, using GLDs for neutralisation of AMD can be an effective symbiotic process that can benefit two industries in managing their waste discharges: the Kraft pulp industry and the mining industries. The results obtained from the optimisation of the variables (neutralising reagent dosage, process time, and stirring speed) involved in the neutralisation process showed that the reagent dosage was the most significant variable while the stirring speed was the least significant one. The models for all the GLDs and reference materials were proven to be significant because all of them had a p-value of $<0, 000001$ and their R^2 and Adjusted R^2 were close to 1.

ACKNOWLEDGMENTS

I have known the Lord God Almighty for all my life, but it has been through this PhD that I got to experience Him and for that that I will forever shout glory be unto the Lord, Almighty God for His faithfulness, and mercies.

I am grateful to my supervisor, Prof. B.B. Sithole and co-supervisor Mr J.K. Johakimu, for their patience, support, guidance, and encouragement that they gave me throughout my study. Your leadership is treasured; thank you.

My utmost gratitude goes to the National Research Foundation (NRF) and the Council for Scientific and Industrial Research (CSIR) – Biorefinery Industry Development Facility (BIDF) for financial support. I would also like to express gratitude to the CSIR-BIDF for providing laboratory space and equipment for my experimental work.

I acknowledge:

- ✓ Sappi Ngondwana and Mondi Richards bay for supplying me with green liquor samples.
- ✓ Mr P.J. Hobbs and Ms L. Hill (both CSIR) for helping out with acid mine drainage sampling.
- ✓ Dr R. Bucher from Ithemba laboratories and Mr P. Suthan from UKZN's Discipline of Geological Sciences for their XRD expertise.
- ✓ Mr V Bharuth from UKZN's Microscopy and Microanalysis Unit for assistance with SEM/EDX analyses.
- ✓ Ms M. Grobbelaar-Moolman from Central Analytical Facilities, Stellenbosch University, for providing analytical assistance.

To my acquired BIDF family, thank you for being such a phenomenal support system. Special thanks go to Dr. V.P. Dladla, Dr A.R. Ocwelwang, Ms. E.S. Sibande, Mr. T.P. Kekana Mrs. G. Andrews, and Ms. O. Molelu. Thank you for your encouragement and for believing in me. To my foster family, Mr Themba and his beautiful wife Delfina Mabindisa, not forgetting their wonderful daughters Angela and Inathi, I would not be writing this if it were not for the love and risk you had to take for me to realise my goals. Thank you for your prayers. You are appreciated and loved; may the Lord God be with you to the thousand generations. Ms. D.S. Itholeng, A.U. Badela, and N. Mathebula, thank you for being sisters to me, time with you have been nothing but a blessing to me.

Finally, I would like to thank my family, tautona Ntuboy Solomon Sebogodi, my sisters, Kesejwang Eva Sebogodi and Mokhutshwa Maria Sebogodi-Leotwane, my brother, Tshepo Magagane, nephews, Orapeleng Ronald Itholeng, Ontiretse Benedict Itholeng, and Bokamoso Leotwane, and my nieces, Reaobaka Leotwane and Kabelano Sebogodi. Thank you for your support, love, and prayers. Thank you for continually asking me when will I finish for many times I went beyond feeling like just giving up to deciding to give up. It was during this time when I got to remember my why that came through all your voices together saying, “you can do this”. It is impossible to acknowledge everyone individually. Thus, I would like to express my sincere gratitude to all those who have been there for me, from the day I was born, I enrolled for pre-school, to this pinnacle of Ph.D., it indeed takes a village to raise a child thus big thumb up to Lobatla village people. Everything and anything about us is never about us as an individual but about all of us. An individual may go through the fire, but victory is for all of us!!

It may seem like it is too late, but behold, even now He can do it, He can still do it, He is the Lord of suddenly. It is never too late for Him. Trust the process

DEDICATION

I dedicate this work to my late mothers

Mampho Aletta Sebogodi (24 September 1953 - 07 January 2016)

and

Banyana Elizabeth Itholeng (24 September1969 -14 April 2016)

TABLE OF CONTENTS

TABLE OF FIGURES

LIST OF TABLES

LIST OF ABBREVIATIONS AND SYMBOLS

Abbreviations

AMD	Acid mine drainage
EDX	Energy dispersive x-ray
Ec	Electrical conductivity
Fe_2S	Pyrite/ iron sulphide
GDP	Gross domestic product
GLDs	Green liquor dregs
HCl	Hydrochloric acid
H_2SO_4	Sulphuric acid
ICP-AES	Inductively coupled plasma atomic electron spectroscopy
ICP-MS	Inductively coupled plasma atomic mass spectroscopy
Micro-meter	µm
mg/L	Milligram per litre
Min.	Minutes
mS/cm	MilliSiemens per centimetre
NaOH	Sodium hydroxide
pH	Power of hydrogen
rpm	Revolutions per minute
SEM	Scanning electron microscopy
SO_4^{2-}	Sulphate
XRD	X-ray diffraction
XRF	X-ray fluorescence
μg/L	Microgram per litre

CHAPTER 1: INTRODUCTION

1.0. INTRODUCTION

Industrial waste management has become one of the significant challenges that the different states around the globe are facing nowadays. Although waste management acts suggest landfilling as the last resort of waste disposal [1], it has been apparent that landfilling seems to be the customary practise for most industries. Thus, regardless of the nature of the landfills-they range from open field to containers, which may store toxic and radioactive slurries, these sites need to be maintained, and this is not a cost-effective practice.

On the other hand, we have witnessed about 178 countries unite together and come up with 17 goals in a Blueprint called The 2030 Agenda for Sustainable Development" [2]. These goals are intended to among the others sustain the planet for now and into the future that we want to see. In a pursuit to devise the solution towards adhering to the waste management acts and to achieving the 17 Blueprint goals, scientists came up with what is known to be the green economy. This phenomenon has been in the core of most research and invention and thus proving to be indeed the bridge between the two worlds-waste management act and the 17 goal Blueprint world. This bridge offered us to view the landfills with the mindset of searching for their hidden treasure.

Nevertheless, the Kraft pulp manufacturers produce about 80% of the total pulp in South Africa (SA) [3]. Along with this Kraft pulp, diverse types of inorganic wastes including slaker grits and green liquor dregs (GLDs) are also produced in Kraft pulp mills [4], [5]. The grits are the waste generated at the bottom of the slacker tank during the recausticising process. These are mainly composed calcium carbonate ($CaCO_3$) and small quantities of lime (CaO), slacked lime ($Ca(OH)_2$) and sodium carbonate (Na_2CO_3). On the other hand, GLDs are the solid suspensions that have been removed from the green liquor during the green liquor clarification process. The GLDs are mainly composed of the sodium and calcium carbonates and the non-process elements that may have originated from the feedstock or the process tank walls [6]–[8].

Years of pulping parallels the amount of wastes that gets piled up in landfills. This leads to congestion of landfills, obliging pulp producers to purchase additional land to use as dumping sites. This is a burden because acquiring land is expensive these days, and there will be more money going out on waste maintenance as there will now be more than one waste site to maintain. In South Africa, acquiring land for landfilling is a rather tedious process that would take years before it could be licenced. Additionally, the South African government is looking into implementing a disposal/environmental tax on top of the disposal/landfill tipping fees [9]. The solution to all these problems is simply to revert to waste regulation acts and look for ways of adhering to the waste management hierarchy, e.g., the technology employed in the manufacturing process could be optimised to the one that would produce no or few wastes. While there is still no technology that can be used to eliminate these wastes at the source, i.e., "cleaner production," it is imperative that we continue to explore both short- and long-term solutions. Thus, the main aim of this study is to characterise GLDs generated in South African Kraft pulp mills and explore their potential for use in treating AMD from both coal and gold mines.

1.2. SIGNIFICANCE OF THE STUDY

Disposal of GLDs is a huge problem worldwide and in South Africa. For example, Brazil and Sweden produce about 300 000 and 240 000 tons of GLDs per year, respectively [10]–[12], while each of Finland and South Africa produces about 100 000 tons of GLDs per year [13], [14]. Currently, these wastes are landfilled. Unfortunately, this practice costs a single mill, anything from $1.2 to1.4 million per annum, indicating that landfilling is not only an environmentally unfriendly practice but also costly. Although landfilling is not yet subject to tax [10], [15], some countries, such as Finland, are already paying around $67.63 per ton of GLDs [13], implying that the pulp and paper industry ought to seek solutions of avoiding, minimising, reusing, recycling or recovering their wastes as stipulated by the National Environmental Management Act (NEMA) [1]. Recovering these wastes will help the pulp and paper manufacturers to decrease inflated costs involved in landfill management, avoid pending NEMA penalties, provide other industries with sustainable resources and more importantly it would not be necessary for them to acquire new land (to use as landfill) which is now becoming more expensive. This practice would help us to get closer to the phenomenon of sustaining the planet.

Although the mining industry is an essential pillar of the South African economy, it may, however, leave the country devastated as its activities may lower the quality of water by contaminating it with acid mine drainage (AMD). This AMD is caused by oxidation of sulphide-bearing minerals by water and oxygen, leading to low pH water with heavy metals and high sulphate concentrations [16]. This oxidation process can be exacerbated by other factors, such as the presence of acidophilic micro-organisms.

Due to differing characteristics of AMD in terms of acidity, heavy metals, volumes generated, one solution cannot be applicable to all AMDs [16]. Hence, understanding the factors mentioned earlier in implementing strategies for treating AMDs. It had been reported that the most popular AMD neutralising reagent is limestone and lime [17], [18]. The problem with using limestone and its derivatives involves the possibility of depleting these natural resources reserves. Having highlighted that, there is a global need to look for new materials that may either partially or wholly replace the traditional natural resources which are being depleted and to seek ways of handling industrial waste in a cost-effective and environmentally friendly way. As a result, this study will be exploring the use of South African green liquor dregs (GLDs) as an alternative for the traditional calcareous materials for AMD treatment.

This is the first time that such studies would have been conducted in the South African context and its outcome will not only help pulp and paper industry to avoid capital involved in handling its wastes, but it will also help mining industry (particularly the mines with sulphide-bearing minerals such as gold and coal mines) to source sustainable raw material at a low cost.

1.3. RESEARCH QUESTION

Is there any possibility of beneficiating the South African Kraft mill's green liquor dregs into an AMD neutralising agent?

1. What are the characteristics of the green liquor dregs?

2. Are the GLDs compatible for use as AMD neutralising agents?
3. How do the neutralisation properties of the dregs compare with currently used neutralisation reagents sourced from natural raw materials?

1.4. AIMS

The main aim of this study was to characterise and evaluate green liquor dregs produced by the South African Kraft mills as a possible sustainable alternative for the $CaCO_3$ and its derivatives in the pre-treatment of acid mine drainage.

1.5. OBJECTIVES

1. Characterise GLDs and quantify if their characteristics are comparable to those of $CaCO_3$.
2. Use dregs as an alternative raw material in ameliorating AMD (from coal and gold mines) and evaluate their effectiveness as compared to the present practice of using natural calcareous materials.
3. Optimise the variables (neutralising reagents dosage, process time, and stirring speed).

CHAPTER 2: LITERATURE REVIEW

2.1. INTRODUCTION

AMD and GLDs remain to be a prominent eco-environmental challenge that needs an urgent solution. It is therefore for this reason why various institutions (including governments, academic, and private sectors) have, for decades, joined hands to search for solutions on how to better address the challenges posed by these waste streams and to seek for opportunities that may be concealed in them. protect the environment and lead sustainable manufacturing and production. For this reason, for the mining and pulp and paper industries. Thus, chapter two gives an in-depth description of what AMD and GLD are i.e., characteristics and how they are formed. Additionally, research on how these by-products have been addressed and/or taken advantage of is explored.

2.2. ACID MINE DRAINAGE

2.2.1. Mining Industry in South Africa

The trajectory of the South African economy was primarily founded and shaped by the mining industry between the 1850s and 1990s. The first mine started at Springbokfontein in the Northern Cape in 1852 [19], [20]. This was followed by the discovery of coal in 1864 in Molteno, Eastern Cape. Three years later, the diamond was found in Kimberly, Free State. These historic achievements were proceeded by the gold, coal, diamond, and platinum across the country in Gauteng, Mpumalanga, Limpopo, and North-West. Other minerals, such as manganese, chrome, vanadium, and vermiculite were later discovered [20]–[22].

Along with the industry's rapid growth, towns grew more prominent, and other economic structures such as banking, manufacturing, and retail were introduced/developed [22]. Thus, the mining industry had shaped the wealth and economy of South Africa directly and indirectly. In 2019, the South African mining industry contributed $24.5 billion to the country's gross domestic product (GDP) [21].

2.2.2. Impacts of Mining Activities on the Environment

Despite its significant contribution towards SA's economy, mining activities left the country with a bad legacy which perils the biota, soil, water sources, as well as crippling the country's economy (e.g. by destroying historic or educational places- dissolving the parent rocks in caves) with its 170 million litres of acidic water production per day [23]. This acidic water from mines and mine-workings is known as acid mine drainage (AMD). Its major components are sulphates, ferric oxide-hydroxide, and sulphuric acid and different metals. Thus, AMD contaminated water poses different threats to the environment, depending on its composition [24].

2.2.3. Formation of AMD

The formation of acid mine drainage is a naturally occurring process that involves oxidation of sulphide-bearing mineral rocks, Table 1, in the presence of dissolved oxygen (DO) and water. In the absence of earth-moving activities, small quantities of this acidic leachate are produced. At this production rate, this leachate does not cause any problem because the surrounding rocks (e.g., carbonates and clays) are capable of neutralising it [25]. However, this phenomenon becomes a problem when it occurs on a disturbed mineral rock, such as at mining operations. This is because disturbing the rock enlarges its surface area, making it to be more prone to oxidation. The mechanisms for the formation of AMD are shown in Eqns. 1-4 using pyrite, FeS_2, as an example [14], [17], [26], [27].

Table 1: *Sulphide bearing minerals and their products* [28]

Element	**Mineral Name**	**Sulphide Mineral**
Iron (Fe)	FeS_2	Pyrite or marcasite
	$Fe_{(1-x)}S$	Pyrrhotite
Zinc (Zn)	ZnS	Sphalerite
Copper (Cu)	$CuFeS_2$	Chalcopyrite
	CuS	Covellite
	$CuFeS_4$	Bornite
	Cu_2S	Chalcocite
Arsenic (AS)	FeAsS	Arsenopyrite
	AsS	Realgar
	As_2S_3	Orpiment
Lead (Pb)	PbS	Galena
Nickel (Ni)	NiAs	Niccolite
	$(Fe,Ni)_9S_8$	Pentlandite
Mercury (Hg)	HgS	Cinnabar
Cobalt (Co)	CoAsS	Cobaltite

AMD leachate formation starts when ferrous (Fe^{2+}), sulphate (SO_4^{2-}) and hydrogen (H^+) ions are formed from the oxidation of FeS_2 in the presence of water and oxygen, Eqn. 1 [14], [17], [26], [27].

$$FeS_{2(s)} + 7/2\ O_2 + H_2O \rightarrow Fe^{2+} + 2\ SO_4^{2-} + 2\ H^+ \qquad \textbf{\textit{Eqn. 1}}$$

The above reaction may go forward depending on the pH of the leachate, microbial activity, and the presence of the DO. Thus, in acidic environment, the initiator ion, Fe^{2+}, is oxidised by oxygen to form ferric ions, Fe^{3+}, Eqn. 2. The presence of acidophilic micro-organisms accelerates the rate of this reaction [14], [17], [29], [30].

$$Fe^{2+} + \tfrac{1}{4}\ O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\ H_2O \qquad \textbf{\textit{Eqn. 2}}$$

Fe^{3+} precipitates as a hydrated ferric oxide-hydroxide, ($Fe(OH)_3$), as pH level raises up to ≥ 3.5, Eqn. 3 [14], [17].

$$Fe^{3+} + 3\ H_2O \rightarrow Fe(OH)_3 + 3\ H^+ \qquad \textbf{\textit{Eqn. 3}}$$

If the alkalinity in Eqn. 3 is not enough to precipitate all of the Fe^{3+} in the medium, then this ion will further be reduced by FeS_2 (Fe^{3+} acts as a FeS_2 oxidising agent), as depicted in Eqn. 4 to produce Fe^{2+} and more acid. This proceeds at $pH<3.5$ [14], [17], [30], [31].

$FeS_2 + 14\ Fe^{3+} + 8\ H_2O \rightarrow 15\ Fe^{2+} + 2\ SO_4^{2-} + 16H^+$ ***Eqn. 4***

The produced acidic leachate would then dissolve the surrounding tailings, rock waste, or mineral ores, thereby liberating and introducing heavy metals such as uranium (U), nickel (Ni), radium (Ra), thorium (Th) and aluminium (Al) into it. In the presence of moving water, the acidic, heavy metal tainted leachate will find its way into freshwater bodies and hence pollute them [32], [33].

2.2.4. Occurrence of AMD

2.2.4.1. Factors affecting the formation of AMD

The rate of AMD generation is determined by physical, chemical and biological factors, as illustrated in Figure 1, and some of the factors are interrelated [34].

Mine type: Minerals are mined using either underground or open cast mining. The type of mining used could affect the rate at which AMD is formed, as well as its overall character. That is, the open cast mine would be prone to faster rates of Fe_2S oxidation as compared to the underground mine. These elevated rates are due to the unlimited atmospheric oxygen that can easily permeate into the mine rocks. The higher rates of Fe_2S lead to extremely low pH of the water. This acid will now be able to dissolve the surrounding aluminosilicates, such as feldspar and clays, as illustrated in Eqn. 5. This dissolution would (1) introduce some alkalinity, which may precipitate some of the Fe^{3+} and (2) introduce Al and other minerals into the solution. The overall process leads to the AMD with high acidity, which is caused by high Al:Fe. On the other hand, the AMD from the underground mine would have low Al:Fe and thus low acidity. This is due to limited atmospheric oxygen that permeates through to induce oxidation [35], [36].

$KAlSi_3O_8 + 10H_2O + 3Fe^{3+} + SO_4^{2-} \rightarrow KFe_3(SO_4)_2.(OH)_6 + 3\ H_4SiO_4 + 2H^+ + Al^{3+}$ ***Eqn. 5***

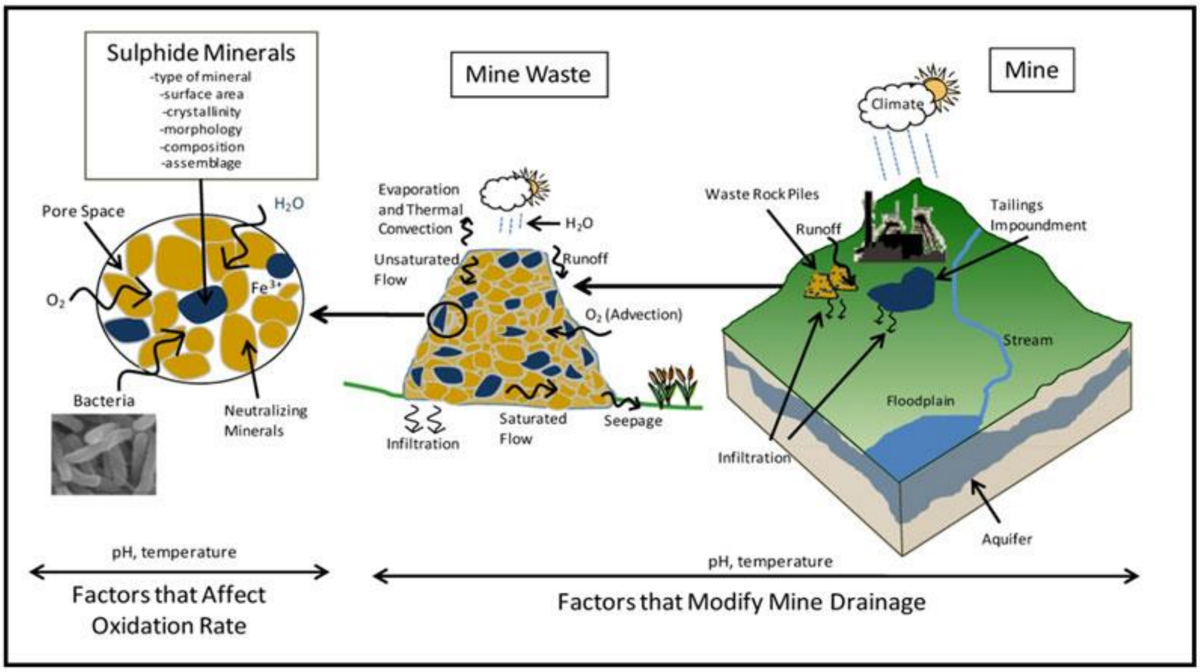

Figure 1: *Factors affecting sulphide-bearing mineral oxidation* [34].

Hydro-geology: Flooded mines would have low acidity and higher pH values than the free-draining mines. This is because the copious standing water would limit the oxygen from inducing oxidation. This is the same phenomenon behind the mine tailings water cover [35], [36].

Rock type: Crystallinity and particle size of the mineral could influence its rate of oxidation. It has been reported that lower crystal symmetry and crushed waste rocks can be easily oxidised due to magnified surface area exposed to the oxidising environment [37]. Furthermore, it has been reported that the crystalline structures are less prone to weathering and oxidation as compared to the amorphous structures [35], [38].

Weather factors: Chemical reactions are dependent on temperature. Arrhenius law stipulates that reaction rate is directly proportional to an increase in temperature [37], [39]. One study showed that the reaction order of asernopyrite ($Fe_2(SO_4)_3$) increased with increasing temperature. Precisely, a 0.41 order was observed when the experiments were carried out at temperatures between 15 and 35^{O}C. However, a 0.64 order was observed when the same experiments were carried out at 45^{O}C [40]. This showed that a different mechanism must be involved at higher temperatures. Furthermore, the phenomenon known as the climate change has and is continuing to change the processes and livelihood on earth by directly influencing the increase in temperature. This increase in temperature has a direct influence on the rate of evaporation, glacial meltdown, local and global climate, and rainfall pattern which would all impact on the mechanism of AMD formation and its overall characteristics as described on reviews by (Corkhill and Vaughan (2009) and Anawar (2013).

Chemical factors: The pH of the leachate can also influence the rate of reaction. That is, the forward reaction that occurs after the initial oxidation of the sulphide mineral is dependent on the surrounding environment. If the surrounding soils could add high alkalinity into the leachate, then acidity would be consumed. This may be accompanied by precipitation of different metal constituents present in the leachate. This precipitation is dependent on the metal type and its oxidation state, e.g., Fe^{3+} precipitates at pH ≥ 3.5 while Fe^{2+} precipitates at pH≥ 6 [37], [43]. Redox character of metals can play a role in the amount of acid that is produced, e.g., in acidic conditions, Fe^{3+} oxidises pyrite, and hence more acid is produced [35]–[37].

Biological factors: The presence of acidophilic micro-organisms can accelerate the rate of sulphide mineral oxidation. That is, under typical microorganism-free environments, conversion of Fe^{2+} to Fe^{3+} ions reaction in the rate-determining step (Eqn. 2) is slow, but it becomes very fast in the presence of the active *Thiobacillus fero-oxidans* and hence increases the rate of AMD formation [30], [36], [43], [44].

2.2.4.2. The Difference between the Gold and the Coal AMD formation.

Earth-moving activities such as mining exacerbate the production of AMD. This is because they expose the sulphide-bearing minerals that might be confined within the mineral host rock or the mineral itself. Thus, the mechanism in which the AMD is formed differs according to the mineral that is being mined.

Gold mining: Gold is found in layers of sedimentary rocks and veins. Its mining involves the extraction from gold-rich conglomerates, which would be transported to the earth's surface where the gold would be extracted by dissolution in a cyanide solution. The waste rocks or mine tailings resulting from this entire process will then be disposed of in what is known as mine/tailing dams. Generally, the conglomerate itself contains ~3 % of Fe_2S. Therefore, AMD formation that is associated with gold mining occurs when the Fe_2S constituted in both the gold host rock dams and mine channels is exposed to oxidising conditions[25].

Coal Mining: Coal is a black or brownish-black sedimentary rock. It can be exhumed from the ground by using either opencast or underground mining techniques. Coal will then be moved from the site with minimal waste or surface dumping. In this case, both the coal and the host rock constitute sulphide-bearing mineral, but it is more concentrated in the coal itself. The pyrite in this mineral is said to be 8% [30]. As the mine ceases operations, water is used to fill mine voids, and the Fe_2S is oxidised and decanted at the lowest opening discharge points in the form of AMD. If the open cast mining method was used, the landscape is often rehabilitated by backfilling with the crushed host rocks and covering them with soil. Rainwater will, however, penetrate through the soil and find its way into the Fe_2S deposits. This O_2 abundant water will then oxidise the pyrite and produce AMD. Resurfacing of this contaminated water may occur ten years after the backfilling[25].

2.2.1.3. Geomorphology and distribution of AMD in South Africa

Water does not only act as a reactant but also as an AMD carrier. Thus, the extent of AMD distribution from the source relies on the geomorphology of water drainage. In SA, there are three major water basins in the Gauteng province, which are associated with AMD. These are the Central, Western and Eastern basins, accounting for 60, 30 and 80 million L of acid water produced per day. Fortunately, these basins do not overflow into each other as they are not interconnected [23]. Witpoortjie boundary separates the Western and Central basins while the Boksburg boundary separates the Central and Eastern basins. However, these basins are joined to different river systems. Thus, the mine water can pollute water streams of places that are not subjected to the site of AMD formation. For example, the Orange and Vaal Rivers' water is subjected to AMD contamination because they are underlain by AMD producing mines. These rivers are unfortunately flowing throughout the country, meaning that they distribute their pollutants in all the places that they pass through, Figure 2 [25], [31].

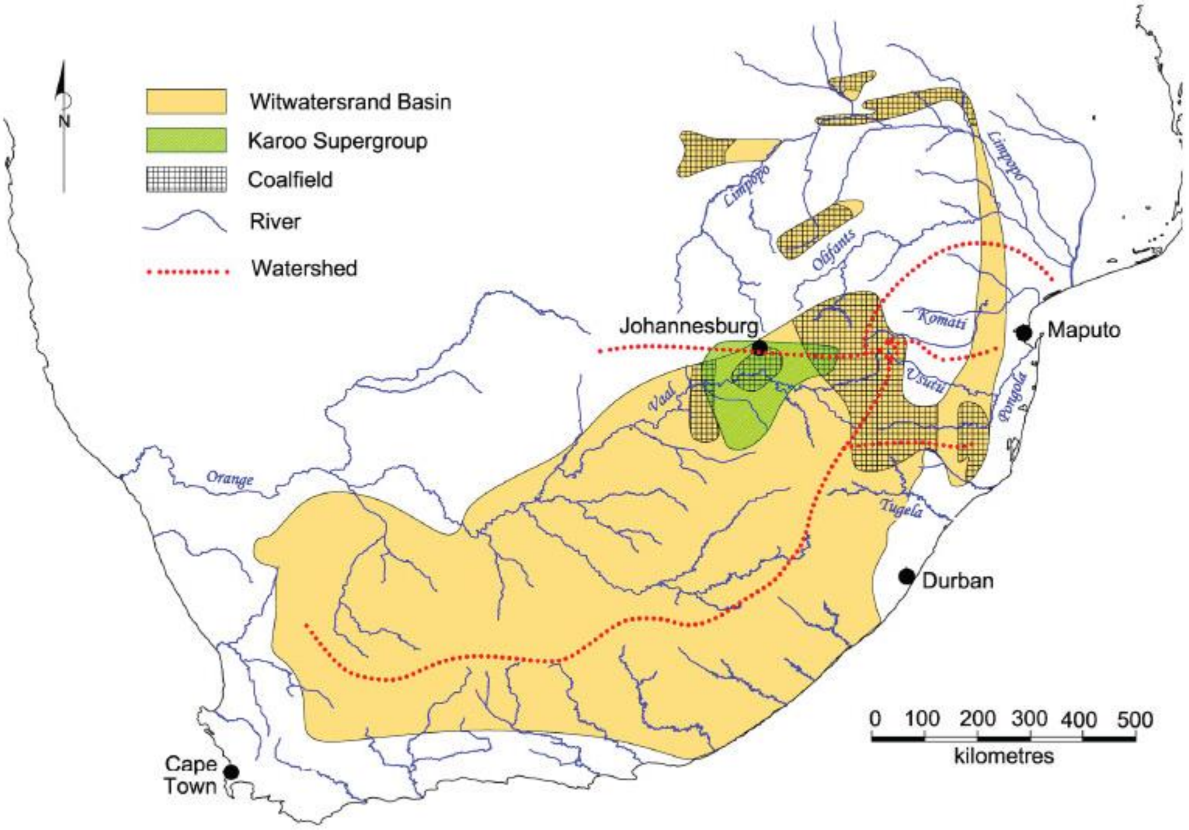

Figure 2: *Topography of the water drainage system in SA* [25]

2.2.4.4. **Socio-economic impacts of AMD**

AMD has dramatically impacted negatively on the socio-economic factors such as endangerment of biota, human health, tourism, and educational sites, and this will ultimately impact negatively on the economy [45]–[47].

Biota: AMD is primarily characterised by having a low pH and high concentration of heavy metals. These two characteristics can impact negatively on the wellbeing of both the aquatic and terrestrial plants and animals. For example, generally, the presence of metals in high concentrations can impact negatively on the homeostasis, sprouting, and growth of plants, and this may disrupt their physiology and morphology. Ultimately, different metals affect the wellbeing of plants in different ways, which are listed in Table 2 [48], [49].

The pH of the soil/water thereof taken up by plants can influence the accessibility of the nutrients to the plants. For example, low pH suppresses the availability of potassium (K), nitrogen (N) and phosphorus (P) while it increases the availability of aluminium (Al), manganese (Mn) and iron (Fe) to the plants. This low pH may also decrease microbial activities that help in improving the soil drainage, tilth, and aeration [50].

Table 2: *Effects of metals on plants* [48]

Metal	Effects
Cadmium (Cd)	Decreases lipid content, seed germination, and plant growth; induces phytochelatins production.
Chromium (Cr)	Decreases enzyme activity and plant growth; produces chlorosis, membrane damage, and root damage.
Copper (Cu)	Inhibits photosynthesis, plant growth, and reproductive process; decreases the thylakoid surface area.
Mercury (Hg)	Decreases water uptake and antioxidant enzymes, photosynthetic activity, accumulates in phenol and proline.
Nickel (Ni)	Reduces seed germination, chlorophyll, protein production, dry mass accumulation, and enzymes; increases free amino acids.
Lead (Pb)	Increases superoxide dismutase; reduces chlorophyll production and plant growth.
Zinc (Zn)	Reduces Ni toxicity and seed germination; increases plant growth and ATP/chlorophyll ratio.

Just like terrestrial biota, aquatic organisms also need to survive at certain pH and acceptable mineral concentrations. Thus, when these organisms are exposed to low pH water and high metal concentration, decreased fertility and death may result [51].

High mortality rates of aquatic biota can be experienced due to exposure to AMD. For example, studies on Lake Loskop, which is in Olifant's River (South Africa, SA) downstream of AMD discharged from a coal mine, showed high mortality rates (60%) of *Crocodylus Niloticus* (Nile crocodile). These rates were reported to have been due to pansteatitis (a yellow fat disease), which is caused by consuming the dead rancid fish. The mortality of the fish themselves was associated with the impacts of AMD. That is, the low concentration of DO and high concentrations of Al, Fe, and Mn introduced into the lake body through AMD contamination has been reported to cause cardiovascular failure in the fish and hence resulting in their death[52], [53].

Oberholster *et al.* (2010) investigated the response of phytoplankton when exposed to AMD and other pollutants that originate from both the industrial and domestic sewage systems. The sampling sites were divided into three sections: the inflowing riverine, transitional, and lacustrine zones. These differed in the flushing and flow water rates, from high to low rates, respectively. The study reported that the phytoplankton species at the inflowing riverine zone were susceptible to the elevated levels of contaminants entering the lake body. Thus, at this zone, there was a minimal amount of species, but the species number increased as you go from the transitional to the lacustrine zones. The study also suggested the possible bioaccumulation of lethal metals along the food chain.

Human Health: Human beings can be exposed to the AMD contaminants indirectly through the food chain or directly through drinking or dermal contact. Accumulation of metals may cause organ disruption, and some may even cause ailments such as cancer. The effects of some of the metals on human beings are listed in Table 3 [55]–[57].

Animal: Milk producing cows are one of the animal species that require a lot of water intake, which forms a considerable part of milk. A dairy farmer that was located 500 feet away from an active coal mine experienced low milk production. In addition to this, the cows in this farm were reported to suffer from other ailments such as substandard reproductive performance, miscarriage, and anaemia. Neither the pathological nor the blood tests revealed the cause of these problems. The water analysis indicated the presence of various metals with variable pH values. The authors attributed the variable pH levels and the presence of some metals such as Pb, Fe, Mn, and Zn to the mine water contamination. The presence of these metals reduced the palatability of the water due to high concentrations of Fe and Mn, and low pH values led to acidosis. Thus, the reduced palatability of water affected the water intake of the cows, which affected the milk production rate [58].

Tourism and or Educational sites: The Cradle of Humankind is a dolomite cave that was bestowed a World Heritage Site by the United Nations Educational, Scientific and Cultural Organisation (UNESCO) in 1999 due to its exceptional natural and cultural legacy. This site is known to many as an archaeological and palaeontological research centre as well as a tourism site (Durand, Meeuvis and Fourie, 2010). This cave, now known as the Cradle of Humankind World Heritage Site (COHWHS), is located adjacent to the Witwatersrand Supergroup gold deposits. The AMD from these gold deposits has already found its way into water bodies such as the Bloubankspruit spring that, unfortunately, runs through the COHWHS. Due to the dissolution character of carbonates when exposed to acidic conditions, the integrity of the COHWHS walls is threatened. As the dissolution progresses, sinkholes may be formed, and the site's roof may collapse in, and this may lead to the closure of this remarkable tourism, educational and business site [45], [59].

Economy: like all the above-mentioned socio-economic factors manifest, the economy of the affected country is negatively affected. For example: (i) the government should relocate people who reside next to the AMD contaminated areas as well as mine dams because, in the long run, the same government will be liable to fund their health issues when they become affected by consumption and effects of exposure to AMD; (ii) once total karstification of the COHWHS has occurred, this historic heritage, educational and tourism site will be part of the dead history, and the country would lose a valuable resource. Buildings can also collapse into the sinkholes that result from karstification. This may leave people homeless, and thus, the government may be liable to step in to assist financially.

Table 3: *Effects of metals on human health* [56]

Metal	Effects
Arsenic (AS)	Bronchitis, dermatitis, and poisoning.
Cadmium (Cd)	Renal dysfunction, Lung disease, Lung cancer, Bone defects (Osteomalacia, Osteoporosis), increased blood pressure, kidney damage, bronchitis, gastrointestinal disorder, bone marrow, cancer.
Lead (Pb)	Mental retardation in children, developmental delay, fatal infant encephalopathy, congenital paralysis, sensor neural deafness and, acute or chronic damage to the nervous system, people with epilepsy, liver, kidney, gastrointestinal damage.
Manganese (Mn)	Inhalation or contact causes damage to the central nervous system.
Mercury (Hg)	Tremors, gingivitis, minor psychological changes, acrodynia characterised by pink hands and feet, spontaneous abortion, damage to the nervous system, protoplasm poisoning.
Zinc (Zn)	Cause damage to the nerve membrane.
Chromium (Cr)	Damage to the nervous system, fatigue, irritability.
Copper (Cu)	Anaemia, liver and kidney damage, stomach and intestinal irritation.

2.2.5. Prevention of AMD Formation

AMD is formed when the sulphide bearing mineral when the mine waste rock or tailings react with water and oxygen. Hence keeping the ingress of either one of the factors that initiate AMD formation out of the system offers an opportunity of retarding/prohibiting the formation of AMD [24]. Several techniques such as bactericides [60]–[62], organic coating [63]–[65], micro-encapsulation [60], [66], [67], silane-based coating [68]–[70] and carrier-micro-encapsulation [71]–[73] have been studied and explored in preventing the formation of AMD. The basis of these technologies is discussed in Table 4. However, other methods such as sealing layer (barriers) application on top of mine wastes and blending mine wastes with alkaline sources are discussed below.

2.2.5.1. Barriers to prevent AMD formation

Barriers are described as materials that protect the mine tailings from being in contact with either of the factors that induce their oxidation. These barriers are classified as water or soil barriers [16], [74], [75].

Water barrier: Although not widely practised, water can be used to prevent the formation of acid mine drainage. This is made possible by the relatively low amount of oxygen present in water (30 times less than that found in the atmosphere). Thus, the limited amounts of dissolved oxygen in water barriers retard the reaction rate and possibly inhibit it once all oxygen is exhausted [74].

Soil barrier: One of the most effective ways of ensuring that mine waste or tailings do not undergo oxidation processes is to use a cover that serves as either a water or an oxygen barrier. The covers are typically single or multi-layered (in 3-5 layers). These may include (but not limited to) the tailings/waste rocks containing sulphide-bearing minerals, sealing layers, protective layers, and topsoil, as illustrated in Figure 4 [74], [75].

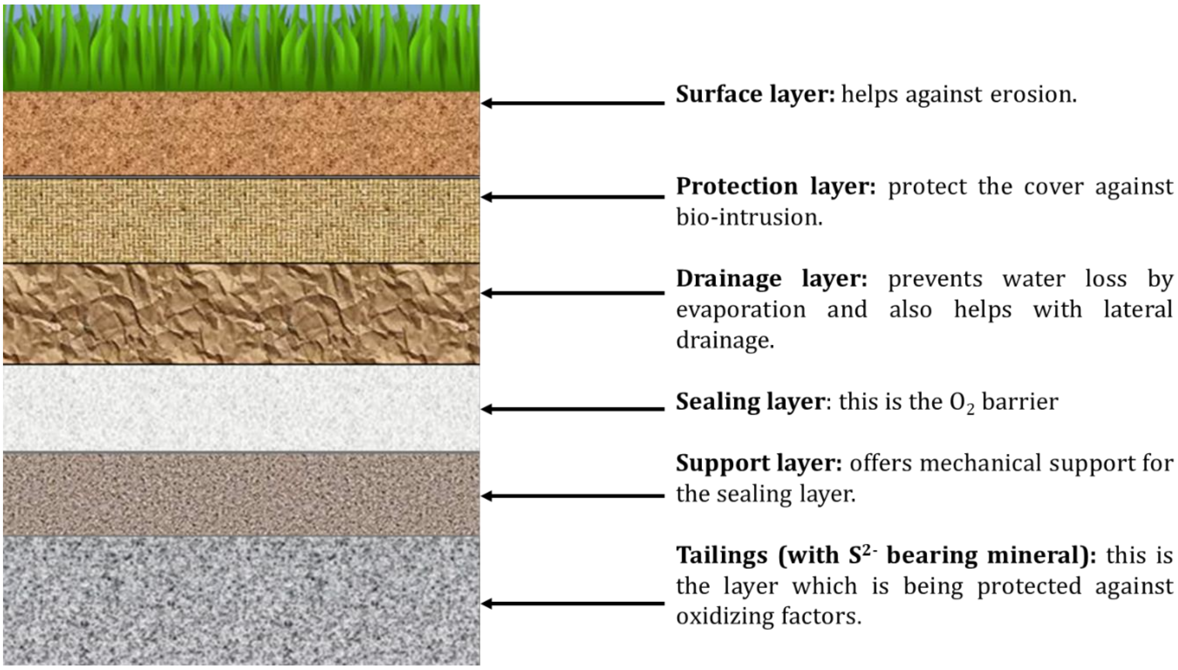

Figure 3: AMD soil cover (adapted from [24])

2.2.5.2. Blending and co-disposal of tailings and alkaline materials.

Blending the reactive mine tailings with alkaline materials such as limestone, dolomite, and lime could be considered as one of the promising methods of reducing low pH mine leachate, especially where backfilling the mine voids is desired. However, the homogeneity and stoichiometry between the S^{2-} source and the buffering material should be considered as the wrong combination may result in disastrous consequences [76], [77]. For instance, low quantities of the alkaline source may lead to the formation of AMD whereas the high quantities may lead to the production of highly alkaline (pH ~10, suitable for Mn and SO_4^{2-} precipitation) leachate which may be rich in toxic metals that precipitate at slightly lower pH levels [78]. When done correctly, this method's effectiveness will not only aid in neutralising the AMD that may be formed but would also immobilise the toxic metals through precipitation, reduce the rate of AMD formation by disengaging the acidophiles with the alkaline environment, and in the long run, the formation of gypsum hardpan may reduce the ingress of O_2 into the S^{2-} source [76].

Table 4: Methods of preventing /and or minimising the AMD formation [18].

Prevention Method	Materials used	Features	Advantages	Limitations
Oxygen barrier	•AMD treatment sludge, ash, clay, industrial alkaline wastes, low sulphide tailings, natural till/soil, non-reactive mine residue, organic materials	•Placing the covers composed of fine-grained materials, basic materials, and organic substrate over-reactive mine wastes. •Submerging mine tailings underwater.	•Dry and water covers suppressed the formation of AMD by limiting water and/or O_2 availability to mine wastes.	•The alkaline cover may enhance the solubility of some heavy metals and toxic metalloids. •Organic cover can cause a reductive dissolution of iron (Fe) precipitates. •Water cover does not apply to arid and semi-arid regions.
Bactericide	•Acetic acid, lactic acid, sodium dodecyl sulphate, sodium dodecyl benzene sulfonate, sodium lauryl sulphate	•Reduction of biological activity or extermination of bacteria present in mine wastes.	•Bactericides effectively inhibit the growth of micro-organisms, thereby suppressing AMD formation.	•It cannot permanently inhibit microbial activity, so repetitive addition is required.
Organic coating	•DETA, DTC-TETA, humic substance, phospholipids, sodium oleate, TETA, 8-hydroxyquinoline	•Formation of hydrophobic coatings on sulphide minerals.	•Organic compounds render sulphide minerals hydrophobic, which inhibits mineral-water interactions.	•The long-term stability of these organic coatings, which could be degraded by some micro-organisms, is unknown.
Microencapsulation	•Coating agents: Apatite, cement, MgO, $KMnO_4$, manganite, phosphate, sodium metasilicate	•Formation of inorganic coatings like iron-oxyhydroxide, iron-phosphate, and iron-hydroxide/silica.	•Iron-oxyhydroxide, iron-phosphate, and iron-oxyhydroxide/silica coatings were effective in suppressing	•Excessive use of phosphate may cause eutrophication of water bodies.

	•Oxidants: H_2O_2, NaClO •Buffer: Sodium acetate		AMD formation by preventing mineral contact with oxidants like O_2 and Fe^{3+}.	•H_2O_2 is challenging to handle and store. •The techniques are non-selective.
Silane-based coating	AAPS, APS, MTMOS, NPS, PropS-SH, PropS-SH/SiO_2, TEOS, TMOS, VTMS	•Formation of coatings composed of both inorganic and organic components.	•Silane-based coatings combine the advantages of both inorganic (i.e., durability and superior adhesion) and organic components (i.e., flexibility, crack-resistance, and compatibility). •Does not require any pre-oxidation step using H_2O_2.	•It has little selectivity for sulphide minerals.
Carrier micro-encapsulation	•Metal(loid) ions: Al^{3+}, Fe^{3+},Ti^{4+}, Si^{4+} •Organic carrier: Catechol	•Selective formation of metal(loid)-oxyhydroxide coatings on sulphide minerals	•Redox-sensitive metal(loid)-catecholate complexes were able to target sulphide minerals to form surface protective coatings specifically.	•The effects of coexisting minerals and the long-term stability of the coating remain unclear.

2.2.6. Mitigation of AMD

The impact of AMD becomes more prevalent when the mines are no longer operational. This is due to the water that becomes accumulated in mine voids (as it is no longer being pumped out), together with the leachate that is produced from the uncovered mine wastes outside the mine voids. This low pH metal leachate may pose a danger to species and activities (e.g., agricultural or tourism activities), which are dependent on the water streams that the leachate may flow into. Thus, different mechanisms such as pH control, adsorption, biological treatment, redox, ion exchange, and crystallisation have been adopted and developed as the driving forces behind the various AMD treatment processes [79]–[81].

2.2.6.1. Mechanisms used in AMD treatment processes

Redox: oxidation of AMD components may occur in two ways. First, this process occurs in abiotic conditions whereby the solution needs to be aerated. In active systems, O_2 may be aerated into the reaction tank under mechanical stirring. The same aeration is, however, dependent on the natural exposure of the AMD to O_2 in the passive systems. Thus, because of the absence of mechanical stirring in the passive systems, the longer residence time is required for the AMD in the system (e.g., aerobic wetlands).

On the other hand, oxidation may occur under biotic conditions. The oxidation process is dependent on the chemoautotrophic micro-organisms present. These species act as catalysts of metal oxidation and act as electron donors. Reduction processes involve a reduction of SO_4^{2-} to HS^- by sulphate-reducing bacteria (SRB) in the presence of organic substrates, which act as electron donors. The differences between oxidation (under biological conditions) and reduction processes are the type of electron donors (micro-organisms and organic substrate respectively), the presence and absence of O_2 and that metals precipitate as oxides/hydroxides and sulphates respectively [82]–[84].

Ion exchange: The ion exchange process is a process where resins are used to absorb cations and anions from the AMD contaminated water. This absorption process is known as the demineralisation process, as shown in Eqns. 6 & 7. The contaminated water requires that the particulate matter is filtered out prior to the treatment process. After absorption, the resins are regenerated using acid for cation absorbing resins and a base for anion absorbing resins, Eqns. 8 & 9. High-quality gypsum is produced during the ion exchange process [32], [85]–[88].

AMD demineralisation

Cation demineralisation : $2RH^+ + Ca^{2+} \rightarrow R_2Ca^{2+} + 2H^+$ ***Eqn. 6***

Anion demineralisation :$2ROH^- + SO_4^{2-} \rightarrow R_2SO_4^{2-} + 2OH^-$ ***Eqn. 7***

Resin regeneration

Cation resin regeneration : $R_2Ca^{2+} + H_2SO_4 \rightarrow 2RH^+ + CaSO_4$ ***Eqn. 8***

Anion resin regeneration : $R_2SO_4^{2-} + Ca(OH)_2 \rightarrow 2ROH^- + CaSO_4$ ***Eqn. 9***

Where: R represents the resin with either a cation or an anion.

Adsorption: This mechanism can be defined as a chemi-physical sorption process in which the AMD contaminants (both organic and inorganic) adhere to the surface of the adsorbents. This adherence forms a film on the surface of the adsorbent. Unlike the ion exchange mechanism, the adsorption mechanism does not require prior filtering. Varied materials such as biomass, fly ash, blast furnace slag, and kaolinite may be used as adsorbents of heavy metals found in AMD. Technologies that use adsorption mechanism in AMD treatment entail minimal area, low capital, and simple design [89]–[91].

pH control: Different AMD effluents have distinctive characteristics such as acidity, pH, flow rate, metal load (Fe, Al, and Mn are of high importance in terms of treatment) and DO. Using pH control as a mechanism of choice is dependent on both the neutralising reagent and the treatment technology that will be used to treat the AMD. Thus, different treatment technologies, as discussed below, were designed to achieve a specific outcome of which the main one is to neutralise the AMD. Metal precipitation may also occur during the neutralisation process. As a result of their chemical properties, these metals precipitate at different pH levels. Careful decisions should be taken in deciding on the dosage (especially in the active systems) because the stability of amphoteric metals such as Al is affected by pH levels. Such metal precipitates are usually stable at neutral pH.

Oxidation states of metals are also vital. For example, Fe^{2+} is preferred for most passive systems because Fe^{3+} will cause armouring on the surface of limestone ($CaCO_3$). On the other hand, Fe^{3+} is preferred for the active systems because it precipitates at relatively low pH as compared to Fe^{2+} [81].

Different chemicals such as $CaCO_3$, hydrated lime ($Ca(OH)_2$), quicklime (CaO), sodium carbonate (Na_2CO_3), caustic soda (NaOH), and ammonia (NH_3) can be used for AMD neutralisation. A vast number of researchers and or AMD treatment institutions have shown a great interest in using $CaCO_3$ and its derivatives because of their lower costs as compared to the other chemicals [17], [29].

2.2.6.2. Processes for Treatment of AMD

AMD treatment has been proven to be a costly practice as compared to AMD prevention. This is because the production of AMD may last for decades or even centuries before the S^{2-} embedded in the mine tailings could be consumed. Moreover, the continual exposure of S^{2-} through the ongoing mining of precious minerals assures that both the current and the future generations are bound to suffer the devastating challenges associated with AMD. Nevertheless, scientists have developed biotic and abiotic methods that are further classified as either passive or active AMD treatment technologies and further sub-divided into biotic and abiotic systems (D. Barrie Johnson and Hallberg, 2005; Kefeni, Msagati and Mamba, 2017).

The fundamental choice between these two technologies is based on the amount and characteristics of AMD, the material used for treatment, labour, management, the objectives of AMD treatment (protection of the site infrastructure, downstream aquatic ecosystems or agricultural activities, or human consumption), and the overall cost. Between the two, passive technologies have been reported to be cost-effective as they require no/low maintenance, management, labour, material (chemical) addition. However, their employment may, unfortunately, be limited by various factors such as prolonged time (~12 h) necessary for effective treatment, not applicable to all types of AMD, is designed to treat low volumes of AMD per day, and require large surface areas [24], [92], [93]. The methods categorised in this technology include aerobic and anaerobic wetlands, compost bioreactors, anoxic $CaCO_3$ drains, open $CaCO_3$ ponds, and permeable reactive barriers [92], [94].

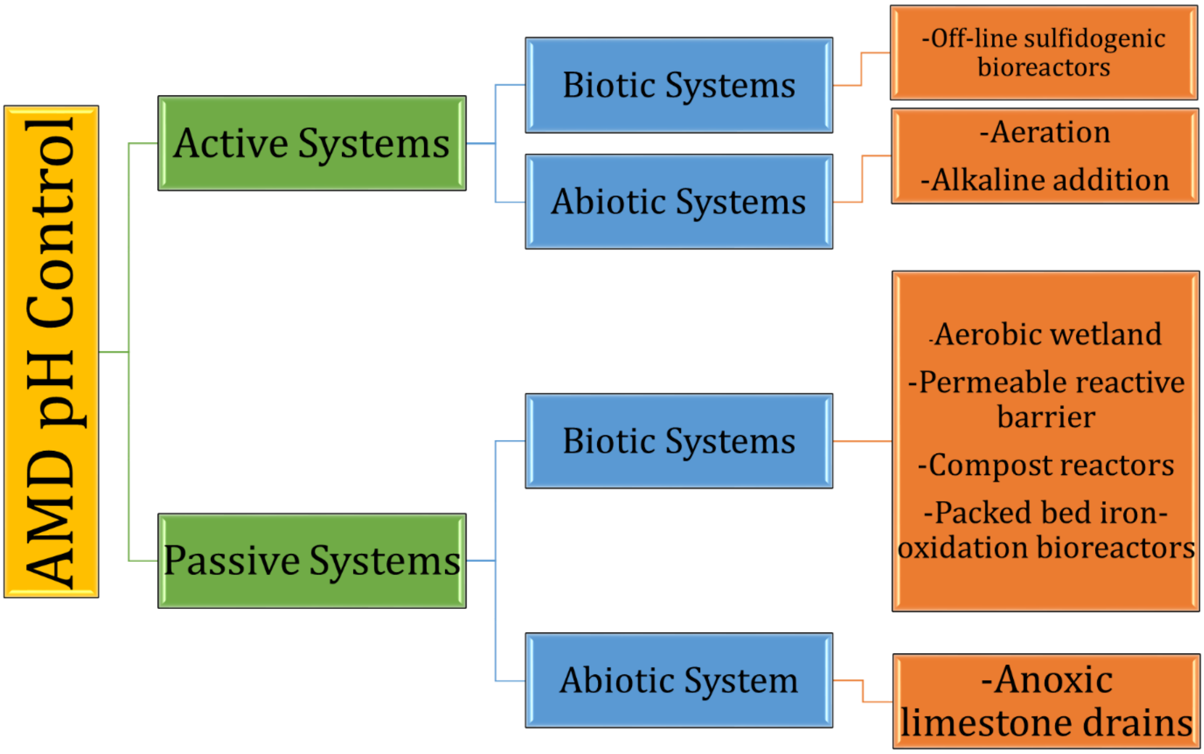

***Figure 4**: Passive and active processes used in AMD treatment (adapted from* [24]*)*

On the other hand, active treatment technologies are the most versatile of these technologies because they could be used to treat all types and volumes. This versatility is made possible by their ability to be custom designed/modified to achieve effective treatment for a specific AMD character. Also, these technologies require less operating space as compared to the passive ones. However, active technologies suffer from not being cost-effective because they are labour, material, and energy-intensive, produce large quantities of toxic sludge that is mainly landfilled and may cause ecological disturbances [24]. These technologies include off-line sulphidogenic bioreactors, the addition of alkaline reagents (neutralisation), flocculants/coagulants, ion exchange resins, electro-dialysis, zeolites, and membrane technologies. Their advantages and disadvantages are listed in Table 5 below.

Table 5: *Summary of advantages and disadvantages of AMD treatment technologies* [17]

Treatment technology	Principle/Mechanism	Conventional material used	Advantages	Disadvantages
Alkaline addition	•The most common approach for the treatment of AMD •Involves neutralising the pH with one or more alkaline materials, after which the metals are insolubilised and removed •Metals are precipitated according to as (oxy) hydroxides, sulphides, and carbonates •Sulphate is removed as gypsum, but removal efficiency is low	•Limestone, quicklime, hydrated lime, dolomite, kiln dust, sodium bicarbonate, ammonia, potassium hydroxide, barium carbonate, barium hydroxide, magnesite, calcium peroxide	•Neutralising agents can be applied to any form of AMD treatment, e.g. ponds, pits, streams •Is a quick temporary solution for AMD treatment	•Conventional substrates are prone to armouring •Lime cannot raise the pH above 8 resulting in some metals not being removed •Sludge produced is voluminous, has a low solid content and is difficult to settle •Metals in the sludge are sensitive to pH
Desalination (sulphate removal)	•Involves the use of multiple alkaline agents sequentially to remove sulphate •There are various processes some of which include the ettringite process, barium sulphate process, and nano-filtration	•Lime, aluminium hydroxide, barium sulphate	•Ettringite process can lower sulphate to below 200 ppm •Nano-filtration can remove more than 99% of sulphate •Hybrids of desalination processes eliminate most of the disadvantages	•Produces large amounts of sludge that is difficult to settle •Treatment reaction times are too long •Unpractical for large-scale treatment •Barium sulphate process produces toxic barium salt, poisonous hydrogen sulphide gas and is expensive

				•Nano-filtration requires a pre-treatment step and produces large amounts of waste brine
Adsorption	•Involves the use of adsorbent materials to selectively adsorb metals from AMD while releasing oxides and hydroxides to neutralise the pH	•Dead biomass, clay, tree bark, tea leaves, blast furnace slag, fly ash, natural zeolite, commercial chemical oxides and hydroxides	•Simple to operate •Efficient •Low volume of sludge produced •Do not require the use of chemicals	•The adsorption capacity of conventional materials is low •Cannot treat AMD containing suspended solids •Some commercial adsorbents are expensive •Regeneration of adsorbent is costly, and significant amounts of material are lost with each cycle •Conventional adsorbents have a limited lifespan
Anaerobic (sub-surface flow) constructed wetlands	•Forms the basis of passive treatment of AMD •Are natural wetlands that are engineered to naturally and biologically produce alkalinity •Treat AMD primarily through DSR by *Desulfovibrio* bacteria •Other mechanisms include dilution; filtration; sedimentation; hydrolysis;	•Wetlands typically comprise of a bedrock (limestone/gravel), soil, plants and an organic substrate (compost, manure, hay bales, peat, wood chips, leaf mulch, sewage sludge, cellulose, ethanol, acetate, lactate)	•Natural treatment for AMD •Environmentally friendly •Can be used for land and habitat rehabilitation •Removes both metals and sulphate •Metal precipitates are stable in the wetland and need not be removed	•Long retention times •Difficult to remove high concentrations of metals •Requires vast land space •Chemical substrates are expensive •Organic substrates can be costly for treatment in remote areas

	ion exchange by plants, soil and organic matter; other microbial redox reactions		•Low volume of sludge is produced •High long-term performance •Low maintenance •Cost-effective	•Gravel can be steep in some countries
Sulphidogenic bioreactors	•Treats AMD through DSR in batch, continuous or semi-continuous reactors •Dependent on an organic carbon source •Continuously stirred reactors are most common •Other types include fluidised bed reactor, up-flow anaerobic granular sludge bed (UASB) bioreactor and submerged membrane bioreactor (MBR)	•Animal manure, compost, sawdust, wood chips, spent mushroom compost, cellulose waste, limestone, bark Installation is simple	•Easy to install •Low cost •Removes high concentrations of metals and sulphate well •Performance is predictable •Allows for differential removal of metals	•Long-term performance is not understood due to complex biogeochemical processes •Lifetime is limited •Mn metal removal is poor •Requires continuous additions of organic substrates
Anoxic limestone drains	•Used to improve the efficiency of wetlands •Usually serve as a pre-treatment step by passing the AMD through a bed of limestone under reducing conditions	•Consists of a sealed trench buried in the ground which is filled with limestone and covered with an impermeable substrate such as clay	•Requires little land space •Cheaper than CWs •Requires lower maintenance than CWs •Good short-term performance	•Anoxic conditions are challenging to maintain •Prone to clogging of limestone •Conventionally known to fail in the long-term run

	and raising its pH, while metals are still in their reduced form •This allows a higher concentration of metals to be removed when sent to a CW/ settling pond			•Cannot handle high metal concentrations •Can only remove metals in their reduced states, e.g., Fe (III) and Al •Removes sulphate in low concentrations
Permeable reactive barriers	•Recent and emerging technology •Is an in-situ passive treatment •Are underground trenches filled with porous reactive materials, through which an AMD plume passes through •Similar to sub-surface flow wetlands in that DSR is used to remove metals and sulphate •Contaminants can also be immobilised in the reactive material through adsorption, ion exchange, and precipitation processes	•Granular iron, zero-valent iron, limestone, dolomite, quick lime, zeolite, compost, sewage sludge, wood chips, bone char, apatite, bauxite, activated alumina, fly ash, peat moss, ferric oxyhydroxides	•Low-cost in-situ treatment •Prevents cross-contamination with surface waters •Prevents loss of large amounts of groundwater •No land space required •Does not require any waste disposal	•Needs multiple substrates for effective treatment •Capital and implementation costs can be high if substantial barriers are needed •Mine site must be well characterised and modelled before treatment, which is time-consuming •PRBs are site-specific and are limited to AMD plumes that are less than 20 m below the ground •Long-term performance is unknown

AAPS→N-(2- aminoethyl)-3-aminopropyltrimethoxysilane ;APS→γ-amino-propyltrimethoxysilane ,DETA→diethylenetriamine ; DTC-TETA→sodium triethylenetetramine- bisdithiocarbamate ;MTMOS→methyltrimethoxysilane; NPS→n-propyltrimethoxysilane; PropS-SH→γ-mercaptopropyltrimethoxysilane;TEOS→tetraethoxysilane ;TETA →triethylenetetramine ;TMOS→ tetramethoxysilane; VTMS→vinyltrimethoxysilane

The addition of alkaline reagents to the AMD has been popularly adopted across the globe. The traditional chemicals that have been used for the past decades are sodium hydroxide (NaOH), $CaCO_3$, CaO, hydrated lime ($Ca(OH)_2$), dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), and ammonia (NH_3). The selection of these chemicals is, however, dependent on several factors, e.g., pH, acidity level, and volume of AMD to be treated. Amongst these, $CaCO_3$ and its derivatives are widely used because of the copiousness $CaCO_3$ and or its derivatives, and low cost as compared to other chemicals [14], [95]. In most cases, $CaCO_3$ is used to raise the pH of AMD to values between 6 and 8. This step will then be followed by the post-treatment step which, uses $Ca(OH)_2$ or CaO to raise the pH of the neutralised AMD to values around 12 [96], [97]. Thus, the initial step of $CaCO_3$ addition is used to precipitates all the metals which need not higher pH levels to precipitate, e.g., Fe^{3+} and Al, precipitates at pH values of 3-4 and 7 respectively. This step is crucial as it ensures that some of the metals which may be amphoteric do not re-enter the AMD through dissolution (if the pH were to be allowed to rise to values around 12). The subsequent step (post-treatment) is designed to precipitate ions such as Mn and SO_4^{2-} [97], [98].

Maree *et al.* (2004) used limestone to neutralise coal mine originating AMD. They reported that limestone could change the properties of the AMD. For example, the acidity of AMD changed from 12 000 to 300 mg/L (as $CaCO_3$), SO_4^{2-} from 15 000 to 2 600 mg/L, Fe from 5 000 to 10 mg/L, Al from 100 to 5 mg/L and pH from 2.2 to 7.

Researchers have conducted studies on treating AMD using integrated limestone and lime[100], [101]. Wilmoth's (1978) study was focused on precipitating out Fe^{2+} from solution, and this was achieved by first raising the pH to 6 by adding $CaCO_3$ and then to 9.5 by CaO addition, which aided Fe^{2+} precipitation. Geldenhuys and colleagues reported that the pH of AMD was raised from 2.1 to 7.68 thereby decreasing the acidity of AMD by up to 96% after $CaCO_3$ addition. After lime addition, Mn and SO_4^{2-} decreased appreciably after their precipitation at a pH of 9.5 and 12.26, respectively [100].

Magnesite, $MgCO_3$, is one of the naturally occurring carbonates, and it is mainly comprised of high quantities of MgO (~89%) and small quantities of Fe_2O_3, CaO, SiO_2, and Al_2O_3. Due to its high solubility and ability to raise pH to ~10 ($CaCO_3$ can only raise pH to values between

6 and 8), this reagent has been explored by Masindi *et al.* in the neutralisation of AMD. The initial AMD properties of pH 2.30, total dissolved solids of 10 237.30 mg/L, EC of 22 713.12 µS/cm and SO_4^{2-} of 4 635.6 mg/L changed to 10.30, 4 345.21 mg/L, 4 635.60 µS/cm, and 1 912.9 mg/L, respectively after reaction with $MgCO_3$. Although this treatment yielded much improved results as compared to $CaCO_3$, elevated levels of some ions such as Na, Zn, Ni, and Cd remained present in the treated AMD. This suggests that post-treatment may be required for alkali removal [102].

The main advantage of using carbonates is that they are cheaper than other neutralising reagents. However, there are environmental and economic issues tied up to their usage. These include the greenhouse gases, energy consumption involved in mining and or calcining and transportation, and depletion of the natural resource.

2.2.6.2.3. Sustainable AMD treatment options

Due to the diminishing limestone reserves, alternatives to limestone or lime alternative materials that are environmentally friendly, cheap, and sustainable are desirable for mitigation of AMD. Such chemicals include pulp and paper limestone wastes (Maree *et al.*, 2013; Vadapalli *et al.*, 2015) and fly ash from coal firing energy stations (Petrik *et al.*, 2003; Gitari *et al.*, 2006; Vadapalli *et al.*, 2008). These high concentrations of CaO in these materials enable their practical usage as alternative options.

Kraft pulp mill $CaCO_3$ ***wastes:*** Maree *et al.* (2013) used precipitated $CaCO_3$ (lime mud) from Kraft pulp mills, chemical recovery loop to treat AMD from coal mine dumps. The AMD, whose concentration of Fe^{2+} was 6 000 mg/L, acidity was 18 000 mg/L $CaCO_3$, and SO_4^{2-} was 25 000 mg/L, was treated with the precipitated $CaCO_3$ in a sequencing batch reactor (SBR). This neutralisation process was followed by lime treatment to elevate the pH to values above 9, thus precipitating out metals such as Mg. The authors reported total Fe removal during the pre-treatment step and total heavy metal removal during the post-treatment with lime. The study concluded that the use of precipitated $CaCO_3$ in an SBR could treat 1 ML/day of AMD at the cost of R3.5 million.

Vadapalli *et al.* used pulp and calcium carbonate by-products from the paper mill to treat gold mine AMD in an SBR. The neutralising by-products used were pure and waste calcium carbonates (PCC and WCC, respectively). After neutralisation, some of the raw AMD chemical characteristics were improved, as depicted in Table 6. Although the quality of the neutralised water from these by-products was not the same, with PCC showing better results, both by-products showed potential as alternatives to natural $CaCO_3$ usage in AMD neutralisation, especially in active treatment technologies [104]. Here again, the practical utility of this treatment option is limited by the availability of the calcium carbonate by-products-these are produced in low quantities.

Table 6: *Chemical properties of AMD sample before and after PCC and WCC neutralisation* [104]

Parameter	**Units**	**Raw AMD**	**After SBR neutralisation**	
			PCC	**WCC**
pH	-	5.4	7.6	6.8
Acidity	mg $CaCO_3$ /L	1998	107.0	221.0
Fe^{2+}	mg/L	1089	0.540	4.500
Na		110.0	108.0	152.0
Mg		180.0	200.0	212.0
Mn		46.00	46.00	68.00
Al		<0.100	<0.100	<0.100
Ca		580.0	875.0	1041
Co		0.240	0.230	0.430
Ni		0.120	0.120	0.300
Zn		0.031	0.030	0.152
SO_4^{2-}		2939	2929	3109

In another study, Pérez-López and colleagues neutralised AMD samples from two different streams. These were collected from Cueva de la Mora (CM) and Tharsis (TH) at Québec in Canada. The pH, EC, and SO_4^{2-} of these samples were 3.61, 5.09 mS/cm, and 3 873 mg/L and 2.62, 11.09 mS/cm, and 15 558 mg/L, respectively. After reaction the pH, EC and SO_4^{2-} removal efficiency values were 8.15, 2.35 mS/cm and 48%, respectively, for AMD_{CM}, and 8.05, 5.38 mS/cm and 75%, respectively, for AMD_{TH}. However, the utilisation of lime mud for

AMD treatment is limited because the production of this material in pulp mills is deficient [108].

Slaker Grits: In the same study mentioned above, Pérez-López *et al.* also used Kraft mill slacker grits to treat the same AMD samples. The results indicated that pH, EC, and SO_4^{2-} reduction and removal efficiency values changed to 6.68, 2.25 mS/cm and 44%, respectively, for AMD_{CM}, and to 6.03, 6.30 mS/cm and 55%, respectively, for AMD_{TH} [108].

Coal fly ash: Both coal mining and power plants (during energy production) lead to the generation of copious amounts of waste in the form of AMD and fly ash, respectively. Fortunately, the latter has been proved to be beneficial in treating the former. The logistics of this is also improved by the fact that coal-firing power stations are usually situated close to coal mines for easy transportation. In turn, this could beneficiate the mine when transporting the fly ash back to the mine for AMD treatment. Generally, fly ash comprises CaO, $CaSO_4$, MgO, Fe_2O_3 (periclase), Fe_3O_4 (hematite), Al_6SiO_3 (mullite), and SiO_3 (quartz). The widely renowned utilisation of fly ash in AMD treatment is due to its alkalinity contributed by the presence of CaO. A study conducted by Gitari *et al.*, 2006 concluded that the dissolution of fly ash oxides contributed towards increasing the pH of AMD, which in turn reduced the ions concentration through precipitation. Optimum results were achieved with increasing fly ash dosage. Although some ions reached ~100% removal efficiency, some increased due to the leaching effect from fly ash. Thus, this leaching effect may limit the full utilisation of fly ash in AMD treatment.

Zeolites: Zeolites are tetrahedral, interlinked cage frameworks of aluminosilicates with water and alkali or alkaline earth metals. The open cage framework structure of zeolites imparts excellent sorption characteristics on them; hence they can be used effectively as molecular sieves and ion exchangers, Figure 5 [109], [110]. Generally, zeolites have a varying affinity of metals, and the adsorption efficiency of metals is dependent on the pH of the solution. At low pH values, zeolites will have a higher affinity towards H^+ than to metals. This means that strongly acidic solutions will favour the removal of metals through precipitation (the pH of water increases due to the formation of OH^- which is produced as H^+ is adsorbed by zeolites), and the high pH solutions would have high adsorption efficiency of metal species and fewer precipitates. It has also been reported that alteration of the cage framework by dehydration decreases the adsorption efficiency capacity of metals because this process decreases the cage size [109].

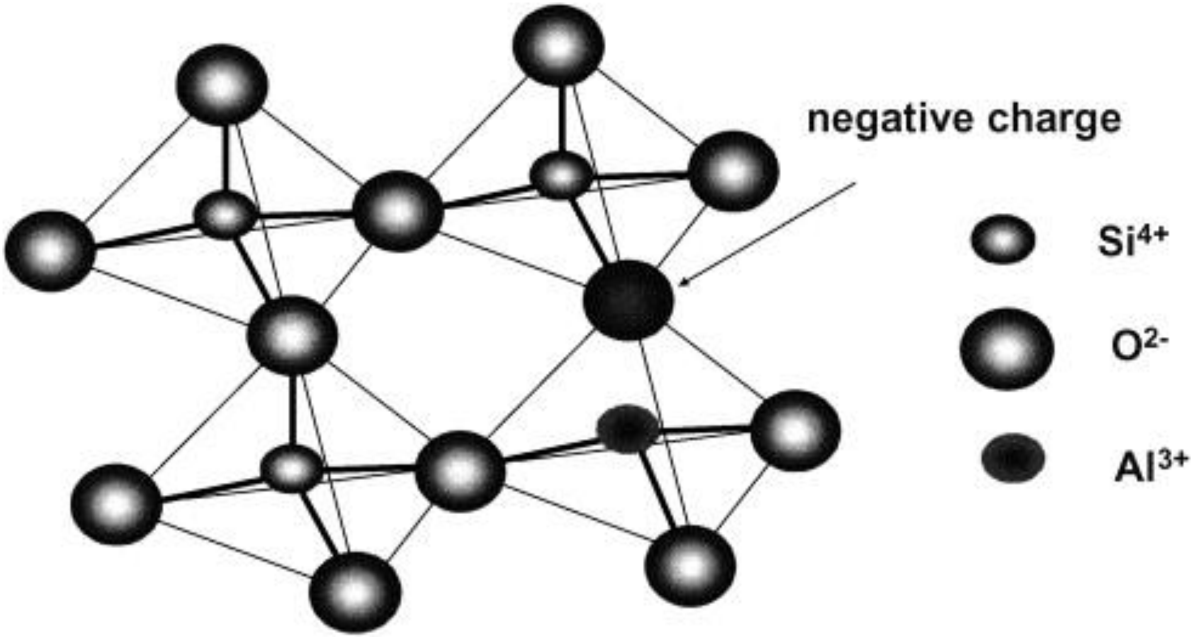

Figure 5: *Zeolite framework of tetrahedral SiO_4^{4-} with a Si/Al substitution AlO_4^{5-} yielding a negative charge, and consequently a cation exchange capacity* [110]

2.26. AMD TREATMENT TECHNOLOGIES THAT WERE DESIGNED BY SOUTH AFRICANS

After adding the alkalinity into AMD using limestone and/or lime, the effluent produced contains salts, rendering it unsuitable for regular consumption and use. When released into water bodies, this effluent adds salinity to them. To avoid this or to treat this alkaline effluent further, desalination technologies should be used. These technologies are designed to remove salts from water and hence convert this previously contaminated water into a portable one. One instance of such an integrated active AMD treatment solution is currently ongoing at the Optimum Water Reclamation Plant in Mpumalanga, SA [93].

More SA developed desalination technologies include the Magnesium-Barium-Alkali (TUT MBA) process from the Tshwane University of Technology (TUT), the Alkali-Barium-Calcium (CSIR ABC) process from the Council for Scientific and Industrial Research, the SAVMIN process from MINTEK, Savannah Mining and The Wren Group, the Rhodes BioSure, Environmental and Remediation Technology Holdings Ion Exchange (EARTH), and High-Pressure Reverse Osmosis (HiPRO) developed by Aveng water [93].

CSIR ABC: The alkali-barium-calcium (ABC) AMD technology developed by the CSIR is based on reducing the SO_4^{2-} in AMD by using and recovering barium carbonate ($BaCO_3$). The technology is a three-step process. The first is a pre-treatment step that is aimed at buffering the H^+ acidity and precipitating the dissolved metals using lime. A certain percentage of sulphate may also be reduced, probably due to gypsum crystallisation. The second process uses $BaCO_3$ to precipitate the SO_4^{2-}. At this stage, the SO_4^{2-} concentration is reduced from the AMD in the form of $BaSO_4$, and the resulting water will be clean. Finally, in the third stage, the sludge produced is calcined in a kiln to produce alkali (A), barium (B) and calcium (C), hence the name ABC process. The costs involved in treating the sludge make this technology to be economically favourable [111].

TUT MBA: The TUT developed the TUT MBA technology. The technology was designed to precipitate metals and SO_4^{2-} from the laden mine water using economically sound chemicals. The process is similar to the CSIR ABC process. The difference between the two is the reagents that are used. In the case of MBA, $Mg(OH)_2$ and $Ba(OH)_2$ are used to treat the AMD. The highly soluble $Mg(OH)_2$ (as compared to $Ca(OH)_2$) is used for increasing the pH value of the water as well as to precipitate the dissolved metals. After filtering out the precipitates, the filtrate is then treated with cheap $Ba(OH)_2$ (as compared to $BaCO_3$) which serves to precipitate both the SO_4^{2-} and Mg^{2+}. After removing the sediment, CO_2 is bubbled through the water to precipitate $CaCO_3$ [112].

MINTEK SAVMIN: Mintek developed the SAVMIN AMD treatment technology in collaboration with Savannah Mining and The Wren Group. The technology is divided into five stages, as described below [113].

Stage 1-Precipitation of dissolved metals: The first stage is aimed at raising the pH level to ~12 for metal precipitation.

Stage 2-Gypsum de-supersaturation: in the absence of gypsum seeds on the walls of stage 1 tank, the Ca^{2+} and SO_4^{2-} in the solution do not crystallise, that is they remain meta-stable in the solution. In stage 2, gypsum seeds are introduced into the solution to provide the reactive sites for gypsum crystal formation in the water. The resulting crystals will then be filtered out, and their portion will be used in the next cycle.

Stage 3-Ettringite precipitation: further removal of the Ca^{2+} and SO_4^{2-} ions in the solution is carried out at this stage. This process is achieved through the addition of $Al(OH)_3$, which precipitates Ca^{2+} and SO_4^{2-} by forming an ettringite (calcium-aluminum sulphate, $3CaO.3CaSO_4Al_2O_3.31H_2O$) through the following reaction:

$$6Ca^{2+} + 3SO_4^{2-} + 2Al(OH)_3 + 38H_2O \rightarrow 3CaO.3CaSO_4.Al_2O_3.32H_2O + 6H_3O^+ \qquad \textbf{\textit{Eqn. 10}}$$

This reaction takes place at a pH between 11.6 and 12. The ettringite is then separated from the solution through thickening and filtration.

Stage 4-Carbonation: the filtrate from stage 3 is then bubbled with CO_2, which reduces the pH and, at the same time, precipitates pure $CaCO_3$ that is then filtered out.

Stage 5-$Al(OH)_3$ recycling: $Al(OH)_3$ is recovered by decomposing the ettringite that was formed in stage 3. The ettringite is destabilised through the reverse of Eqn. 10- this is achieved by exposing it to low pH, gypsum saturated solution. The $Al(OH)_3$ is then removed from the solution by thickening and filtration and recycled at stage 3. The resulting solution is then treated as described at stage 2, and the filtrate is reused in stage 5 again. This process produces portable water, $CaCO_3$, $CaSO_4.2H_2O$ and metal hydroxides [113].

Rhodes Biosure: The Rhodes Biosure technology was developed by Rhodes University and is the most cost-effective biological AMD treatment technology that has ever been reported. Unlike other biological treatment technologies that reduce the SO_4^{2-} ions and metal precipitation through the addition of electron donors such as ethanol, this technology use sewage sludge as a sustainable carbon and electron donor source. Thus, the Rhodes BioSure is not only cost-effective but also a green initiative that benefits the environment [114].

EARTH: The EARTH ion exchange process was designed to treat lime pre-neutralised AMD using IX resin as absorbents. Thus, after neutralisation, the AMD is filtered through sand and activated carbon to remove solids and organisms, respectively. The resulting filtrate will then be fed into the uranium (U) strong base IX resin columns to remove U in the AMD. The U-rich resins are then eluted with H_2SO_4, and the eluate is stored in tanks, ready to be sold to U processors [88].

A portion of the U deficient AMD is sent back to the feed water point, where it will be used for backwashing the sand filter. The other portion will be fed into the strong acid IX resin columns. The cation-rich resins are then regenerated by eluting them with concentrated HNO_3. During this process, nitrate salts are formed, and the eluent is then aerated to oxidise Fe^{2+} to Fe^{3+} and neutralised with $NH_{3(g)}$ to precipitate Fe^{3+} (at pH ≥3). The Fe precipitate is then filtered out, dried and packaged as pure red oxide pigment. The pH of the filtrate is then further adjusted to 7, concentrated to contain 50% water through hot air evaporation and packaged as a fertiliser [88].

The SO_4^{2-} removal is achieved by feeding the acidic effluent from the strong acid IX resin columns into the week base anion exchange resin columns. After the SO_4^{2-} absorption, the resins are regenerated using an alkaline reagent, in this case, $NH_{3(g)}$. The eluent is then crystallised through evaporation to form ammonium sulphate ($(NH_4)_2SO_4$) and the water from the columns can be used for domestic purposes [88].

HiPRO: The High-Pressure Reverse Osmosis (HiPRO) system is a desalination process that was designed by Aveng Water to treat AMD at eMalahleni in Mpumalanga, SA. This technology enables a total of 97% portable water recovery and brine and solid wastes, which amount to less than 3% of the total initial feed. Both saleable and impure $CaSO_4.2H_2O$, together with metal sulphates, are recoverable in this process. [115].

GYP-CIX: This process is based on an ion-exchange mechanism to treat AMD. The system was designed to treat the net alkaline, and gypsum saturated AMD. The process removes cations and anions in two separate multistage ion-exchange fluidised resin beds. The strong acid cation (SAC) and the weak base anion (WBA) resins are used for the respective ion types. The cations are removed in the first stage, whereas the anions are removed in the second stage. After each type of ion removal, the resins are regenerated using 10% H_2SO_4 and 2% lime solutions for the cation and anion resins, respectively. The end products of this process are clean water and $CaSO_4.2H_2O$ [85], [87]**.** The unique advantage of this technology is that, unlike other ion exchange technologies, it uses cheap chemicals that do not produce undesirable unstable waste products for resin regeneration [87].

2.2.7. Benefits of AMD Treatment

Treatment of AMD does not only produce water with improved mineral content but also produces sludge and gases. The sludge is a soup of heavy metals precipitated as oxides, hydroxides, sulphides, or carbonates. Thus, the slurry is toxic due to its constituents. To abide by environmental regulations, e.g., NEMA guidelines, the sludge also needs to be beneficiated, and this would not only help in protecting the environment but would also lead to self-sustain the AMD treatment plants.

In the pursuit of finding sustainable ways of treating the toxic sludge, it is crucial to develop and/or validate AMD treatment techniques that have the potential to self-sustain themselves by producing saleable by-products. These by-products may include H_2O, metals, salts, oxides, H_2SO_4, HCl, building and construction materials, adsorbents and pigments. The recovery of some of these byproducts has been described in the preceding sections. Generally, the recovery of saleable by-products is dependent on both the mechanism and process used for AMD treatment.

2.3. GREEN LIQUOR DREGS (GLDs)

2.3.1. History of Pulp and Paper Industry in South Africa

Most people do not appreciate the value encrypt in the biomass pulp products that they use daily. When they see these products, they only value what the product has been intended for and not its source. They do not realise the whole story behind the product at hand.

One such product of tree is the pulp that is widely used in every society across the universe is paper. Most people do not appreciate the remarkable story that every sheet of paper carries. They do not realise that it was first a tree, which served distinct roles that sustained the planet and its activities. Thus, every tree pulp should be viewed as a first the source of oxygen, absorbent of carbon dioxide (CO_2) and other greenhouse gases, a job opportunity (directly or indirectly), host for active medicinal ingredients, packaging material, energy source, and should be appreciated for its carbon lock ability, Figure 6.

The history of the South African pulp and paper industry dated to the 1920s when Premier Paper Company was founded at Klipriver. Significant growth in both the establishment and capacity building of this industry was realised around 1950s-this is when the industry started to contribute significantly towards the economy of the country. During these years, companies (such as Mondi and Sappi)and their satellites were established [116].

The virgin source of pulp and paper industry in South Africa (SA) is mainly from Pine and Eucalyptus species. These trees are mainly distributed in areas which receive high rainfalls such as Mpumalanga, KwaZulu-Natal and Eastern Cape provinces [116]. Their distribution has been reported to be about 41, 40 and 11%, respectively. Parts of Limpopo and Western Cape each constitute 4% of the plantation, Figure 7. The 2016 Paper Manufacturers Association of South Africa (PAMSA) industry progress report recorded that the timber plantations produced 15 tons of O_2 and absorbed 20 million tons of CO_2 and other greenhouse gases. Furthermore, the plantations intended for pulp and paper manufacturing made it possible to avoid emissions of 1.3 million tons of CO_2 from fossil fuel burning through biomass energy generation [117].

Figure 6: *Products made from a tree pulp* [117]

There has been a steady decline in the total net production of pulp in SA, pulp and paper industry is continuing to play a significant role in the GDP of the country [117], [118]. For example, the local pulp production dropped from 2.14 million tonnes in the year 2018 to

1.94 million tonnes in the year 2019. However, both these years have contributed 0.53% towards the country's GDP. The 2019 GDP contribution translates to $1.7 billion [118].

Figure 7: *Plantations in South Africa* [119]

2.3.2. Cradle of Green Liquor Dregs

As described in the introduction section, GLDs are non-process elements (NPE) and they ought to be removed from the green liquor. The Kraft pulp mill is divided into two parts viz; pulp manufacturing and chemical recovery system, which represent a closed-loop overall system as conferred below and demonstrated in Figure 8 [120], [121].

Pulping: The Kraft pulverising method yields pulp from wood by cooking the debarked, fragmented wood in a hot mixture of Na_2S and NaOH, known as cooking/white liquor.

This cooking liquor unshackles the cellulose fibres from the lignin matrix that binds the fibres together. This process removes about 90-95% of the lignin from the wood matrix. After cooking, the fibres and the resultant black liquor are separated. The pulp fibres are then sent into the knotter where knots and uncooked wood portions (shives) will be removed. These knots and shives may either be used for energy recovery, repulped, or may be disposed of as waste [5], [8], [122]–[124].

The deknotting process is then followed by the pulp washing step. Multiple washers may be used to ensure efficient cooking liquor recovery and to minimise its carryover to the next processes. From this step, the washed pulp undergoes further cleaning process known as the screening process. The oversized particles found in the washed pulp are removed during this screening process. The screening process is then followed by either paper making (for non-bleached paper applications such as packaging) or bleaching processes (aiming to improve its application possibilities such as in dissolving pulp, white and or coloured paper) depending on the intended application. The spent "black liquor"(also known as brown recovered during pulp washing is then sent to the chemical recovery system, where the Kraft cooking liquor "white liquor" components will be produced and used as cooking liquor during Kraft pulping cycle [5], [8], [122]–[124].

Kraft recovery system: The Kraft recovery system has been referred to as the kidney of the Kraft pulping process. This is because of its diverse vital processes that ensure the overall well-being and sustainability of the pulping plant/equipment. Spent liquor from the pulping process (Black liquor) is very rich in organics, and inorganic salts, which, when are recovered, are used as source energy and cooking chemicals, respectively. The energy regeneration and chemical recovery from the black liquor are discussed below.

Energy regeneration: the black liquor that go into the recovery system is composed of ~15 % solids. These may, depending on the type of wood used, include organics (e.g. lignin, hemi-cellulose, tall oil, resin acids, turpentine, and vanillin), inorganic salts (e.g. Na_2CO_3 and $Na_2SO_)$, and non-process elements (NPEs) (Mg, Si, Se, Cu, Zn and Mn). Optimisation of energy regeneration efficiency from this liquor, the liquor is evaporated in multi-stage effect evaporators to about 60-75% of solids. The resultant liquor would now be referred to as concentrated black liquor. The concentrated liquor is then directed into the bottom of a high temperature furnace, where the organic matter in the liquor is pyrolysed to generate green, sustainable energy. Under these stringent conditions, inorganic salts, Na_2S, and sodium carbonate, Na_2CO_3, are formed [5], [123], [124].

Causticisation: the smelt resulting from the deoxygenated recovery boiler is then sent to the dissolving tank where it is dissolved with a weak white liquor to form green liquor. The green liquor is then transferred to the green liquor clarifying where all non-processed elements (using different technologies) are removed from the liquor, washed and discarded as GLDs in landfills as GLDs [5], [125].

The cleared green liquor is then sent to the slaker where CaO is added. CaO then reacts with water to form calcium hydroxide ($Ca(OH)_2$). At this stage, another form of solid waste is removed from the process and disposed of in landfills as slaker grits. The liquor produced is then directed to the causticising reactor, where Na_2CO_3 reacts with $Ca(OH)_2$ in the liquor to form NaOH and $CaCO_3$. At this stage, liquor is now made up of white liquor (NaOH and Na_2S) and $CaCO_3$. From here, the liquor is fed into a white liquor clearing tank, where $CaCO_3$ is allowed to settle at the bottom. This settled $CaCO_3$ is now referred to as lime mud. The clarified white liquor is then returned to the pulping cycle. Lime mud is washed (producing weak white liquor), filtered with a pre-coat, and used as a limestone make-up in the calcination process to produce CaO. The weak white liquor will be used to dissolve the smelt recovered from the smelt recovered from the recovery boiler [5], [125], and forms part of the chemical recovery loop.

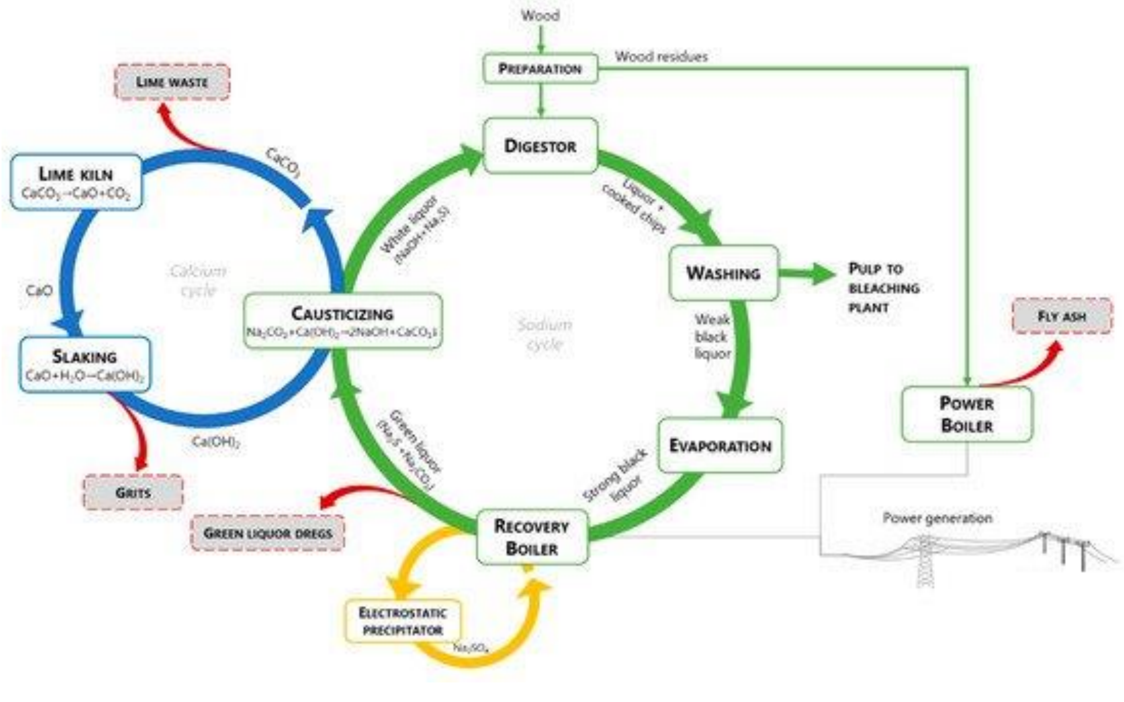

Figure 8: Kraft mill pulping flow diagram [121]

GLDs are found in the green liquor system and contribute significantly to the NPEs found in the chemical recovery operations. Their carryover to the downstream processes has a negative effect on the quality of the cooking liquor produced as well as the operation of the kiln [6], [121]. This carryover relates respectively to the filtration capacity of low dregs in the cooking liquor and mud lime systems. As a result, dregs must be purged from the process through a liquid-solid separation process. Green liquor clarification technologies used are either sedimentation or filtration processes. The standard principle between them is that the pH of dregs should be below the maximum recommended value of 13. Thus, depending on the method used to separate dregs from liquor, a washing step may be necessary to reduce the pH of dregs to the recommended values. [5], [121], [126].

Sedimentation of GLDs: Separation of dregs by sedimentation processes relies on the settling properties of the liquor's solid particulates. The sedimentation technologies that have been invented and used by various Kraft mills around the globe include the green liquor clearing tank and the centrifugal system [119],[120]. These developments vary in the efficiency of the clarification of liquor, the settling rate and the time taken to sediment the solids [4].

Green liquor clarifying tank: This technology uses the rake system to remove the dregs from the liqueur. The process basically begins by allowing the insoluble particles to settle at the bottom of the clarifying tank-this phase can take about 12 hours. Many mills improve the sedimentation cycle with flocculants. It is accomplished by rising particulate surface area and thereby improving settling rate by increasing conglomerate density. After settling, the clarified liquor is then transferred to the causticising plant where it will be reacted with $Ca(OH)_2$, while the sediment slurry is drained from the tank using a rake method. The dregs are then sent to the washer where they are diluted with fresh water, and then the resulting slurry is moved to a washer. The overflow liquor, also known as the weak white liquor, is transferred to the weak wash liquor tank while the underflow is sent to the effluent treatment plant. The washed GLDs are then disposed of in the landfill. [4], [5], [126].

Filtration of GLDs: A number of GLDs filtration processes, including the cross-flow, cassette, tube, pressure disk, and pre-coat vacuum filters, are commonly used. The filtration processes are enabled by membrane processes whereby semi-permeable membranes are used as filters to separate the solid particulates from the liquor. The methods may be driven by either internal pressure (from the liquor feed pump), or external/introduced air pressure [127], [128]. This study will only cover the use of the pre-coat vacuum filter, which is widely used in the Kraft mills.

Green liquor pre-coat vacuum filter: the most commonly used green liquor vacuum filter is known as a pre-coat vacuum filter, Figure 9 A. This filter is fitted with a slurry feed vat, filter drum, filtrate pipe, and knife blade. The sediment slurry is collected in a vat that has an agitator, which prevents the settling of insoluble solids. The filter, which is pre-coated with lime mud, rotates and picks up the slurry from the vat, the liquid is sucked into the hollow filter drum and the solid particulate forms a cake on the filter's external surface and, finally, a knife blade scrubs the cake out of the mesh. This cycle continues until all the liquor has been filtered out, and the cake is then sent for disposal as GLDs, as shown in Figure 9B. The lime mud used to enhance the filtration process ends up increasing the quantities of dregs that are being landfilled. Typically, 1-1.5 Kg of lime mud is used to aid the filtration process of 1Kg dregs [126], [129], [130].

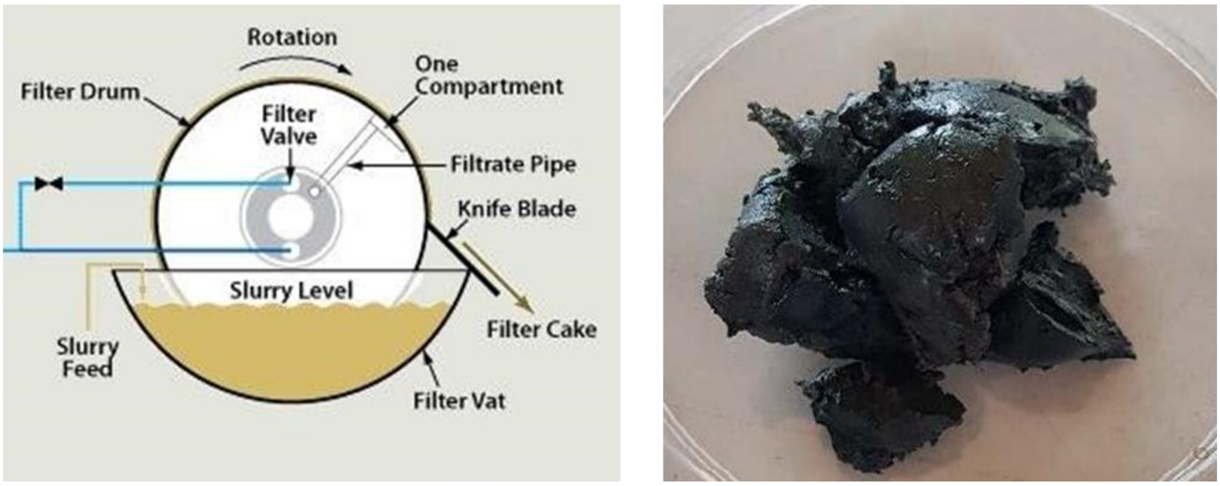

Figure 9: *A rotary pre-coat vacuum filter* [131] *and (B) fresh GLD* [14]

2.3.3. Properties and Applications of Green Liquor Dregs

2.3.3.1. Properties and applications of GLD

Chemical and mineralogical composition: GLDs are generally characterised by having high quantities of $CaCO_3$, sodium carbonate (Na_2CO_3), carbon, and NPEs. The $CaCO_3$ present in the GLD is mainly introduced when the GLDs is filtered with a lime mud-coated vacuum filter while the traces of carbon may be the leftovers of lignin that was not burnt during the energy regeneration step, and the NPEs may have either came through the process through the wood, chemicals used, or the corrosion of pulping equipment [125], [132]–[134]. The NPEs may include magnesium (Mg), iron (Fe), silicon (Si), potassium (K), copper (Cu), calcium (Ca), manganese (Mn), barium (Ba), nickel (Ni), chromium (Cr), and zinc (Zn) and these together with their concentrations may differ from one mill to another. Similar to the NPE composition, the mineralogical composition of GLD differs from one mill to another. This difference in elemental and mineralogical composition is shown in Table 7 Table 8, respectively. [16], [108], [125], [133], [135], [136].

Table 7: *Elemental composition of GLDs* [14]

Parameter	**Concentration (ppm)**			
P	10	0.90-2.10	0.2	98-78
Ca	84500	118.2-347	0,175	18.500-20.700
Na	26100	29.8-144.4	0.0198	311.000-267.00
K	1700	0.90-6.60	1.4	9.830-11.600
Mg	29700	21.0-51.1	0.0959	8.030-12.100
S	10600	N/A	0.0312	N/A
Cu	110	2.60-5.40	0.33	N/A
Zn	1200	0.0488-0.258	6.49	269-313
Fe	4500	2.60-5.40	8.01	6.590-10.600
Mn	10300	1.6-7.8	0.0351	3.980-5.950
Cd	10	0.00407-0.00612	0.011	N/A
Cr	300	0.0474-0.0689	0.16	33-42
Ni	200	0.119-0.254	0.08	32-38
Al	N/A	0.3-4.10	0.0255	1.670-2.050
Pb	N/A	0.0311-0.0624	0.052	N/A
pH	10	12.1-12.3	N/A	N/A

pH and neutralising potential: the presence of carbonic mineral phases together with the fact that the Kraft pulping process virtually an alkaline process, efficiency of filtration, and or NaOH that may sometimes be carried over from the liquor play a substantial role in the pH level of GLDs equipment [125], [132]–[134]. Also, the neutralising potential of GLDs was determined to be comparable to that of limestone [134]. This could be taken advantage of in replacing the use of limestone in specific industries.

Geotechnical properties: Mäkitalo *et al.* (2014) have shown that GLDs have excellent geotechnical properties such as high porosity and water retention capacity, small particle size ~12μm, large surface area ~18 m^2/g and very low hydraulic conductivity. GLDs, however, were stated to have low shear strength.

Table 8: *Mineralogical composition of GLDs*

Mineral Name	Formula	References
Pirssonite	$Na_2CO_3.\ CaCO_3.\ 2H_2O$	[14], [120], [125], [133]
Calcite	$CaCO_3$	[10], [14], [16], [108], [120], [133], [137]–[140]
Portlandite	$Ca(OH)_2$	[120], [133]
Thermonatrite	$Na_2CO_3.\ H_2O$	[125], [133]
Natrite	Na_2CO_3	[16], [133]
Sjögrenite	$Mg6Fe_2^{3+}(CO_3)(OH)_{16}.\ 4H_2O$	[133]
Anhydrite	$CaSO_4$	[14], [133]
Quartz	SiO_2	[133]
Graphite	C	[16], [126], [133]
Halite	NaCI	[133]
Diopside	$CaMgSi_2O_6$	[133]
Pargasite	$NaCa_2Mg_3Fe^{2+}Si_6AI_3O_{22}(OH)_2$	[133]
Vermiculite	$Mg_{1.8}Fe_{0.9}^{2+}AI_{4.3}SiO_{10}(OH)_2.4(H_2O)$	[133]
Dolomite	$CaMg(CO_3)_2$	[137]
Thenerdite	Na_2SO_4	[137]
Cesanite	$Ca_2Na_3(SO_4)_3OH$	[137]

2.3.3.2. Exploitation of GLDs

The properties that GLDs possess had enabled researchers across the globe to explore them to beneficiate various fields/industries such as in agriculture [141], building and construction [12], [137], [142], and mining, pulp and paper, and water industries [7], [10], [16], [108], [134], [143]. In this review, we will be looking only into the beneficiation of GLD in the mining industry and particularly in remediation and amelioration of AMD.

2.3.3.2.1. Remediation of AMD formation

Blending and co-disposal of GLDs

Alakangas, Andersson and Mueller (2013) expropriated the GLDs' neutralising power in blending them with S^{2-} rich mine tailings as an initiative of reducing their landfilling and preserving natural carbonate materials. In their study, different ratios of GLDs were mixed with tailings and exposed to the oxidising environment for stipulated periods. At the end of their experiments, GLDs was proven to be effective in buffering the AMD that would have otherwise been formed had it not been the presence of the alkalising effect produced by GLDs. In other words, the presence of GLDs assured the production of leachate with pH values that were above 7 and had low metal concentration as compared to the leachate that was produced from the tailings that were not blended. Nevertheless, the authors also outlined that the actual particle size of mine rocks/tailings may negatively impact blend ratios and that the longevity of using GLDs as the alternative for traditional unsustainable carbonates needs to be investigated. The other problem that was not highlighted by the authors of this study is that the versatility of NPE and their concentration thereof must be carefully studied before using GLDs for this purpose and that further treatment may be required to turn the neutralised AMD into potable water. Additionally, high $CaCO_3$ content may be a preferred mineral phase composition of the GLDs as this phase is not prone to fast depletion as compared to other phases such as $Na_2CO_3.CaCO_3.2H_2O$. On the other hand, the gradual formation and accumulation of precipitates, especially the $CaSO_4$, use of this technology may, in a long-term turn into a non-porous surface that may inhibit the proliferation leachate.

Mäkitalo *et al.* (2014) studied the potential use of GLDs as a sulphidic rock's sealing layer and concluded that GLDs could effectively avoid or lessen the formation of AMD due to several properties they have. These include high porosity, water retention capacity, the small particle size of ~12μm, the great surface area of ~18 m^2/g, and very low hydraulic conductivity. The high porosity allows water to flow through the cover. Due to the large surface area (which is the result of the small size of the particles), the water entering the GLDs is imbibed by chemical interactions with the GLDs. This results in a high-water saturation of ≥85 % that inhibits or limits the penetration of O_2 into AMD tailings. The high-water saturation helps to keep the sealing layer intact as it prevents shrinkage and cracking of the layer that could occur due to seasonal changes.

However, it was also determined that GLDs' effectiveness and or durability might be affected by various factors. Other studies in which GLDs were used as sealing layers evaluated factors that could impact the efficacy and or durability of the layers. These factors included weather conditions, CaO quantities, pH, and topography of the area. However, Maurice, Villain and Hargelius (2009); Jia *et al.* (2013); Jia, Maurice and Öhlander (2014)b; Mäkitalo *et al.* (2014) had also reported that the that GLDs' effectiveness and or durability may be affected by various factors such as the CaO content, pH, and weather conditions as shown below.

High CaO content: The high amounts of CaO in GLDs may increase the hydraulic conductivity of the layers and negative impact on the efficiency of the sealing layers. This means that water and O_2 may infiltrate through the till and induce oxidation [140], [146].

pH: batch leaching tests conducted by Jia, Maurice and Öhlander (2015) showed that GLDs could immobilise different metals. This is accomplished when carbonate salts or metal hydroxides are exposed to high pH levels. For example, high pH levels mobilise As by reducing its hydroxide's stability. The same scenario applies to Cr in which the alkalinity above the neutral value facilitates the conversion of Cr^{3+} to Cr^{4+} ,thus promoting the mobility of Cr [136], [140], [143].

Land topography: It has been recounted that GLDs cannot be used on hillsides because of their weak uniaxial compressive strengths. Consequently, several studies investigated ways to enhance this geotechnical property of GLDs. Maurice, Villain and Hargelius (2009) ascertained that GLDs from the clarifying tank (GLDs removed from the process by allowing them to settle at the bottom of the clarifying tank) exhibited lower hydraulic conductivity than pre-coat segregated GLDs. The high hydraulic conductivity in the pre-coat segregated GLDs is caused by the high amount of CaO in the AMD. This means that using pre-coat segregated GLDs as a sealing layer may not be as effective as soils with lower hydraulic conductivity and thus runs a risk of perhaps sliding down/tearing apart and hence unveils the S^{2-} bearing minerals to the oxidising environment. The addition of fly ash or biological sludge will reduce GLD's hydraulic conductivity by a magnitude of 1. With all these alteration materials integrated, the hydraulic conductivity decreased by a further magnitude of 1[140], [145], [146].

Weather conditions: In very cold areas, the freeze-thaw cycles may cause shrinkage and expansion, which, may in turn, lead to the cracking of the sealing layer, thus allowing the ingression of water and O_2 into the tailings. This intrusion will lead to oxidation of the sulphide-bearing minerals within the tailings [140], [146].

Using GLDs as a single dry cover

Other studies have focused on using GLDs as partial or alternative materials for traditional sealing layer materials in AMD treatment to reduce the costs sustained when synthetic materials or soils are used as sealing layers. For example:

Ragnvaldsson *et al.* (2014) investigated the feasibility of using GLDs, on a pilot scale, and in an operational mine, to replace high-density polyethylene sealing layers. In short, two waste rock piles with sloped sides and flat tops were constructed on top of 1-2% sloped polyethylene liners. The liners were there to collect the leachates that might be formed. One pile served as control, whereas the second pile was covered with a 30 cm layer of GLDs, on the top and sides. The top side was then covered again with a high-density polyethylene liner that diverted water away from the pile, thus reducing the amount of water that might infiltrate the piles. Flow meters were installed at each pile to measure the quantities of the leachates. The leachate from each pile was collected biweekly for one year and analysed for metal content. The results indicated that the test pile produced 40% less leachate than the control pile. This indicated that the GLDs that was mounted on the sides of the waste rock pile also contributed towards the reduction of water infiltration. Chemical analysis of the AMD showed that although there was no significant difference in pH levels of the two leachates, the concentration of metal load in the test leachate decreased by ≥50% for 13 of the 20 metal elements. The researchers postulated that such differences in metal concentrations might have been due to: (i) the GLDs might have increased the pH of the incoming water hence initially minimising the sulphide oxidation induction rate which ultimately reduces the dissolution of other metals found in the rock waste, and; the precipitation of Fe could have impacted on the chemistry of other metals. The study concluded that this technology could reduce the AMD treatment costs of an operational mine by ~10 % due to the 40% lower leachate production as well as the low concentrations of most metals in the leachate. These findings could benefit not only the mine but also the environment as the carbon footprint involved during the synthesis of polyethylene used for sealing mine wastes, and mining, burning, and transportation of $CaCO_3$ limestone/lime (CaO) and the sludge produced if vast quantities of AMD were to be treated. Although the results of this study have shown the positive effects of using GLDs in partially substituting the polyethylene, which is sometimes used for covering tailings, careful considerations on the integrity of the cover should be considered. For example, a cover should always be able to block away either one or both of the elements needed for sulphide oxidation. That is, using GLDs in the open air means that they will dry out and may eventually crack, and this would allow water and oxygen to infiltrate the tailings.

Later on, Mäkitalo *et al.* (2015) investigated two ways of blending GLDs and till. A mobile asphalt plant and a construction loader with a crushing bucket were used, as seen in Figure 10. Different ratios of GLDs: till (till with about 30% and less than 10 % of particles which are less than 0.063 mm) were mixed for varying periods. The GLDs ratios used ranged from 5 -15%. The study confirmed that blending fine till with GLDs depletes its good hydraulic conductivity, thus implying that fine tills should not be amended. Vigorous mixing resulted in the mix having high water content (due to the water that is unbound from GLDs), high porosity, and low hydraulic conductivity. Decreased hydraulic conductivity was also noticed after long mixing times. When using a loader, long mixing times affected the consistency of the results because it is possible that the loader could have incorporated the particles from the ground. The addition of coarse material may decrease the conductivity, whereas finer particles may increase it. This is because, naturally, fine soil particles have low hydraulic conductivity and blending them may only lead to depletion of their suitable hydraulic conductivity property.

Figure 10: *A construction loader and asphalt plant used in mixing till and GLDs [7]*

High water content and low dry density on the asphalt blended 10% GLDs: till (30% sand) was observed, whereas the same blend of the loader had precisely the opposite properties. The overall conclusion of this study was that if either technology were to be used, 5% GLDs should be blended with till with high sandy particles. In this way, the blends produced a high compaction degree, which is observed when the blend has high dry density and low water content. This indicates that the compaction degree is preferable to hydraulic conductivity (Mäkitalo *et al.*, 2015).

GLDs amendment using other materials

Makitalo and Siren have investigated soils that are used in mine waste rock or tailings as sealing layers need to meet specific geotechnical properties such as low hydraulic conductivity, small particle size, and high density of compaction. If the soils found in the periphery of mines are not suitable to be used for constructing sealing layers, the mines will have to procure soil for this purpose. This is a costly endeavour. Therefore, to curtail these costs, cheaper materials may be used to improve the properties of the surrounding soils as layers. Sirén *et al.* (2016) studied the effect of adding different quantities of green liquor dregs into diverse types of soils and evaluated the feasibility of using the resulting mixtures as sealing layers. This was a pilot-scale study that used 400 m^2 cells that constituted construction of a 0.2 m foundation, 5 m sealing, and 1.5 m protection layers. Clay, sandy, and fine-grained tills were used as layers to which were added ~10% GLDs. The mixtures were compacted using a hydraulic plate compactor. The results showed that the addition of up to 10% GLDs to the clay soils increased its naturally low hydraulic conductivity. On the other hand, the same quantities of GLDs lowered the hydraulic conductivities of fine-grained and sandy soils. Thus, GLDs could only be used as local soil amendment material in soils that generally have poor geotechnical properties.

2.3.3.2.2. Mitigation of AMD with GLDs

GLDs are generally alkaline waste materials. One of the first studies in which GLDs were used in the neutralisation of the acidic effluents was conducted by Pöykiö and his group (2006). They used GLDs to neutralise Kraft mill acidic wastewater and reported that GLDs were excellent as neutralising agents due to their high pH (~10.7), comparable liming value to that of $CaCO_3$ (39%), and fast-acting capacity [134].

In 2011, Pérez-López *et al.* characterised GLDs and used them to neutralise two different AMD leachates. SEM/EDX and XRD analyses of the GLDs samples were conducted before and after the reaction with AMD. XRD analyses showed that the GLDs contained 80% calcite. These XRD results were confirmed by the presence of rhombohedral structures, which were evident on SEM micrographs. Furthermore, this study showed an effective metal removal from the AMD, as presented in Table 9. It could be concluded that GLDs is effective in raising the pH of AMD and reducing some metals even to 100%. However, it should be noted that the dosage used here may not be taken as the universal dosage because GLDs may sometimes constitute mineral phases, as per Table 4, which may have preferential dissolution to calcite and hence limiting its dissolution- this obviously depends on the pH of AMD and the mineral phase quantities. However, Sebogodi *et al.* (2019) showed that the different carbonic mineral phases composed in the GLDs play a significant role in the AMD neutralisation mechanism. That is, their nature, quantities, degree of solubility facilitate the neutralisation process. Thus, other minerals dissolve readily in the medium, while some like $CaCO_3$ require lower pH values to dissolve.

Additionally, the quantities of the respective NPEs in GLDs should be considered as they may leach out into the AMD and increase the costs of post-treatment. Therefore, it is imperative to keep the dosages as low as possible. The pH at which other metals precipitate is vital in choosing the GLDs feed quantities. Thus, some may be immobilised by adding excess neutralising reagent.

Table 9: *Chemical composition and properties of AMD samples used in a study by [108]*

SAMPLE	SO_4^{2-}	Al	As	**Ca**	**Cd**	**Cu**	**Cr**	**Fe**	**K**	**Mg**	**Mn**	**Ni**	**Si**	**Zn**	**pH**	**EC**	**Eh**
AMD$_{CM}$*	3783	95	0.45	284	0.43	2.2	3.7$^{\#}$	348	2.2	324	17	0.81	40	399	3.61	5.09	510
AMD$_{CM}$$^{+}$	24	100	100	-	75	100	100	100	-	-	-	47	-	32	6.60	6.01	
AMD$_{TH}$*	15558	657	1.6	272	0.88	54	0.18	2172	3.5	1423	109	4.2	32	332	2.62	11.09	605
AMD$_{TH}$$^{+}$	38	100	100	-	74	100	100	100	-	-	-	70	-	64	6.01	8.57	

* Mineral concentrations are in (mg/L) except for # which is in µg/L before treatment

$^{+}$Mineral removal efficiency in % (after treatment)

$^{-}$Not accounted for in terms of removal efficiency

EC = Electrical conductivity (mS/cm)

Eh = Redox potential(mV)

2.4. CONCLUSIONS OF LITERATURE REVIEW

Conventional methods of using naturally sourced materials for handling AMD are not only causing ecological disturbances, but they also lead to depletion of these resources. Thus, there is a need to use alternative AMD treatment procedures that are sustainable and eco-friendly. This review indicates that GLDs can be used as an alternative for the treatment of AMD. Its use is a symbiotic process that is beneficial to both the mining and Kraft pulp mills, leading to avoidance of disposing GLDs of in the landfills and emission of hazardous wastes into the environment, a beneficial contribution to the circular economy.

However, its use and applicability may be limited by several factors, including:

- Characteristics of GLDs that are mill specific: this means that there could never be a universal way of using GLDs in treating AMD just as there is no universal way of treating AMD. Therefore, every GLDs produced should be characterised before valorisation for AMD treatment.
- Transportation costs between AMD and GLDs sources may be prohibitive.
- Post-treatment costs of AMD may be high if GLDs dosages are not optimised. The costs are related to the leaching of NPEs from GLDs into the AMD during treatment.
- The quality of the GLDs concerning its constituent quantities of calcite will affect its AMD treatment efficacy.

Furthermore, research concerning the upscaling of the already available experimental work needs to be conducted, the longevity of using GLDs in sealing layers and in blending them with tailings, post-treatment and its costs need to be studied and evaluated, and possible repurposing of the wastes that may be produced during AMD handling. In pursuit of using ecologically sound methods of treating AMD, polishing off the neutralised AMD with algal biomass that absorbs metals from the water should be explored.

CHAPTER 3: MATERIALS AND METHODS

3.1. INTRODUCTION

Chapter three lists the reagents and describes the equipment and the experimental procedures that were used to achieve the aims and objectives of this study. The materials section describes how and where the samples used were collected and handled as well as listing the chemical reagents used. The methods section lists and describes the analytical equipment used. Furthermore, a detailed description of the steps followed in determining the neutralising values of the carbonic samples and the AMD neutralisation design and procedures are given. Equations used are also given in this section.

3.2. MATERIALS AND METHODS

3.2.1. Materials

3.2.1.1. Neutralising reagents

Green liquor dregs (GLDs) were collected from two Kraft mills and were labelled GLD A and GLD B. Both these samples were in a paste form. These samples were dried in an oven at 105 °C and milled using a rod mill and sieved through a 75μm mesh. Limestone ($CaCO_3$) and lime ($Ca(OH)_2$) samples were supplied by Idwala Industrial Holdings (Durban, South Africa) and were used as reference materials.

3.2.1.2. Acid mine drainage (AMD)

AMD from two distinct origins was used in this study. The first one was collected from the goldfields in 18 Winze decant point of the Western basin, Johannesburg (Gauteng province, South Africa), whereas the other was from coalfields in the Kromdraai catchment in Witbank (Mpumalanga province, South Africa).

3.2.1.3. Chemicals

Sodium hydroxide (NaOH) and hydrochloric acid (HCl) were procured from Sigma Aldrich (South Africa).

3.2.2. Methods

pH, Electrical Conductivity (Ec) and Sulphate (SO_4^{2-}) Analysis

Figure 11: *Hanna HI 98195 multiparameter*

pH and Ec were measured using a Hanna HI 98195 multiparameter, Figure 11. Ec was measured in milliSiemens per cm (mS/cm). Turbidity measurements were used to determine SO_4^{2-} concentration in AMD samples before and after the neutralisation process.

Particle size analysis

The particle size distributions of the ground GLDs samples, $CaCO_3$ and $Ca(OH)_2$, previously sieved through a 75µm mesh, were determined using a Shimadzu SALD-3101, shown in Figure 12 below. (WingSALD II: version 3:4) flow cell with a sampler.

Figure 12: *Shimadzu SALD-3101 particle analyser*

Surface morphology and elemental analysis

The morphological anatomy of the samples was studied using a CARL ZEISS LEO 1450 Scanning Electron Microscope (SEM) (Germany) fitted with Oxford Energy Dispersive X-ray (EDX) probe for elemental analysis, as shown in Figure 13.

Figure 13:*CARL ZEISS LEO 1450 SEM/EDX*

Further elemental analysis was determined by inductively coupled plasma (ICP) technology. A Thermo iCAP 6200 ICP-atomic emission spectroscopy (ICP-AES), Figure 14A, was integrated with Agilent 7900 ICP-mass spectroscopy (ICP-MS), Figure 14B, for this analysis. ICP-AES was used for both major and minor elemental analysis while ICP-MS was used for detection of ultra-trace elements.

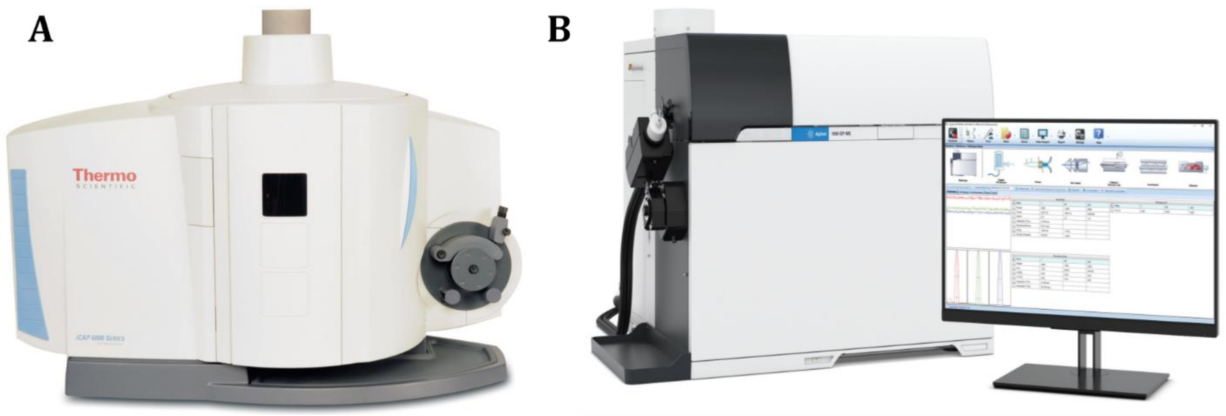

Figure 14: *Thermo iCAP 6200 ICP-AES(A) and Agilent 7900 ICP-AES (B)*

A Malvern Panalytical Axios FAST wavelength dispersive x-ray fluorescence (XRF) spectrometer, Figure 15 ,which was fitted with an Rh tube was used for a non-destructive, rapid but qualitative elemental analysis of all the solid samples.

Figure 15: *A Malvern Panalytical Axios FAST XRF*

Mineralogical analysis

The limitations that come with the elemental analysis were curbed by determining the mineral phases of the reagents. These were done using X-ray diffraction (XRD) spectroscopy. Panalytical Empyrean diffractometer, Figure 16 using Cobalt radiation generated at 40 mA and 40 kV, with the scanning range of 3-9^{o} was used for XRD analysis. The mineral phases were quantified using a Rietveld method that is built in a Malvern Panalytical X'Pert Highscore plus software (Almelo (the Netherlands), and Malvern (United Kingdom).

Figure 16: *Panalytical Empyrean XRD*

Neutralising value (Nv)

The neutralising value of all the neutralising reagents was determined by following the method that was described in Figure 17 [150].

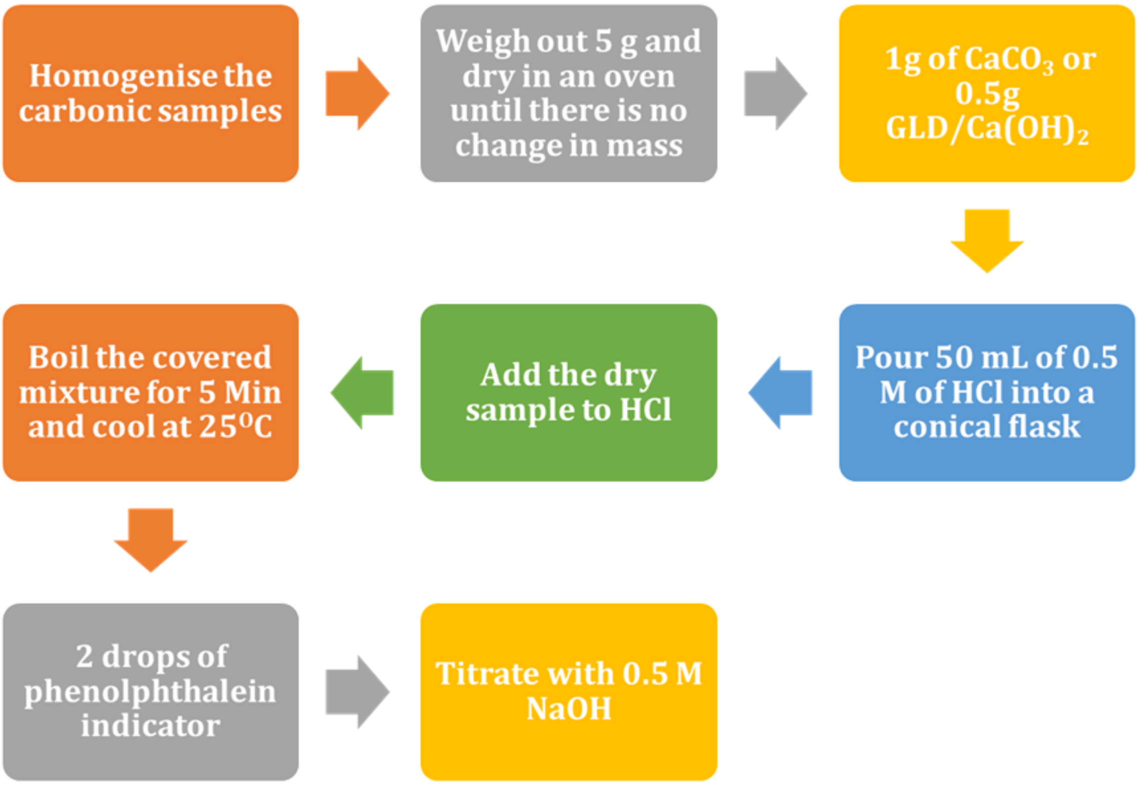

Figure 17: *Determination of neutralising value*

The neutralising values of the carbonic materials were then calculated using the Eqn. 11 below;

$$Nv = \left(\mathrm{Y} \times \frac{0.01402}{\mathrm{X}}\right) \times \; 100\;\%\; CaO \qquad \textbf{\textit{Eqn. 11}}$$

Where:

Y=

Acidity

The pH, Ec, and ICP-AES/ICP-MS results were used to estimate the acidity level of the AMD.

$$\text{Acidity}\left({}^{\text{mg}}/_{\text{L}}\,\text{CaCO}_3\right) = \; 50\left(10^{(3-\text{pH})} \; + 2\,\frac{C_{\text{Fe}}}{55.8} + 2\,\frac{\text{C}_{\text{Mn}}}{54.9} + 3\,\frac{\text{C}_{\text{Al}}}{27.0}\right) \qquad \textbf{\textit{Eqn. 12}}$$

This

Where: C is the concentration of a specific metal in mg/L.

Neutralisation processes

The neutralisation process used in this study was similar in both cases of treating the (goldfields and coalfields) AMD samples, Figure 18. Generally, the neutralisation process was performed by charging a beaker with 1000 mL of AMD and placed under a pre-set overhead stirrer. The samples were conditioned by stirring for 30 min to help remove any CO_2 that may be trapped in the sample. This was then followed by adding the relevant quantities of neutralising reagents and the stirring continued for a specified period. At the end of the neutralisation process, the samples were first filtered through 45 µm Whatman filter paper and then through Whatman Cellulose nitrate filter: this is essential for ICP analysis. pH and Ec of the samples were measured before and after the neutralisation process. The filtrate samples were then stored in airtight containers in a cold room until further analysis. The resulting sludge was dried in a vacuum oven, at 105^oC, to constant mass. The samples were kept in airtight containers until analysis.

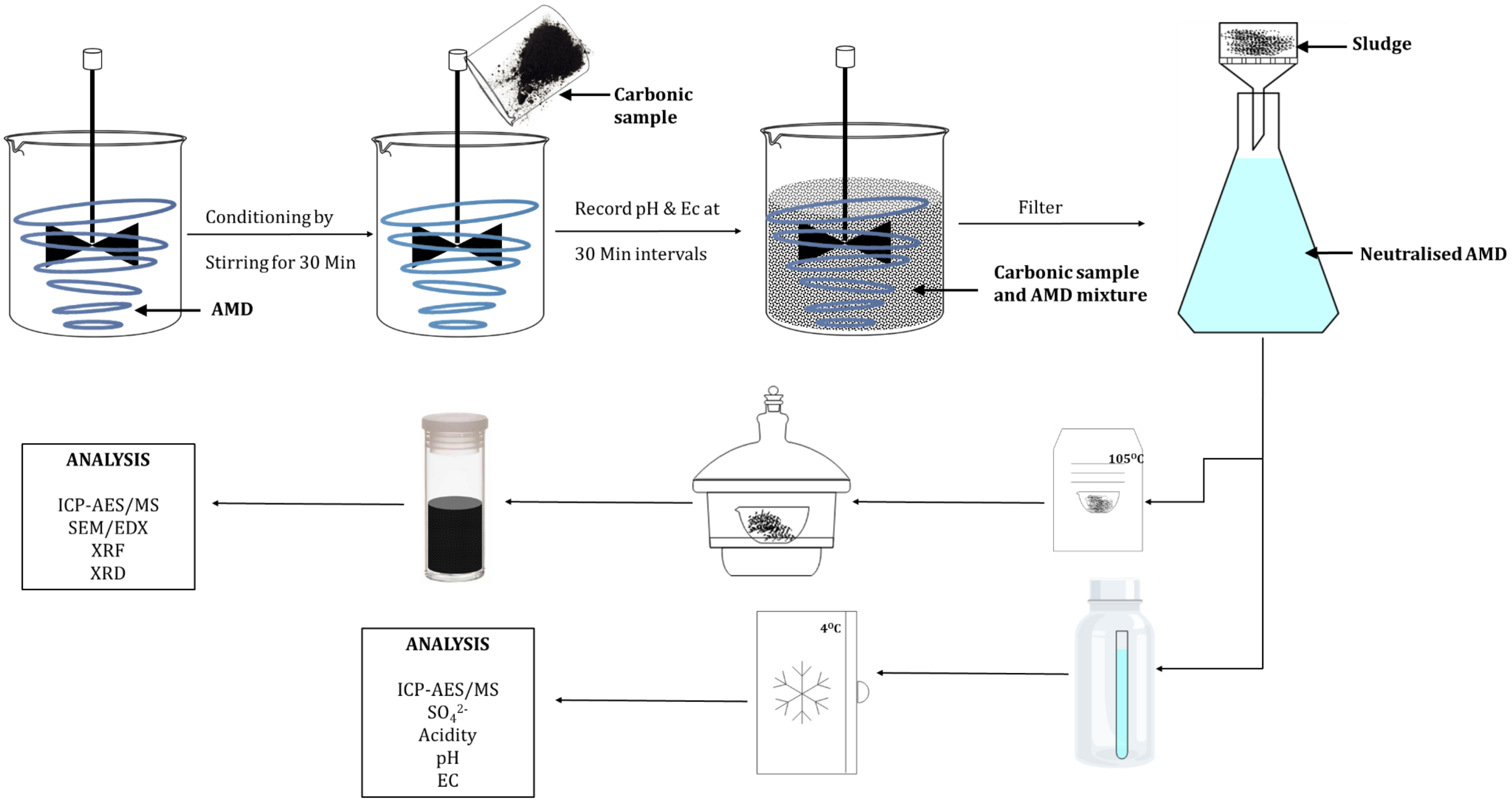

Figure 18: *AMD neutralisation process*

3.2.2.7.1. Neutralisation of goldfield AMD

This AMD was neutralised by adding different dosages (1, 2, 6, 10, and 20 g/L) of neutralising reagents, $CaCO_3$, GLD A, and GLD B to it. The reaction was allowed to proceed for 6 hours. During this time, pH and Ec were measured at 30 Min intervals.

3.2.7.2. Optimisation of neutralisation and optimisation parameters of coalfield AMD using statistically designed experiments

The study was conducted by neutralising AMD samples with four neutralising reagents viz., $Ca(OH)_2$, $CaCO_3$, GLD A and GLD B. Variation of parameters (contact time, dosage, and mixing speed) were performed according to data shown in Table 10 to facilitate the neutralisation process. The interaction that results between this variation and the response variables (pH and Ec) was designed and studied using a Box-Behnken Design (BBD). That is, fifteen (15) experimental runs, Table 11, were designed and analysed for each neutralising reagent using Statistica 13.4 Software (TIBCO Software Inc., California, USA).

Table 10: *Coded values of the AMD neutralisation used in BBD*

CODED VALUES	**INDEPENDENT VARIABLE**	**-1**	**0**	**1**
X_1	Dosage (g/L)	0.5	0.75	1.0
X_2	Time (Min)	60	210	360
X_3	Speed (rpm)	100	175	250

Table 11: *BBD experimental runs.*

Runs	Dosage (g/L)	Time (Min)	Speed (rpm)
6	1.000000	210.0000	100.0000
5	0.500000	210.0000	100.0000
15	0.750000	210.0000	175.0000
10	0.750000	360.0000	100.0000
8	1.000000	210.0000	250.0000
11	0.750000	60.0000	250.0000
13	0.750000	210.0000	175.0000
7	0.500000	210.0000	250.0000
3	0.500000	360.0000	175.0000
14	0.750000	210.0000	175.0000
12	0.750000	360.0000	250.0000
2	1.000000	60.0000	175.0000
9	0.750000	60.0000	100.0000
1	0.500000	60.0000	175.0000
4	1.000000	360.0000	175.0000

CHAPTER 4: RESULTS AND DISCUSSIONS

4.1. Introduction

4.2. Neutralising Reagents

GLDs were explored as alternatives for the traditional carbonate neutralising materials. GLD A was black, and it had clear crystals that looked like NaOH, whereas the GLD B sample was greenish black in colour. $CaCO_3$ and $Ca(OH)_2$ were used as reference materials. All samples were sieved through the 75 µm mesh. Figure 19 below shows the photographs of the GLDs paste sample and the sieved reagents, respectively. The picture shows that although the GLDs samples were produced from the same procedure, their physical characteristics of colour and fineness were different.

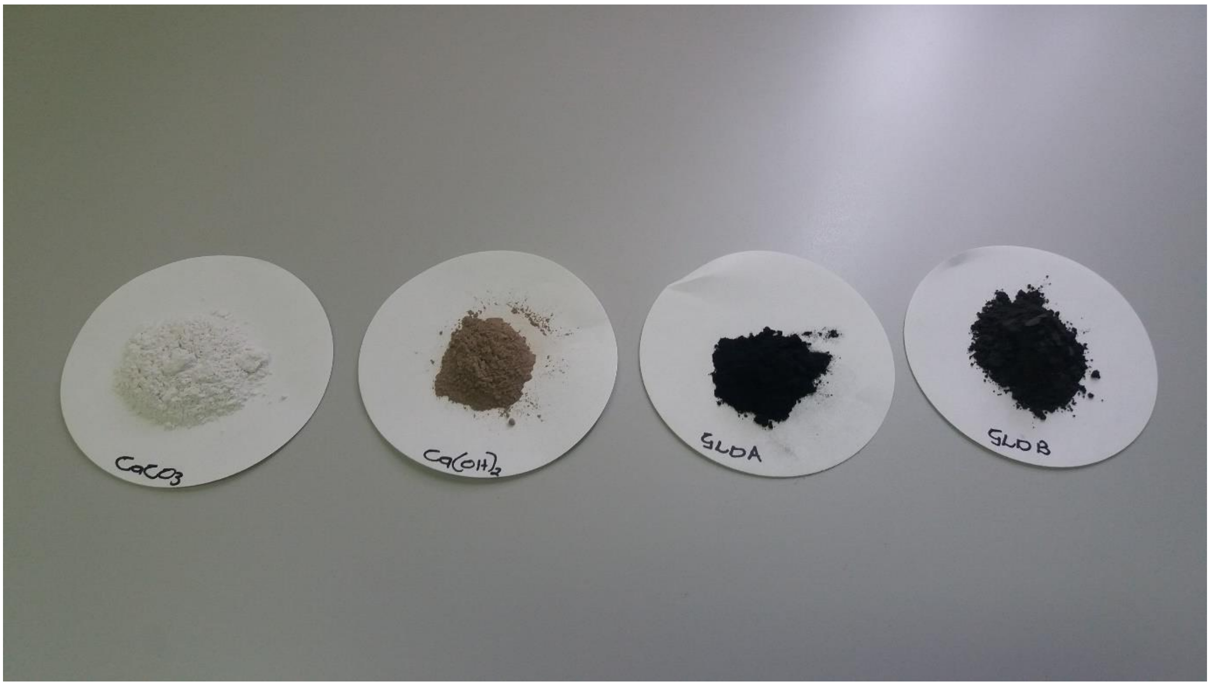

Figure 19: *Photograph of neutralising reagents that were used to neutralise AMD*

The results from the particle size analyser indicated that the median fines (*d_{50}*) of $CaCO_3$, $Ca(OH)_2$, GLD A and GLD B were 13.880, 13.553,19.597, and 17.528, respectively. These results suggested that the reactivity of these samples decreased from $Ca(OH)_2$ > $CaCO_3$

>GLD B> and >GLD A. The higher reactivity is heightened by the large surface area, which is associated by smaller particle size [95]

4.2.1. pH and the Neutralising Value (Nv)

The pH value of GLDs samples was recorded before the samples were dried. The results that were obtained agreed with the previous studies, which suggested that GLDs samples were [151], [152]. Thus, the pH meter read 13.4 and 12.5 for GLD A and B, respectively. These samples are traditionally identified to be rich in $CaCO_3$, which may, in most cases, be responsible for the high pH values [10], [151], [153]. While this is true, it should be noted that GLD A had visible grains of NaOH, which could have contributed towards the high pH value of the sample. The neutralising values of $Ca(OH)_2$, $CaCO_3$, GLD A and GLD B were determined to be 64.5, 26.0, 21.2, and 21.0 %CaO. These values are lower than that were reported in the literature; that is, neutralising value of 38 and 34.2% Ca [125] and 38 and 39.6 % Ca [134] for $CaCO_3$ and GLD samples, respectively.

4.2.2. Surface Morphology and Elemental Analysis

Figure 20 below shows the SEM/EDX micrographs of the raw samples. The SEM micrographs indicate the presence of calcite ($CaCO_3$) in all samples. This is depicted by the rhombohedral structures which are present in all the micrographs [8], [10], [108], [133], [134], [151]. However, these structures were in small quantities on the micrographs of GLD A. The GLD A SEM micrograph demonstrates that the samples was dominated by orthorhombic structures which suggested the presence of another form of carbonate mineral which could be pirssonite ($Na_2Ca(CO_3)_2.2H_2O$) [154], [155]. The EDX data indicated that there were other elements which could not be identified as distinguished mineral phases. These elements included magnesium (Mg), iron (Fe), silicon (Si), copper (Cu), sodium (Na), aluminium (Al), and manganese (Mn). The presence of these elements in $CaCO_3$ may be attributed to the origin of this sample, i.e., this is a naturally occurring material which its constituents may differ from one place to another due to the surrounding soil type and numerous factors that may contaminate its reserves. $Ca(OH)_2$ is obtained by calcining $CaCO_3$ and slacking it with water. Thus, the contaminants in this sample may have been retained from the parent material or may have been imparted in it by water and or the fuel that was used for calcining. GLD samples are the non-process elements (NPEs) that originated from Kraft pulping process. Thus, the EDX confirmed and gave a preview of what kind of NPEs were present in the samples.

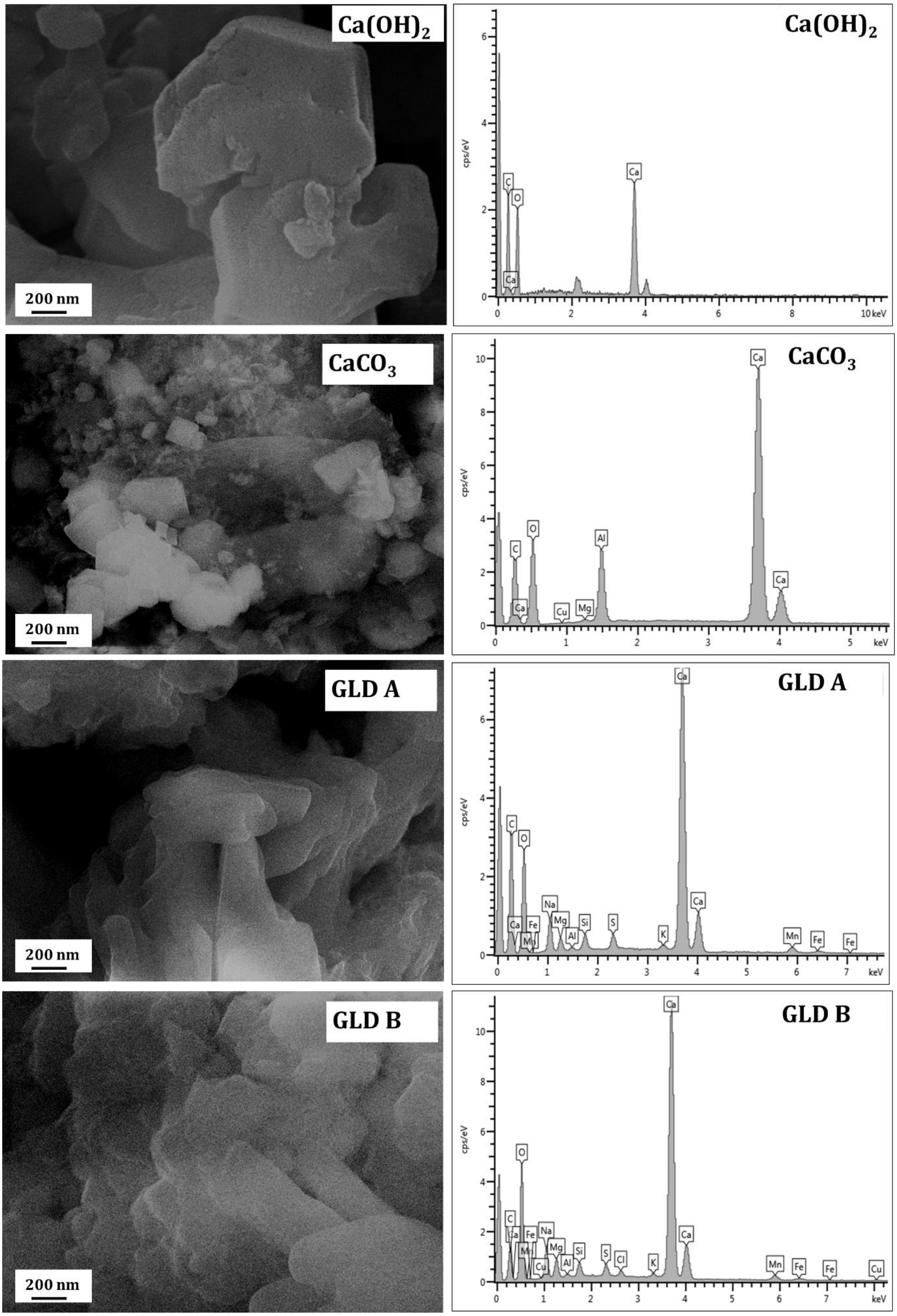

__Figure 20:__ SEM/EDX micrographs of raw neutralising reagents

The integrated ICP-AES/ICP-MS was further used to analyse the elemental composition of the samples. The results of this technique, Table 12, clearly indicate that the samples constituted more than 20 elements. Some elements, such as Cu, Zn, Pb, and Ba, were present at trace concentrations. These small concentrations imply that they may be environmentally benign [10]. Cr was detected at very high concentrations. These, depending on the oxidation state, may cause adverse effects on plants, animals, and humans. The adverse effects on humans and animals may include cancer, ulcers, and kidney dysfunction. Physiological and biochemical processes in plants may also be affected negatively [156], [157]. Calcium is the most prominent element that is present in all the samples as it forms the basic structure of the carbonic mineralogy. Results in Table 12 show that this element decreased in the following order $CaOH_2$ $CaCO_3$, GLD B, and GLD A while Na decreased in the opposite trend. The extremely high Na in GLD A is equivalent to the Ca concentration, suggesting further that the sample may be composed of $Na_2Ca(CO_3)_2.2H_2O$ [154], [155]. Na could have also been from the NaOH crystals that were physically identified in the sample. These results agree with the SEM results.

Likewise, XRF was used to determine the overall abundant concentration of elements present in samples and quantified them as their oxides. Table 13 below confirms that the Ca content decreased from $Ca(OH)_2$, $CaCO_3$, GLD B to GLD A and that the Na concentration was higher in GLD A than in other samples. The equivalence of Na and Ca in GLD A further indicates the presence of $Na_2Ca(CO_3)_2.2H_2O$, as revealed by SEM and ICP-AES/ICP-MS [133], [154], [155].

Table 12: *The chemical composition of Neutralising reagents as determined by ICP-AES/ICP-MS (mg/L)*

Element	**Accuracy (%)**	**$Ca(OH)_2$**	**$CaCO_3$**	**GLD A**	**GLD B**
B	95.4	338.00	9.74	67.64	55.01
V	98.9	2.00	4.45	3.23	2.34
Cr	99.2	5.00	10.73	5565	255.03
Co	98.9	12.00	0.88	11.32	13.63
Ni	97.7	168.00	4.68	82.59	37.73
Cu	93.7	4.00	30.25	156.94	161.75
Zn	99.9	159828	11.11	308.80	259.27
As	95.4	1.00	0.81	0.54	2.25
Se	96.9	0.59	0.57	2.99	1.35
Mo	98.8	0.28	0.38	1.17	0.72
Cd	97.3	14.00	0.02	0.39	0.18
Ba	98.1	8.03	10.65	668.62	438.86
Hg	97.4	BLD	0.03	0.02	0.04
Pb	96.7	0.49	2.72	12.38	11.73
Al	96.0	1116.4	92380.32	3759.43	2266.22
Ca	97.0	434 065	268 600.8	101 030	198 049
Fe	97.5	1811.5	870.48	4648.97	3528.13
K	96.9	BLD	259.71	5431.67	5419.11
Mg	95.5	7085	3354.04	36928.39	16381.3
Mn	97.3	5959.0	13.37	7762.37	9547.72
Na	99.8	274.3	306.58	153011.4	71143.6
P	98.7	154.00	153.16	1251.82	760.96
Si	96.5	1994	2517.37	6321.21	6247.69
Sr	96.1	64.00	943.74	639.08	520.48

Table 13: *The XRF analysis of the neutralising reagents.*

Parameter, Wt %	$Ca(OH)_2$	$CaCO_3$	GLD A	GLD B
Al_2O_3	0.24	19.99	0.98	0.57
CaO	56.72	42.42	14.61	31.24
Cr_2O_3	BLD	-	0.72	0.04
FeO_3	BLD	0.13	0.66	0.57
K_2O	0.01	0.02	0.61	0.63
MgO	1.28	0.56	6.13	3.02
MnO	0.68	0.50	0.99	1.34
Na_2O	0.01	0.02	14.38	7.28
P_2O_5	0.01	0.04	0.29	0.26
SiO_2	1.20	0.81	1.18	2.97
TiO_2	0.02	0.03	0.04	0.04
Loi %	38.81	35.07	33.10	39.37
Sum of parameters	99.16	99.09	73.70	87.37

Loi = Loss of ignition

4.2.3. Mineralogical Analysis

XRD was used to estimate the quantities of each element in each neutralising solid. All the XRD diffractograms in **Error! Reference source not found.** show a prominent $CaCO_3$ peak at 34 2 Theta ^{0} ($2\theta^0$). The presence of portlandite ($Ca(OH)_2$) is depicted by peaks at 16, 29, 34, 47, and 55 $2\theta\ ^0$. CaO, which may have remained un-slaked in this sample, is suggested by peaks at 32, 37, and 53 $2\theta\ ^0$. An X'Pert Highscore Plus software was used to determine the XRD mineral phases, and its Rietveld method was used to quantify their percentages. This method calculated the calcite of $Ca(OH)_2$, $CaCO_3$, GLD A, and GLD B to be 92.3, 58.30, 13.3, and 75.4%, respectively. The diffractograms indicate that GLD B constituted a higher concentration of calcite than $CaCO_3$ itself. This could have been because the $CaCO_3$ sample constituted gypsum, which accounted for 25% mineral composition of the sample. GLD B also constituted trona ($Na_2CO_3.NaHCO_3.2H_2O$), which is another form of the carbonate mineral. The samples also exhibited other minerals, which are found in the pie chart insert in **Error! Reference source not found.**. Although calcite is present even in GLD A, its diffractogram shows that it had a very intense peak at

42 ^{0} - a position that has been reported to be associated with $Na_2Ca(CO_3)_2.2H_2O$ [133], [155], [158] .

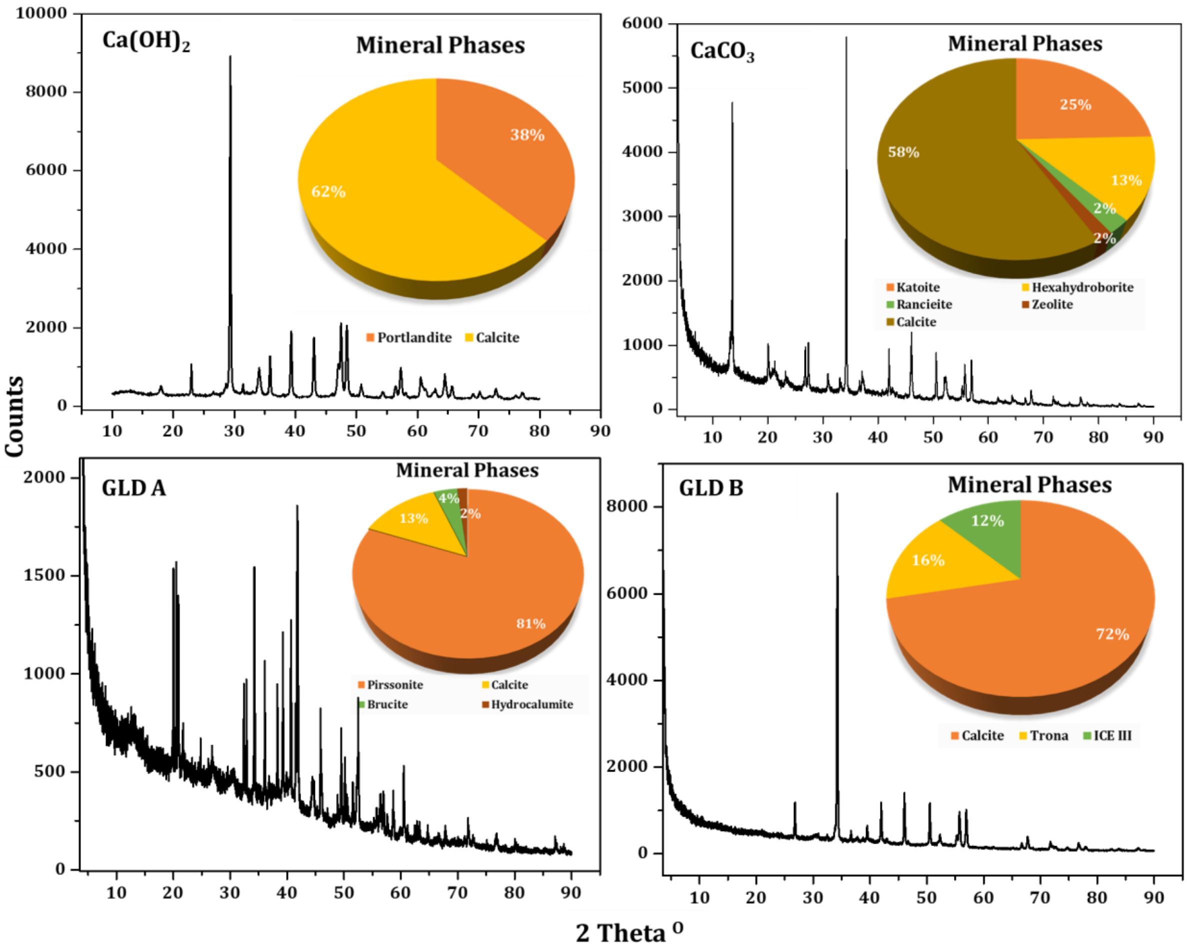

Figure 21: *XRD pattern of neutralising reagent*

Both the trona and $Na_2Ca(CO_3)_2.2H_2O$ minerals that were found in the GLD samples might have been formed during the "upset time." This is the time when the raw green liquor was supersaturated with total titratable alkali (TTA) and when the liquor had low temperatures [155]. It is also possible that trona might have originated from the soda ash, which is sometimes used as a makeup chemical. However, the presence of Ice III assures us that the majority of trona that is present in the sample could have been caused by a rapid drop in temperature (from ~1000 to 25 °C) [159].

`4.3. Acid Mine Drainage

4.3.1. Case study 1: Goldfield AMD

4.3.1.2. Geographical description of the AMD collection site

Johannesburg, the epicentre of the economic growth in South Africa, is one of the cities that grew exponentially during the gold rush years. Today, this town, which receives an average of only 750 mm of summer rainfalls, is estimated to be a home to between 4.4 to 4.9 residents [33]. Unfortunately, the demand for water, not only for domestic purposes but for industrial use, has also increased. This demand could be compromised because the little water that the city receives from annual rainfall is subject to contamination by the 170 million litres of the AMD that is produced daily from the Witwatersrand basin

The AMD sample that was used in case study 1 originated from the goldfields in Randfontein, Johannesburg, Figure 22. The sample was collected at 18 Winze decant point of the Western Basin.

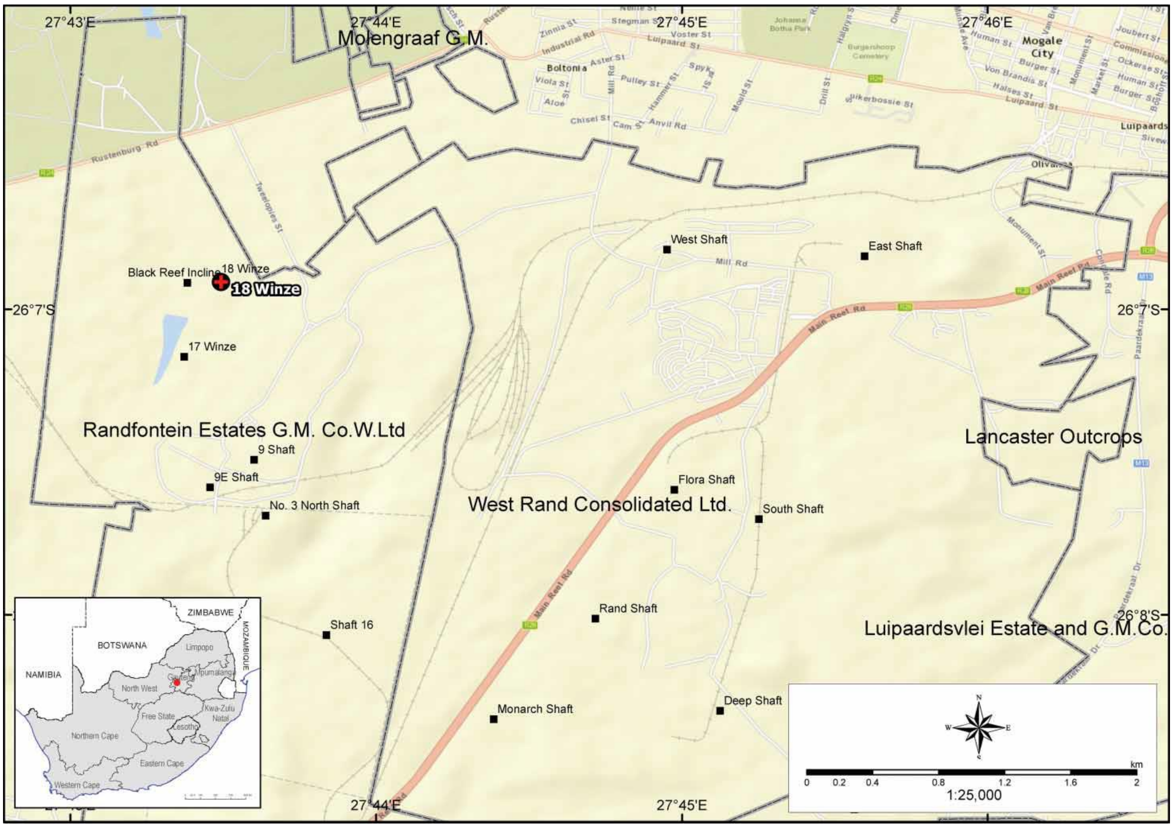

Figure 22: *A map showing the AMD sampling point* [104].

4.3.1.2. Neutralisation of AMD

Naturally, carbonates dissolve in AMD; however, they dissolve at different rates depending on the carbonate type and the pH of the AMD. The interaction of these carbonates and AMD would lead to the dissociation of the carbonate material and increment of pH would dramatically alter the character and composition of the AMD. Similarly, the initial character of AMD used in this study changed after treatment of different neutralising reagents. Before alkalising reagent dosage, the AMD had a pH of 5.6, Ec of 3.6 mS/cm, SO_4^{2-} of 2093 mg/L, and an acidity of 183 mg/L. Figure 23 and Figure 24 show that the pH and Ec of the AMD samples changed dramatically after the addition of the neutralising reagents. This change could be attributed to the dissociation of the calcitic mineral found in both the $CaCO_3$ and GLD samples. However, the nature of Ca^{2+} sources of these neutralisation reagents may have followed different mechanisms as described next:

$CaCO_3$: this reagent may have followed Eqn. 13, however, the XRD results show that this reagent also contained $CaSO_4.2H_2O$ in its matrix. Thus, Eqn. 14 may be used to explain the neutralisation mechanism better. The preference associated with the dissolution of $CaSO_4.2H_2O$ rather than $CaCO_3$ is that the latter dissolves better in more acidic media than the former, which can easily dissolve even in an alkaline environment [160].

$$CaCO_3 + CaSO_4 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + CaCO_3 + H_2O \qquad \textbf{\textit{Eqn. 13}}$$

GLD A: this neutralising reagent's primary Ca source was $Na_2Ca(CO_3)_2.2H_2O$ and small amounts of $CaCO_3$. Similarly to $CaSO_4.2H_2O$, this mineral dissolves readily in the neutral medium [161]. Thus, the $CaCO_3$ in it may not have undergone dissolution, as described in Eqn.15.

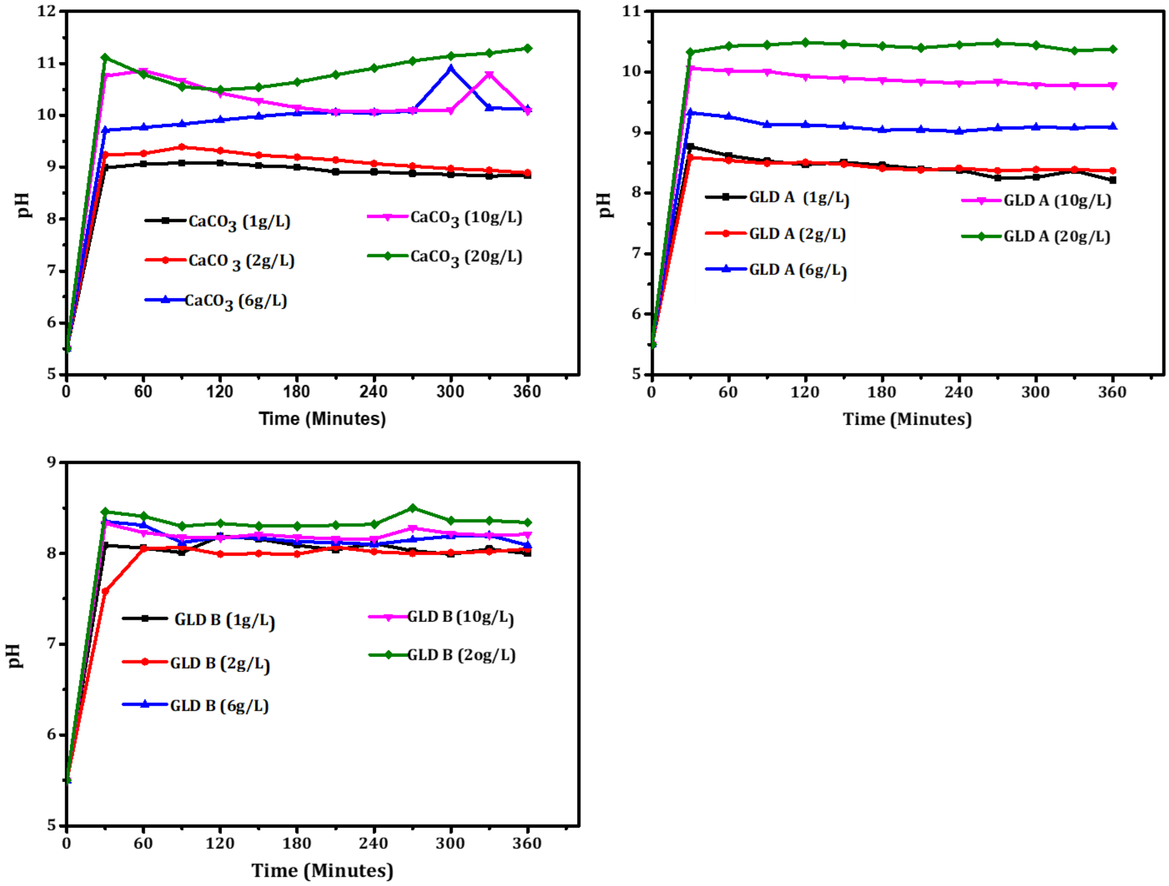

Figure 23: *Effect of neutralising reagent dosage on pH as measured over time*

$$CaCO_3 + Na_2Ca(CO_3)_2.2H_2O + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + Na^+ + CaCO_3 + H_2O \qquad \textbf{\textit{Eqn. 14}}$$

GLD B: of the three reagents used in the neutralisation of AMD in this study, GLD B raised the pH value of AMD to values between 8 and 8.5 only. This is because this GLD had a sufficient $Na_2CO_3.NaHCO_3.2H_2O$ mineral to effectively raise the leachate pH and either wholly or partially impede the dissolution of $CaCO_3$ present in the reagent. The small quantities of $Na_2CO_3.NaHCO_3.2H_2O$ in GLD B in comparison to other Ca^{2+} sources in $CaCO_3$ and GLD A samples could be the reason why the pH of AMD never reached high levels despite the increase in dosages of the reagents. Consequently, Eqn. 16 below may be used to describe the neutralisation process.

$$Na_2CO_3.NaHCO_3.2H_2O + CaCO_3 + H_2SO_4 \rightarrow CO_3^{-} + SO_4^{2-} + Na^+ + CaCO_3 + H_2O \qquad \textbf{\textit{Eqn. 15}}$$

The ion activities presented by different cations such as Ca^{2+}, Na^{+}, Mg^{2+} and anions, which include SO_4^{2-}, CO_3^{2-}, HCO_3^{-} play significant roles in the neutralisation. In this study, Ec was increased with an increase in dosage. This is contrary to what other researchers have reported [97], [108]. However, a different trend was observed on the AMD samples treated with 10 and 20 g/L of $CaCO_3$, whereby the Ec decreased. This decrease could be attributed to the precipitation of SO_4^{2-} in the form of $CaSO_4.H_2O$. This precipitation was only observed on these two samples because the $CaCO_3$ sample that was used contained $CaSO_4$ (which acted as a seed for precipitation) in its mineralogical makeup and the pH values of the AMD were ≥10 [96]. Although the pH of the 6 g/L $CaCO_3$ treated sample was high pH of 10, its Ec did not decrease, and this could be due to insufficient gypsum seed to catalyse its precipitation in the medium, and thus, it remained meta-stable in the solution [108], [162].

Based on the scope of this study, which is to neutralise the AMD, the pH results showed that dosing the sample with 1 g/L of GLD was able to raise the pH to values above the neutral value. Thus, only these samples, together with their corresponding $CaCO_3$ treated sample, were analysed.

The addition of alkalising reagents on AMD does not only impart alkalinity into the sample, but it also reduces its elemental load. For example, Table 14 shows that the concentrations of three main critical elements that drive the AMD formation were reduced after the neutralisation process. Thus, Fe concentrations were reduced by 99% for all samples, Mn by 66, 81, and 13 %, while Al was reduced with -2.0, 76, and 96 % for $CaCO_3$ (1g/L), GLD A (1g/L), and GLD B (1g/L) respectively. The dissolution of carbonate minerals is confirmed by the increment of Ca, Na, and Mg increased in the treated AMD.

This reduction in metal concentration was due to precipitation of the metal constituents of AMD as hydroxides.

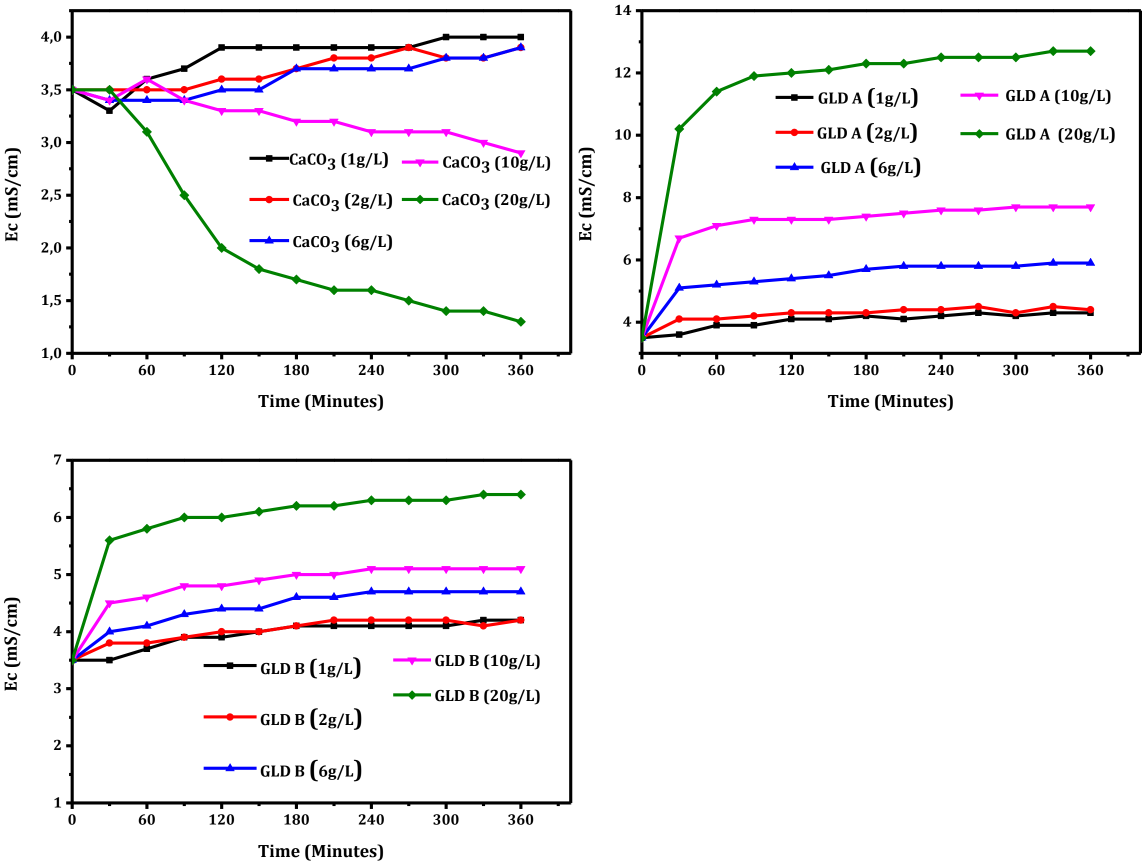

Figure 24: *Effect of neutralising reagent dosage on Ec as measured over time*

The overall outcome of this neutralisation process is that acidity of the AMD dropped from 183 to 21.7, 36.4, and 48.72 mg/L $CaCO_3$, and changed the pH from 5.6 to 8.84, 8.21, and 8.0 respectively for $CaCO_3$, GLD A and GLD B treated samples. However, SO_4^{2-} and Ec had increased from 2093 to 2360, 2538, and 2407 mg/L and from 3.6 to 4.0, 4.3, 4.2 mS/cm, respectively. These changes could be attributed to the origin of the reagent and different carbonate mineral phases and their quantities thereof, which the samples were composed of. This means GLD samples may have increased the SO_4^{2-} in the samples because they originate from a Na_2S driven process, while the presence and dissolution of gypsum ($CaSO_4.2H_2O$) in the $CaCO_3$ sample are the reason behind SO_4^{2-} increment in the $CaCO_3$ (1g/L) treated sample. Additionally, the carbonate minerals other than calcite itself were responsible for the pH augmentation because of their ability to dissolve readily as compared to calcite, which preferably dissolves in acidic medium. The quantities of these minerals were the ones that determined the overall attained pH values. Thus, low quantities of trona ($Na_2C0_3.NaHC0_3.2H_2O$) in GLD B could have limited the dissolution of calcite that was in the sample, and because its quantities were lower than its counterpart, pirrsonite in GLD A, GLD B treated samples only attained the pH values below 9. Thus, this study has, therefore shown that the variable character of GLDs composition is an essential factor that should be considered when pursuing their valorisation in AMD treatment. Furthermore, this study has also shown that the dosages of GLDs should preferably be kept low, this will also be dependent on the pH of the AMD itself, to avoid introducing some ions into the AMD and destabilising ions which precipitate at low pH values.

4.3.1.3. Characterisation of the resulting sludge

Based on the results obtained in the lab during the measurements of both the pH and Ec, only the samples with the lowest neutralising reagents dosages were analysed. These precipitates were reddish. The dominance of this colour was excessively evident for $CaCO_3$ sample while the GLDs sludge was in a transition phase between black and red. The reddish colour could be associated with Fe rich compounds-This is also supported by the results emanating from analytical characterisation of the sludge. $CaCO_3$ (1g/L) had white colour further indicating that $CaCO_3$ may not have completely dissolved.

***Table 14:** The chemical composition of the raw and optimum neutralised AMD samples*

Element	*Accuracy (%)*	AMD	$CaCO_3$ A (1g/L)	GLD A (1g/L)	GLD B (1g/L)
Li	*99.7*	0.08	0.05614	0.06324	0.06431
Be	*98.3*	0.00	0.00100	0.00100	0.00100
B	*95.4*	0.83	0.26442	0.24892	0.40104
Ti	**-**	0.04	0.00009	0.00010	0.00004
V	*98.9*	0.03	0.00011	0.00007	0.00006
Cr	*99.2*	0.06	0.00093	0.00233	0.00062
Co	*98.9*	0.07	0.04327	0.04382	0.06179
Ni	*97.7*	0.05	0.00057	0.01160	0.02993
Cu	*93.7*	4.01	0.00057	0.00547	0.00429
Zn	*99.9*	0.12	0.00042	0.01166	0.02252
As	*95.4*	0.20	0.00156	0.00164	0.00193
Se	*96.9*	0.02	0.00021	0.00026	0.00021
Mo	*98.8*	0.01	0.00010	0.00034	0.00022
Cd	*97.3*	0.00	0.00005	0.00019	0.00015
Ba	*98.1*	0.04	0.02506	0.03102	0,04906
Hg	*97.4*	0.001	<0.00005	<0.00005	<0.00005
Pb	*96.7*	0.01	<0.00001	0.00001	0.00014
Al	*96.0*	0.72	0.73138	0.17016	0.03037
Ca	*97.0*	578.41	595.400	491.600	531.700
Fe	*97.5*	68.94	0.00260	0.00133	0.00325
K	*96.9*	28.64	24.0100	22.8700	21.76000
Mg	*95.5*	135.85	138.30	145.60	146.10
Mn	*97.3*	30.65	9.681	5.986	26.74
Na	*99.8*	146.90	151.50	284.7	184.30
P	*98.7*	<0.02	<0.00005	<0.00005	<0.00005
Si	*96.5*	7.96	0.3881	4.17100	5.60600
Sr	*96.1*	0.51	0.7318	0.9174	0.55857

Figure 25 shows the SEM micrographs, together with their corresponding EDX spectra of the lowest dosage, reacted neutralising reagents. Based on the globular colonies that are evident on these SEM micrographs, it could be assumed that the concentration of elements that were present in the AMD sample could have been reduced through precipitation, co-precipitation, or absorption on the surface of other formed mineral phases. The prominent rhombohedral structures suggest the presence of calcite, which seems to have been armoured by other compounds as they were settling/precipitating on top of them. The EDX spectra confirmed the evidence of the precipitated elements.

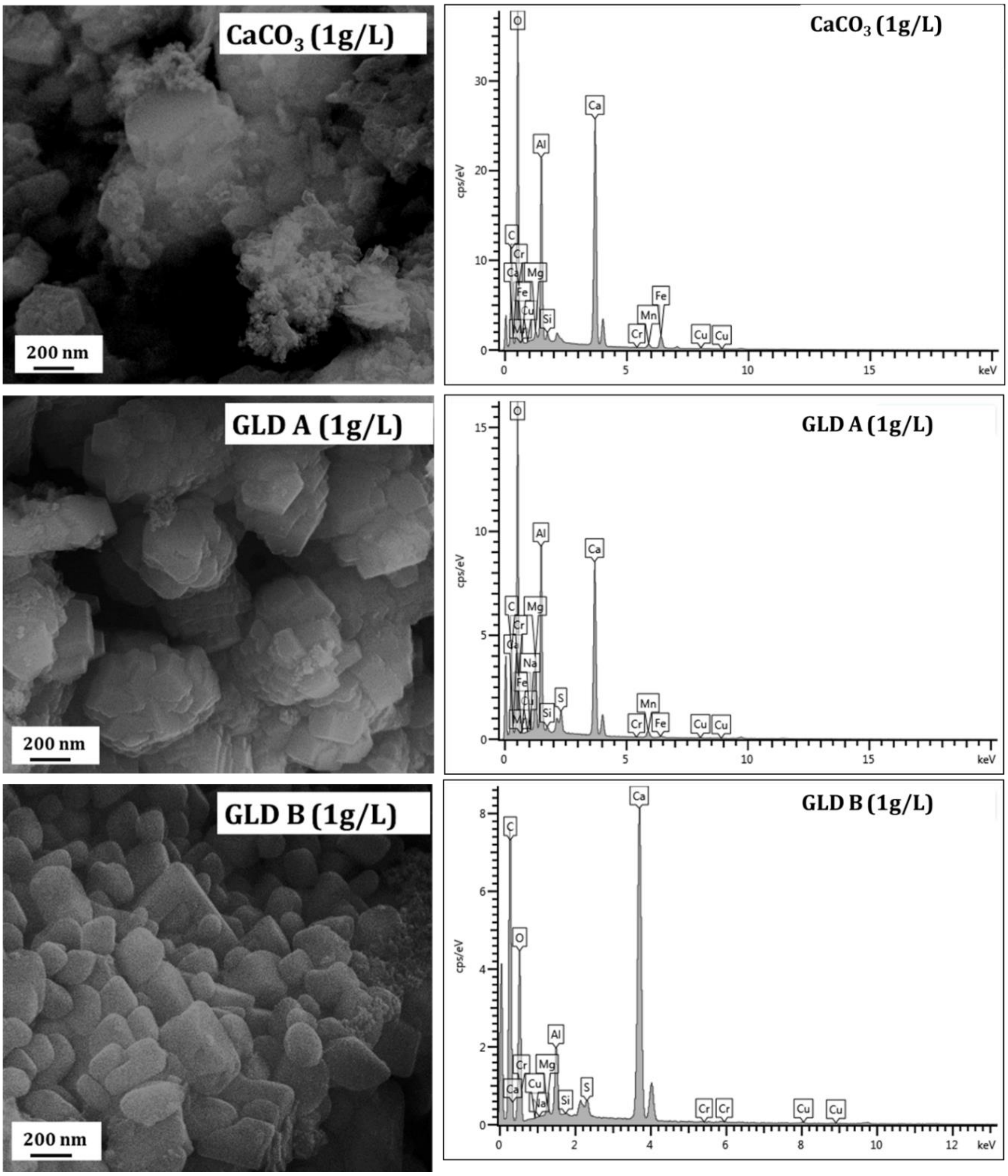

Figure 25: *SEM/EDX of the resultant sludge*

These reacted neutralising reagents were also analysed using ICP-AES/ICP-MS and XRF, as shown in Tables 15 & 16, respectively. These results showed an increase in the concentration of most elements. This confirms that some of the AMD constituents had been reduced and formed part of the sludge.

Table 15: *The chemical composition of Neutralising reagents and sludge samples thereof as determined by ICP-AES/ICP-MS (mg/L)*

Element	Accuracy	$CaCO_3$	GLD A	GLD B	$CaCO_3$ (1g/L)	GLD A (1g/L)	GLD B (1g/L)
Li	*99.7*	2.24	3.40	2.39	7.46	5,42	1.39
Be	*98.3*	0.18	0.18	0.47	< 0.2	0.31	< 0.2
B	*95.4*	9.74	67.64	55.01	25.64	48.45	36.40
Ti	-	100.29	187.42	135.22	66.29	230.97	104.53
V	*98.9*	4.45	3.23	2.34	2.74	3.76	1.51
Cr	*99.2*	10.73	5564.99	255.03	11.39	6269.09	214.00
Co	*98.9*	0.88	11.32	13.63	36.05	63.41	35.63
Ni	*97.7*	4.68	82.59	37.73	45.30	150.59	53.94
Cu	*93.7*	30.25	156.94	161.75	126.61	246.07	164.85
Zn	*99.9*	11.11	308.80	259.27	29.03	369.57	194.29
As	*95.4*	0.81	0.54	2.25	261.30	402.01	285.09
Se	*96.9*	0.57	2.99	1.35	0.08	0.58	0.09
Mo	*98.8*	0.38	1.17	0.72	1.37	2.92	1.47
Cd	*97.3*	0.02	0.39	0.18	0.03	0.47	0.13
Ba	*98.1*	10.65	668.62	438.86	58.91	812.69	392.95
Hg	*97.4*	0.03	0.02	0.04	0.06	0.08	0.04
Pb	*96.7*	2.72	12.38	11.73	3.82	19.05	12.43
Al	*96.0*	92380.32	3759.43	2266.22	77676.43	5149.72	2100.32
Ca	*97.0*	268600.88	101030.03	198049.76	197852.46	187656.40	251152.37
Fe	*97.5*	870.48	4648.97	3528.13	73570.18	113941.61	84317.42
K	*96.9*	259.71	5431.67	5419.11	123.17	173.26	255.85
Mg	*95.5*	3354.04	36928.39	16381.13	10813.11	42186.59	12889.90
Mn	*97.3*	13.37	7762.37	9547.72	11763.95	34930.84	10873.63
Na	*99.8*	306.58	153011.4	71143.63	508.83	3095.06	3246.01
P	*98.7*	153.16	1251.82	760.96	126.65	1770.85	741.22
S	*96.7*	2688.18	34488.36	18271.63	18970.84	9393.13	36399.09
Si	*96.5*	2517.37	6321.21	6247.69	6586.41	5099.52	6464.34
Sr	*96.1*	943.74	639.08	520.48	683.88	443.19	438.37

Table 16: *The XRF analysis of the neutralising reagents and resultant sludge*

Oxide Wt %	**$CaCO_3$**	**GLD A**	**GLD B**	**$CaCO_3$ (1 g/L)**	**GLD A (1 g/L)**	**GLD B (1 g/L)**
Al_2O_3	19.99	0.98	0.57	12.90	0.90	0.42
CaO	42.42	14.61	31.24	27.12	26.16	35.35
Cr_2O_3	-	0.72	0.04	0.00	0.83	0.03
FeO_3	0.13	0.66	0.57	8.87	12.26	8.74
K_2O	0.02	0.61	0.63	0.01	0.04	0.03
MgO	0.56	6.13	3.02	1.92	6.31	2.35
MnO	0.50	0.99	1.34	1.71	4.22	1.40
Na_2O	0.02	14.38	7.28	0.03	0.23	0.14
P_2O_5	0.04	0.29	0.26	0.03	0.38	0.20
SiO_2	0.81	1.18	2.97	1.61	2.32	2.87
TiO_2	0.03	0.04	0.04	0.01	0.03	0.05
Loi %	35.07	33.10	39.37	29.64	36.39	34.37
Sum of concentration	99.09	73.70	87.37	83.86	90.06	85.95

Due to the limitations of the SEM, XRF, and ICP-AES/ICP-MS, of not being able to identify the mineral phases of the sludge, XRD was used to determine the possible precipitates that may have been formed during the AMD neutralisation process. Thus, Figure 26 shows the XRD patterns and mineral phases quantities (pie charts inserts) of the reacted neutralising reagents. These confirmed the presence of $CaCO_3$ in all samples. These results support the assumption of preferential carbonate mineral dissolution instead of the calcite. It should be noted that some of the precipitates that may have been during the neutralisation period may be amorphous and hence would not be detected using the XRD technique. Also, these XRD results confirm the co-precipitation of metals that was hypothesised on SEM results.

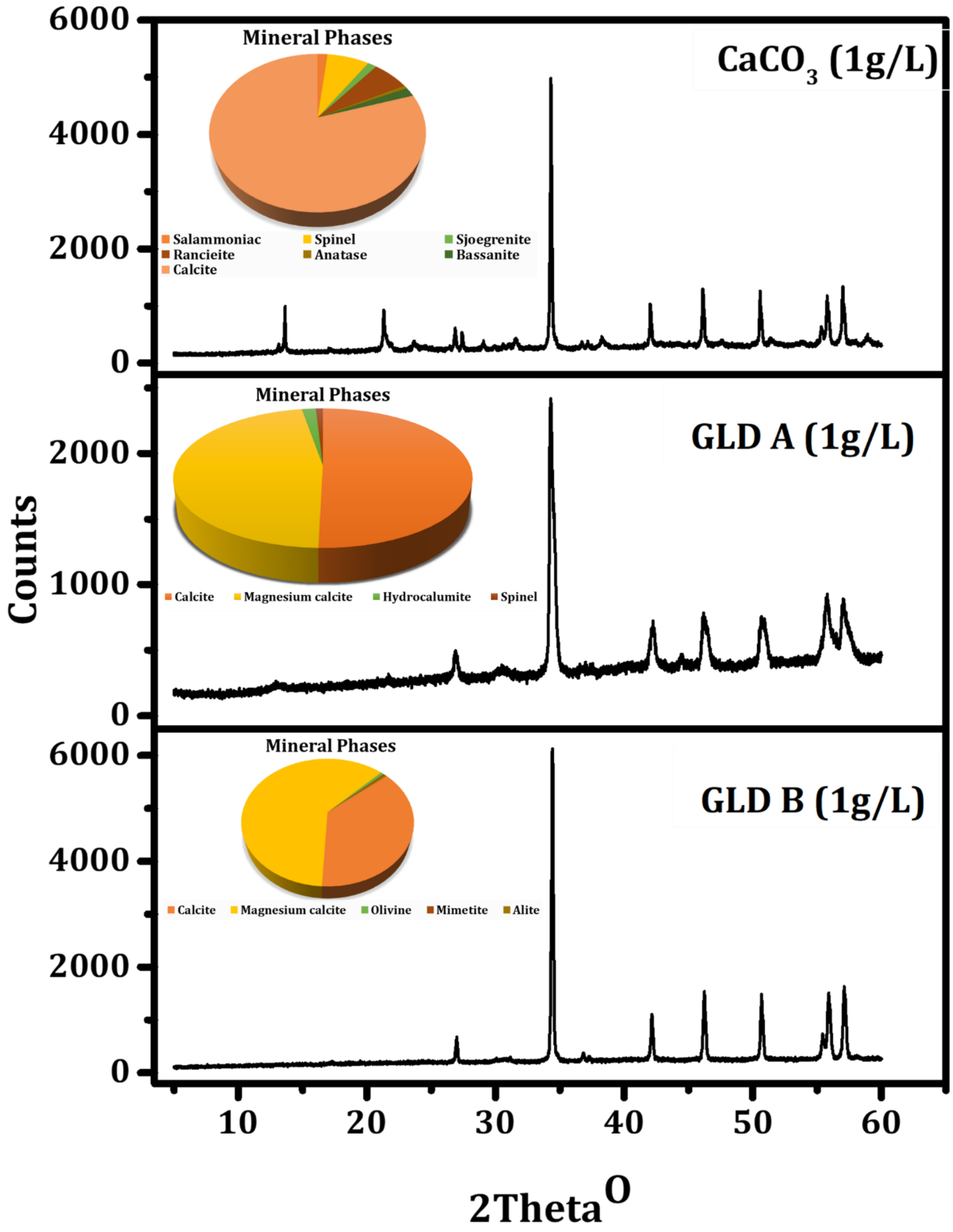

Figure 26: *XRD patterns and mineral mass percentages of raw neutralising reagents*

4.3.1.4. Conclusion

GLD, the inorganic wastes from chemical Kraft mills, can effectively neutralise the pH of AMD. This is due to their chemical properties, namely, high pH, carbonate mineral content, and liming factor that are comparable to those of limestone. However, different GLD samples have different neutralising capabilities that are attributed to the different carbonate mineral phases and their quantities thereof, present in the samples. Thus, this study has shown that GLD wastes from South African Kraft mills are effective in neutralisation of AMD in agreement with studies reported in Finland and Huelva. This indicates that GLD wastes can be beneficiated as agents for neutralisation of AMD, thus leading to environmental benefits for both Kraft pulp and mining industries. Pilot studies concerning the use of GLD in the AMD neutralisation process should be conducted.

4.4.2. Case Study 2: Coalfield AMD

4.4.2.1. Geographical description of the AMD collection site

Coal, the second main mineral in South Africa, is found in about eighteen coalfields. These coalfields are found in Free State, Gauteng, KwaZulu-Natal, Limpopo, and Mpumalanga provinces. However, its largest seams are found in Mpumalanga and KwaZulu-Natal [22], [163]. The pyrite found in this coalfields has been reported to be ~8.5% [30]. However, it should be noted that, unlike in the case of gold, pyrite is more concentrated in the coal itself rather than in the host soils [25]. This substantiates the report that was issued by CSIR (2013) which reported that <3% of pyrite is found in coal. Nevertheless, the Kromdraai coalfields were in 2000 estimated to be decanting 1.6 Mega litres of mine water daily [164].

Figure 27: *Picture of AMD sampling at Kromdraai, Mpumalanga*

The quantities and the period of how long the AMD can be generated in the mine voids and dams of these coalfields are dependent on how big the mine is and the concentration of sulphide mineral. For example, coal in the Highveld coalfield in Mpumalanga contains about 8,5% pyrite [30], and this could mean it could take centuries before its pyrite is exhausted due to oxidation. Additionally, this coalfield generates about 459.9 ML (1.26 ML/day) of AMD annually. The AMD sample that was used in this case study was collected from the coalfields decant point at Kromdraai, Figure 27, Mpumalanga Province [164].

4.4.2.2. Neutralising process

Figures 28-31 show the interactive effects of the three independent variables on pH and Ec, respectively. The graphs show that all the independent variables have played a role in cofounding the response. However, dosage seems to have played the most significant role in this. Thus, an increase in both Ec and pH were realised upon an increase in the dosage of the neutralising reagent. Although all neutralising reagents managed to increase the pH of the AMD significantly, GLD B yielded the lowest response due to the poor dissolution of its carbonic phase. The increase in dosage of both GLD A and $Ca(OH)_2$ resulted in a much increased Ec when compared to the results observed in GLD B and $CaCO_3$. On the other hand, the highest dosage of $CaCO_3$ effected the lowest Ec change (this means that this dosage significantly decreased metal ions in the sample). The increment in Ec was due to the leaching of ions from the reagents used. As expected, $Ca(OH)_2$ dissolved better in the medium than $CaCO_3$, and this means it released higher calcium ions in the AMD than $CaCO_3$, thus resulting in higher Ec values.

The dark red zones of these three-dimensional graphs indicate that the independent variables had a high impact on the response; thus, the effect of the responses intensifies with the spiralling of colourisation from the dark green to dark red zones. All graphs indicate that dosage is the most significant variable that effected most change in both pH and Ec. However, contact time also played a second significant role since it caused change in both the responses.

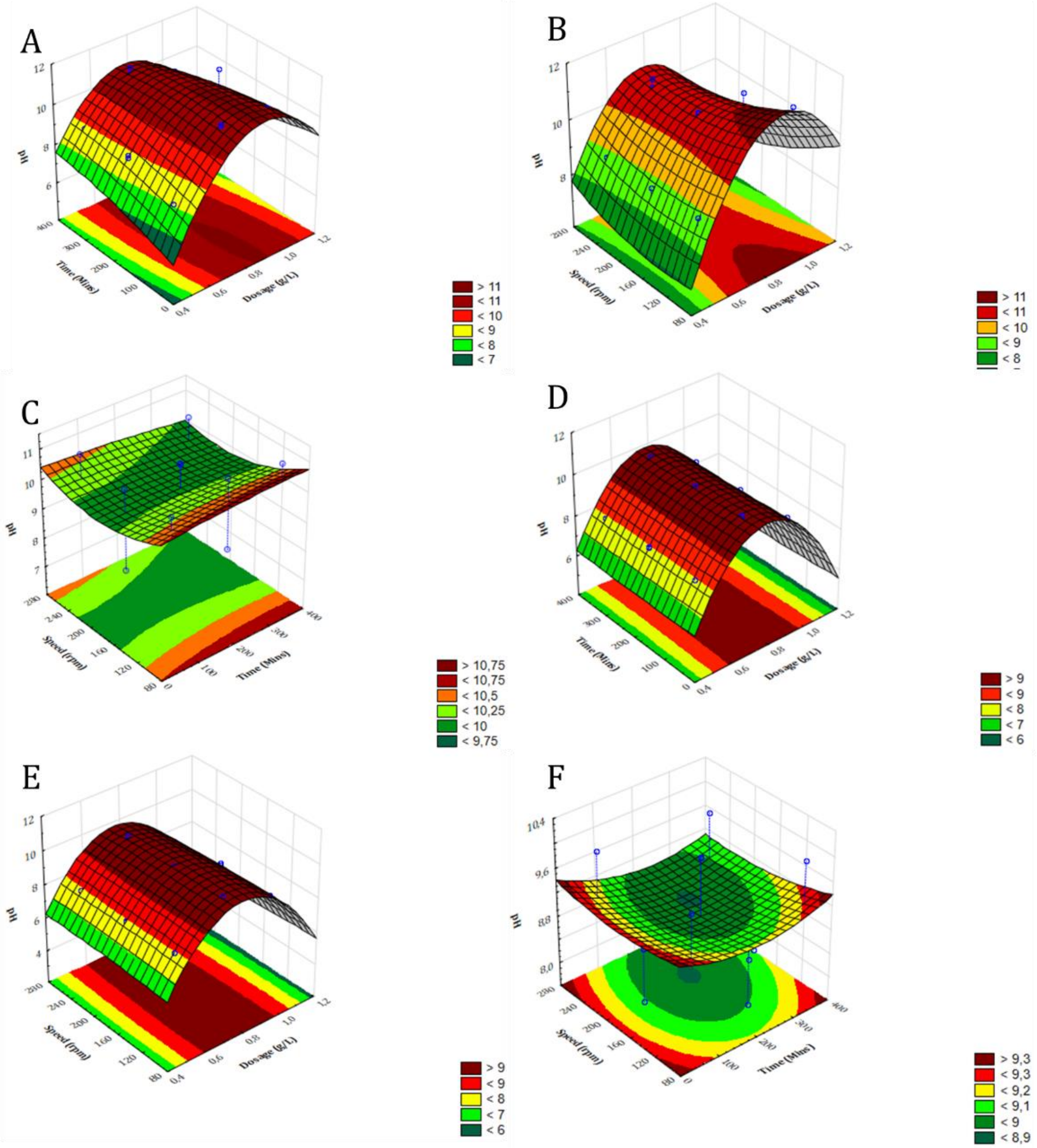

Figure 28: *Three-dimensional plots of the three variables on pH upon neutralisation of AMD with* $Ca(OH)_2$ *(A-C) and* $CaCO_3$ *(D-F). The interaction between dosage and time (A & D), speed and dosage (B&E), and speed and time (C&F).*

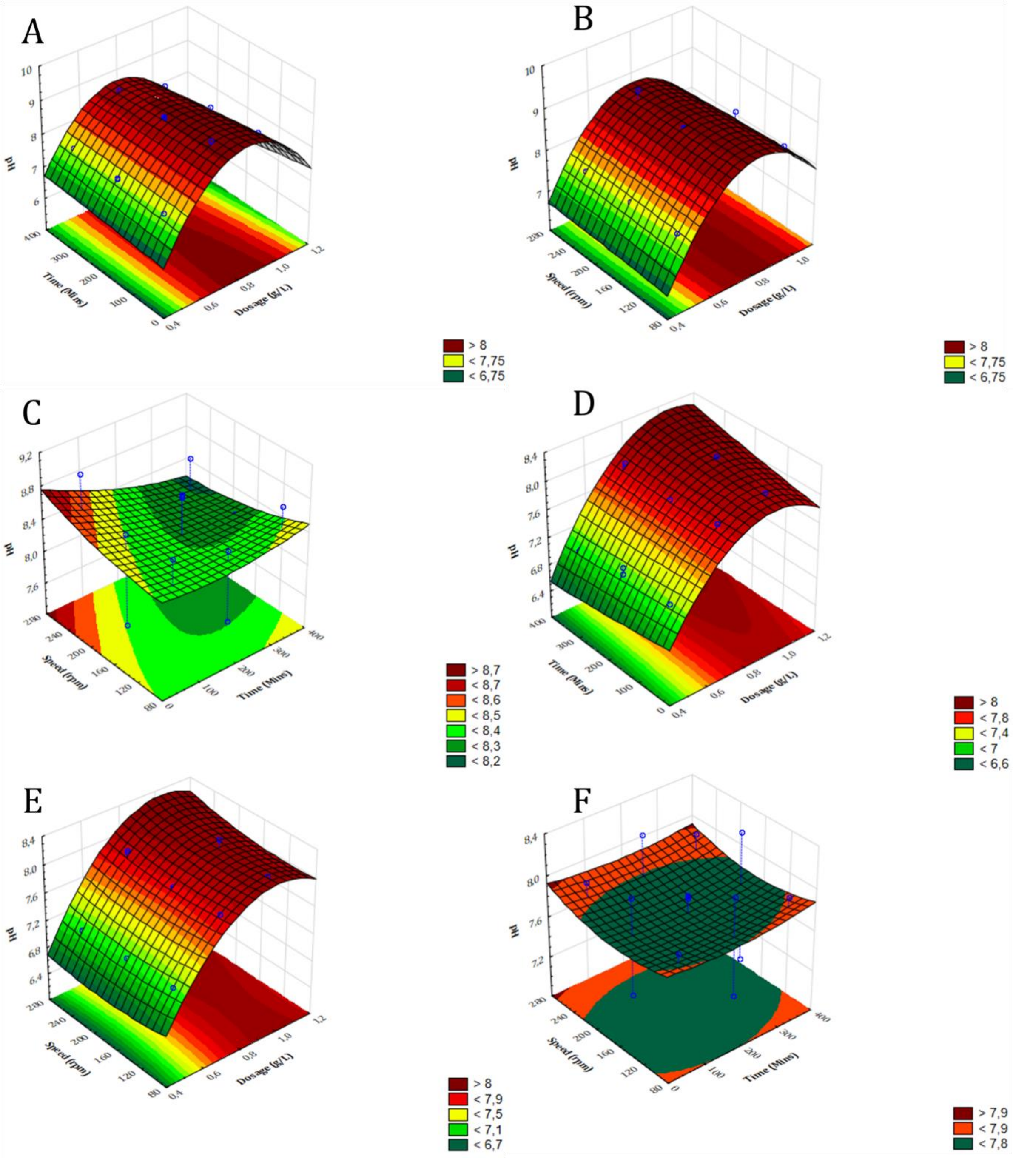

Figure 29:*Three-dimensional plots of the three variables on pH upon neutralisation of AMD with GLD A (A-C) and GLD B (D-F). The interaction between dosage and time (A & D), speed and dosage (B&E), and speed and time(C&F) .*

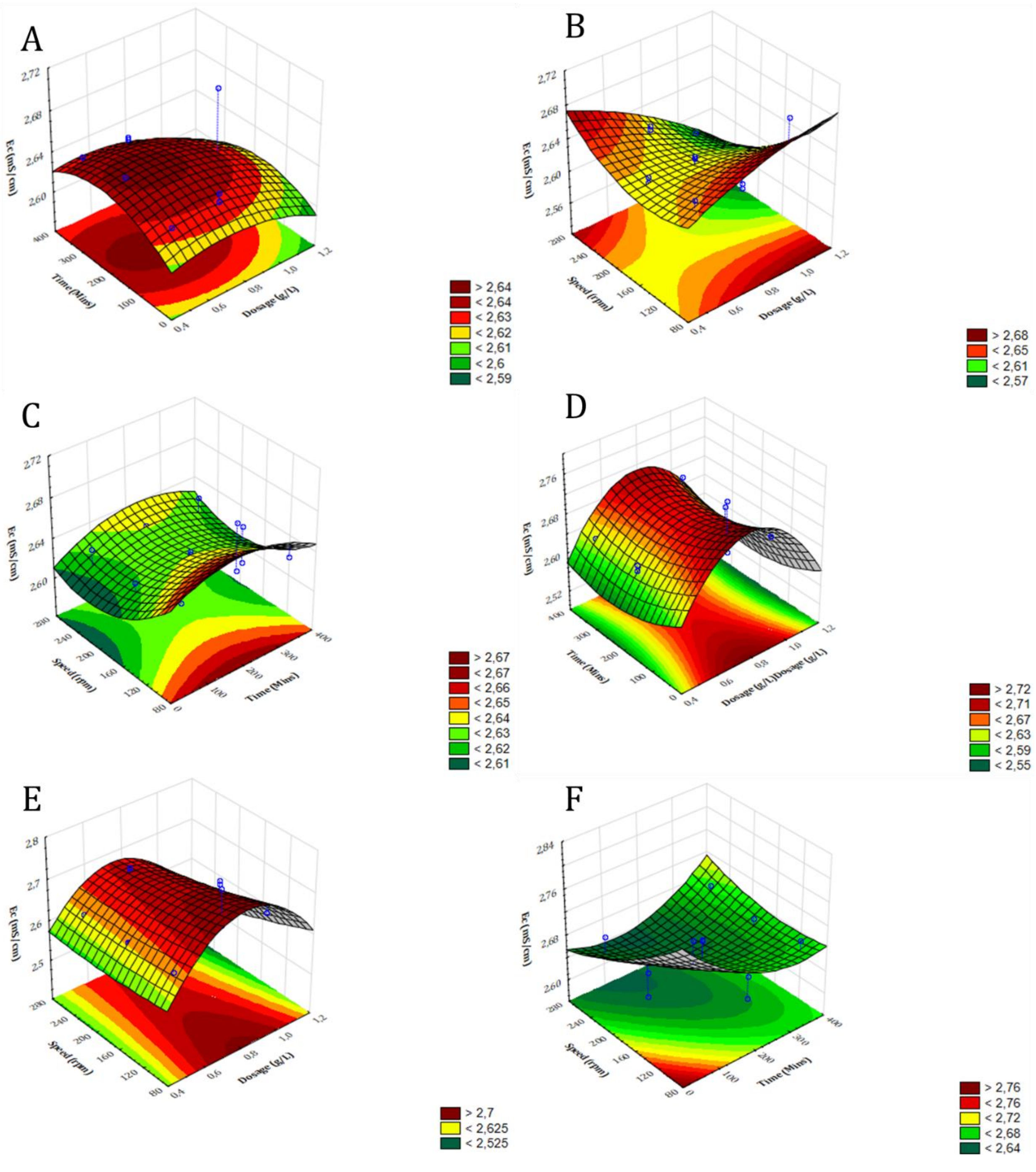

Figure 30: *Three-dimensional plots of the three variables on Ec upon neutralisation of AMD with* $Ca(OH)_2$ *(A-C) and* $CaCO_3$ *(D-F). The interaction between dosage and time (A & D), speed and dosage (B&E), and speed and time (C&F).*

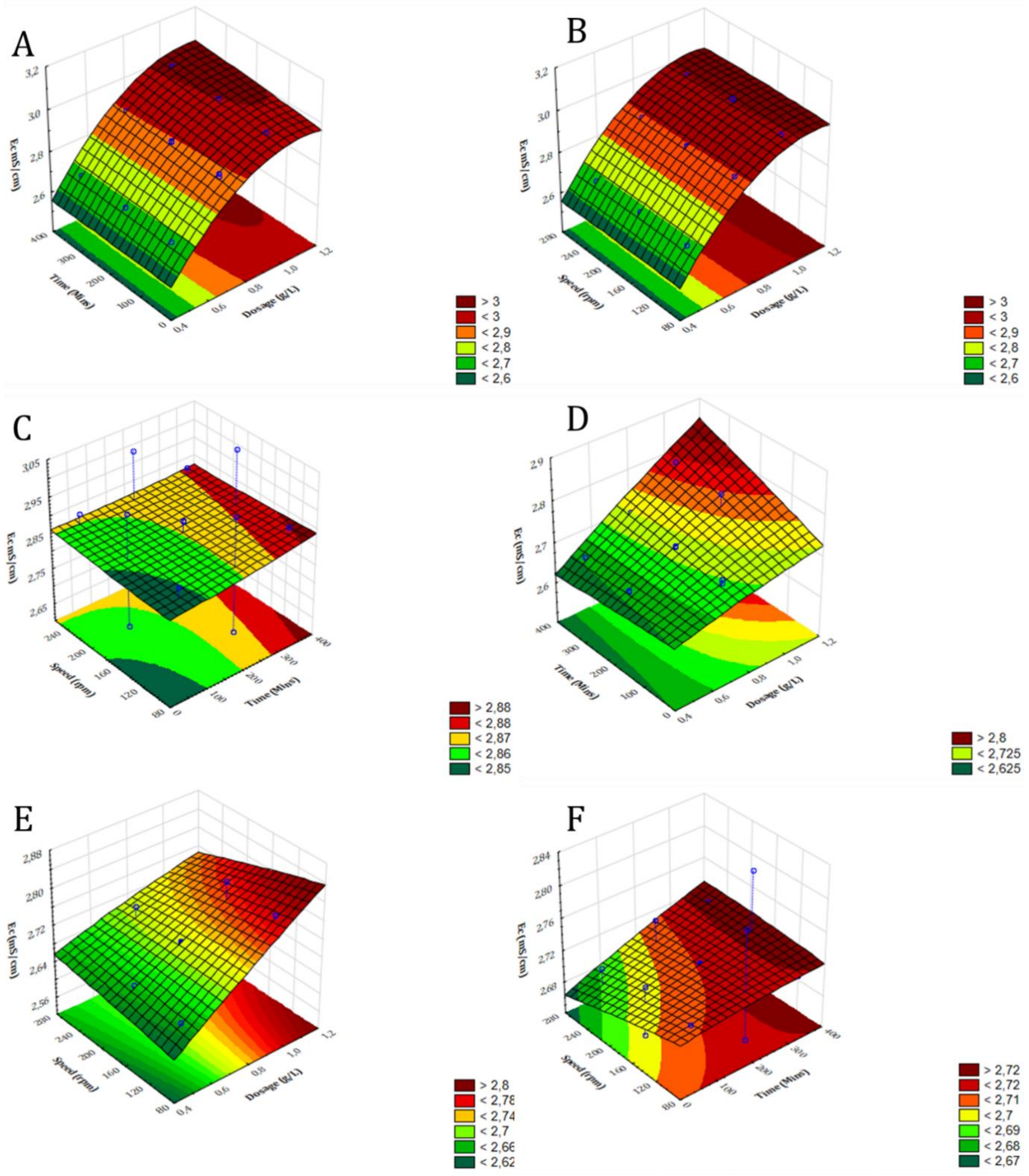

Figure 31:*Three-dimensional plots of the three variables on Ec upon neutralisation of AMD with GLD A (A-C) and GLD B (D-F). The interaction between dosage and time (A & D), speed and dosage (B&E), and speed and time (C&F).*

4.4.2.3. Optimisation of neutralisation by a Box-Behnken design

The fifteen (15) experimental runs, Table 17, that were conducted in this study allowed for determination of the effects of individual and interaction/combination empirical relationship of independent variables on the response (pH and Ec). These empirical relationships (regression equations) could be used to predict the response under any given range. Thus, the regressed mathematical equations Eqns. 17-24 for all the reagents are as follows;

$$\mathbf{pH_{(Ca(OH)2)}} = -1.8657 + 33.8800*X_1 - 20.2467*X_1^2 + 0.0022*X_2 - 5.7963e\text{-}006*X_2^2 - 0.0157*X_3 + 3.6370e\text{-}005*X_3^2$$

Eqn. 16

$$\mathbf{pH_{(CaCO3)}} = -5.4281 + 39.3750*X_1 - 25.2467*X_1^2 - 0.0008*X_2 + 1.3148e\text{-}006*X_2^2 + 0.0018*X_3 - 7.6296e\text{-}006*X_3^2$$

Eqn. 17

$$\mathbf{pH_{(GLDA)}} = 0.5552 + 20.2650*X_1 - 12.3867*X_1^2 - 0.0003*X_2 - 5.1852e\text{-}007*X_2^2 + 0.0008*X_3 - 2.5185e\text{-}006*X_3^2$$

Eqn. 18

$$\mathbf{pH_{(GLDB)}} = 4.2402 + 8.1950*X_1 - 4.0533*X_1^2 - 0.0001*X_2 + 5.1852e\text{-}007*X_2^2 - 0.0029*X_3 + 8.7407e\text{-}006*X_3^2$$

Eqn. 19

$$\mathbf{Ec_{(Ca(OH)2)}} = 2.6903 + 0.0935*X_1 - 0.0780*X_1^2 + 0.0002*X_2 - 5.6111e\text{-}007*X_2^2 - 0.0011*X_3 + 2.5111e\text{-}006*X_3^2$$

Eqn. 20

$$\mathbf{Ec_{(CaCO3)}} = 2.3027 + 1.3110*X_1 - 0.8333*X_1^2 - 0.0004*X_2 + 8.9630e\text{-}007*X_2^2 - 0.0007*X_3 + 1.0963e\text{-}006*X_3^2$$

Eqn. 21

$$\mathbf{Ec_{(GLDA)}} = 1.8888 + 1.9390*X_1 - 0.8633*X_1^2 + 0.0001*X_2 - 9.8148e\text{-}008*X_2^2 + 0.0002*X_3 - 4.8148e\text{-}007*X_3^2$$

Eqn. 22

$$\mathbf{Ec_{(GLDB)}} = 2.5234 + 0.2590{*}X_1 - 0.0387{*}X_1^2 + 0.0001{*}X_2 - 6.2963\text{e-}008{*}X_2^2 + 8.1481\text{e-}006{*}X_3 - 2.5185\text{e-}007{*}X_3^2 \qquad \textbf{\textit{Eqn. 23}}$$

Where: X_1, X_2, and X_3 represent dosage (g/L), time (Min), and speed (rpm), respectively.

Table 17: *BBD experimental runs and the observed results*

RUNS	**Dosage (g/L)**	**Time (Min)**	**Speed (rpm)**	**$Ca(OH)_2$**		**$CaCO_3$**		**GLD A**		**GLD B**	
				pH	**EC (mS/cm)**	**pH**	**EC (mS/cm)**	**pH**	**EC (mS/cm)**	**pH**	**EC (mS/cm)**
6	1.000000	210.0000	100.0000	11.23	2.691	8.73	2.673	8.47	2.993	8.15	2.791
5	0.500000	210.0000	100.0000	8.89	2.645	7.96	2.635	7.60	2.679	7.20	2.656
15	0.750000	210.0000	175.0000	10.71	2.631	9.89	2.683	8.75	2.895	7.88	2.711
10	0.750000	360.0000	100.0000	10.9	2.633	9.92	2.692	8.7	2.899	7.91	2.704
8	1.000000	210.0000	250.0000	9.75	2.602	8.44	2.618	8.27	2.998	8.19	2.73
11	0.750000	60.0000	250.0000	10.89	2.631	9.9	2.68	8.97	2.889	7.96	2.7
13	0.750000	210.0000	175.0000	10.72	2.634	9.88	2.684	8.78	2.892	7.85	2.714
7	0.500000	210.0000	250.0000	8.78	2.631	7.92	2.625	7.56	2.678	7.11	2.657
3	0.500000	360.0000	175.0000	8.80	2.635	7.89	2.63	7.57	2.68	7.00	2.665
14	0.750000	210.0000	175.0000	10.74	2.634	9.88	2.684	8.76	2.894	7.87	2.712
12	0.750000	360.0000	250.0000	10.60	2.635	9.75	2.689	8.6	2.891	7.98	2.725
2	1.000000	60.0000	175.0000	10.70	2.601	8.81	2.67	8.6	2.978	8.09	2.715
9	0.750000	60.0000	100.0000	10.80	2.639	9.91	2.779	8.68	2.876	7.86	2.709
1	0.500000	60.0000	175.0000	8.00	2.628	7.92	2.628	7.49	2.668	7.15	2.655
4	1.000000	360.0000	175.0000	9.81	2.598	8.72	2.679	8.25	3.024	8.26	2.799

Table 18: *ANOVA for the linear model for pH optimisation*

Reagent	Factor	SS	Df	MS	F	p	Significance
$Ca(OH)_2$	Model					<0.000001	Significant
	(1)Dosage (g/L) L+Q	11.66906	2	5.834531	25005.13	0.000040	
	(2)Time (Min) L+Q	0.06965	2	0.034823	149.24	0.006656	
	(3)Speed (rpm) L+Q	0.72914	2	0.364572	1562.45	0.000640	
	1*2	0.73528	3	0.245092	1050.39	0.000951	
	1*3	0.70727	2	0.353637	1515.59	0.000659	
	2*3	0.03803	1	0.038025	162.96	0.006080	
	Error	0.00047	2	0.000233			
	Total sum square	14.31804	14				
	R^2=0.99997						
	Adjusted R^2= 0.99977						
$CaCO_3$	Model					<0.000001	Significant
	(1)Dosage (g/L) L+Q	10.31183	2	5.155915	154677.5	0.000006	
	(2)Time (Min) L+Q	0.01045	2	0.005226	156.8	0.006338	
	(3)Speed (rpm) L+Q	0.04208	2	0.021040	631.2	0.001582	
	1*2	0.02406	3	0.008021	240.6	0.004141	
	1*3	0.01844	2	0.009219	276.6	0.003603	
	2*3	0.00640	1	0.006400	192.0	0.005168	
	Error	10.31183	2	5.155915	154677.5	0.000006	
	Total sum square						
	R^2=0.99999						
	Adjusted R^2=0.99996						

Table 18 continued: *ANOVA for the linear model for pH optimisation*

Reagent	Factor	SS	Df	MS	F	p	Significance
GLD A	Model					<0.000001	Significant
	(1)Dosage (g/L) L+Q	3.544206	2	1.772103	7594.726	0.000132	
	(2)Time (Min) L+Q	0.040108	2	0.020054	85.945	0.011502	
	(3)Speed (rpm) L+Q	0.004946	2	0.002473	10.599	0.086217	
	1*2	0.052538	3	0.017513	75.054	0.013177	
	1*3	0.029513	2	0.014756	63.241	0.015566	
	2*3	0.038025	1	0.038025	162.964	0.006080	
	Error	0.000467	2	0.000233			
	Total sum square	3.816533	14				
	R^2= 0.99988						
	Adjusted R^2= 0.99914						
GLD B	Model					<0.000001	Significant
	(1)Dosage (g/L) L+Q	2.304209	2	1.152105	4937.591	0.000202	
	(2)Time (Min) L+Q	0.001108	2	0.000554	2.373	0.296441	
	(3)Speed (rpm) L+Q	0.009171	2	0.004585	19.651	0.048423	
	1*2	0.029525	3	0.009842	42.179	0.023249	
	1*3	0.010275	2	0.005138	22.018	0.043445	
	2*3	0.000225	1	0.000225	0.964	0.429648	
	Error	0.000467	2	0.000233			
	Total sum square	2.536960	14				
	R^2=0.99982						
	Adjusted R^2=0.99871						

Table 19: *ANOVA for the linear model for Ec optimisation*

Reagent	Factor	SS	Df	MS	F	p	Significance
$Ca(OH)_2$	Model					<0.000001	Significant
	(1)Dosage (g/L) L+Q	0.000704	2	0.000352	117.3000	0.008453	
	(2)Time (Min) L+Q	0.000590	2	0.000295	98.3865	0.010062	
	(3)Speed (rpm) L+Q	0.002984	2	0.001492	497.3122	0.002007	
	1*2	0.000850	3	0.000283	94.4028	0.010500	
	1*3	0.002582	2	0.001291	430.3958	0.002318	
	2*3	0.000025	1	0.000025	8.3333	0.101973	
	Error	0.000003	0.000000	0.000003			
	Total sum square	0.006752	14				
	R^2=0.99911						
	Adjusted R^2= 0.99378						
$CaCO_3$	Model					<0.000001	Significant
	(1)Dosage (g/L) L+Q	0.012284	2	0.006142	18426.71	0.000054	
	(2)Time (Min) L+Q	0.001658	2	0.000829	2487.66	0.000402	
	(3)Speed (rpm) L+Q	0.002832	2	0.001416	4247.42	0.000235	
	1*2	0.001452	3	0.000484	1452.38	0.000688	
	1*3	0.000677	2	0.000339	1016.06	0.000983	
	2*3	0.002304	1	0.002304	6912.00	0.000145	
	Error	0.000001	2	0.000000			
	Total sum square	0.022795	14				
	R^2=0.99997						
	Adjusted R^2=0.9998						

Table 19 continued: *ANOVA for the linear model for Ec optimisation*

Reagent	Factor	SS	Df	MS	F	p	Significance
GLD A	Model					<0.000001	Significant
	(1)Dosage (g/L) L+Q	0.199318	2	0.099659	42711.08	0.000023	
	(2)Time (Min) L+Q	0.001012	2	0.000506	216.87	0.004590	
	(3)Speed (rpm) L+Q	0.000036	2	0.000018	7.61	0.116086	
	1*2	0.000475	3	0.000158	67.87	0.014554	
	1*3	0.000009	2	0.000005	1.96	0.338369	
	2*3	0.000110	1	0.000110	47.25	0.020515	
	Error	0.000005	2	0.000002			
	Total sum square	0.219609	14				
	R^2=0.99998						
	Adjusted R^2=0.99985						
GLD B	Model					<0.000001	Significant
	(1)Dosage (g/L) L+Q	2.304209	2	1.152105	4937.591	0.000202	
	(2)Time (Min) L+Q	0.001108	2	0.000554	2.373	0.296441	
	(3)Speed (rpm) L+Q	0.009171	2	0.004585	19.651	0.048423	
	1*2	0.029525	3	0.009842	42.179	0.023249	
	1*3	0.010275	2	0.005138	22.018	0.043445	
	2*3	0.000225	1	0.000225	0.964	0.429648	
	Error	0.000467	2	0.000233			
	Total sum square	2.536960	14				
	R^2=0.99982						
	Adjusted R^2=0.99871						

The Analysis of Variance (ANOVA) results in Tables 18 & 19, respectively, show the optimisation of pH and Ec that resulted after the AMD neutralisation process. The F-values of both dependent values, which are above 1 are regarded as being significant. Specifically, the F values of the dosage were very high for all the reagents. This indicated that dosage is the most significant variable.

The statistical fitness of the models (pH and Ec) was confirmed by the determination of coefficient values (R^2). The higher values of R^2 that are close to 1 indicate that the variability of the response could be significantly predicted by the models. This significance is shown by the R^2 values in the pH model for $Ca(OH)_2$, $CaCO_3$, GLD A, and GLD B were 0.99997, 0.99999, 0.99988, and 0.99982, respectively, as shown in Table 6. These values indicate that the models can account for more than 99.5% of the response. The high values of the adjusted determination of coefficient (Adj.R^2) also confirmed the robustness of the model. Additionally, the insignificant differences between the R^2 and adjusted R^2, below 0.2, was observed for all samples. This demonstrated that there is a good relational fit between the experimental work and the mathematical models for all the pre-treatment processes.

The p-value was used to determine the significance of the overall model that was used in this study. In essence, the significance of the model and or the independent variables used is said to have strong evidence when the p-value is ≤ 0.05. The ANOVA table indicates that the dosage remained the most significant variable of all the reagents that were used. Its p-values were below 0.0003 and 0.0009 for pH and Ec, respectively. On the other hand, the overall p-values of the model used were below 0.000, which implies that the models are very significant. The graphs in Figure 32 further emphasised the correlation that was depicted by R^2, Adj. R^2, and the p-values of the models; that is, the data points of both the observed and predicted data are not scattered, and this shows the fitness of the model.

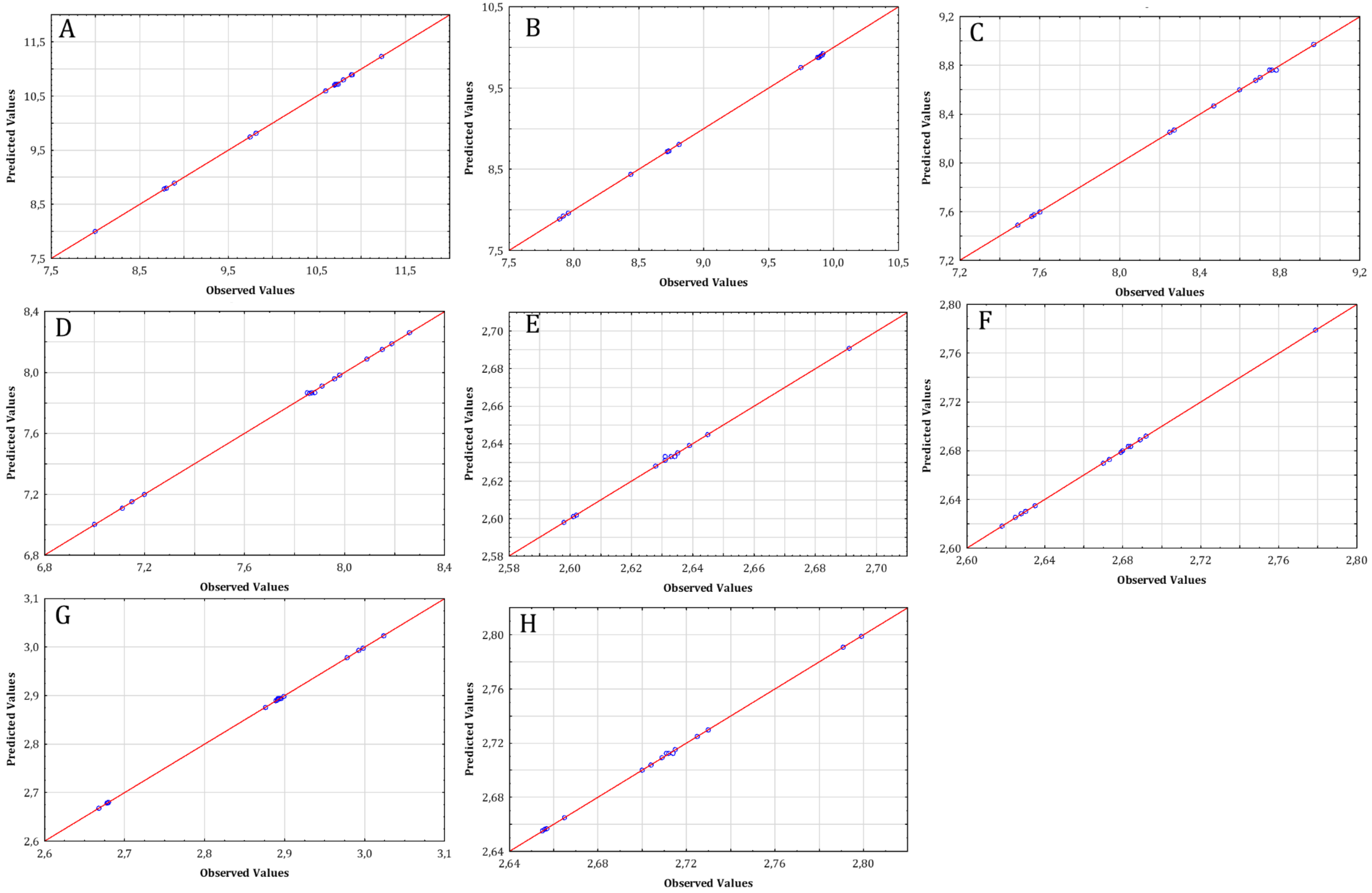

Figure 32: *Predicted vs. observed values of pH (A-D) and Ec (E-H) for Ca(OH)*$_2$*, CaCO*$_3$*, GLD A and G:D B models respectively*

The critical values, Table 20, that were obtained from the software, were favourable for raising pH values above the neutralisation point because they were in favour of using high dosages. However, if these were to be taken as optimum conditions, Ec, especially of the GLD samples, would have increased exponentially as more ions would leach out into the solution. Therefore, the maximum observed (1g/L) dosages of the neutralising reagents were instead chosen as the optimum dosage. The optimisation analysis showed that contact time was the second primary significant variable used for AMD neutralisation. Thus, the 210 minutes was chosen as optimum contact time because it allows efficient time for ion activity to take place- it was noticed that the pH started to stabilise between 2-3 h. It should be noted that the critical values of the reference materials favoured both responses; that is, the higher their dosage, the higher the pH and the more the metal precipitation, which will, in turn, reduce the Ec. However, the same dosage and contact time were used for further analysis for comparison sake.

Table 20: *Critical values as predicted by the DOE software*

Reagent	Factor	Critical Values (pH)	Predicted values (pH)	Critical Values (Ec (mS/cm)	Predicted values (Ec (mS/cm))
$Ca(OH)_2$	Dosage (g/L)	0.5994	10.81594	0.5994	2.631486
	Time (Min)	211.4851		211.4851	
	Speed (rpm)	211.1726		211.1726	
$CaCO_3$	Dosage (g/L)	0.7866	9.92051	0.7866	2.666247
	Time (Min)	241.1467		241.1467	
	Speed (rpm)	301.9426		301.9426	
GLD A	Dosage (g/L)	1.1230	8.950032	1.1230	3.026067
	Time (Min)	562.3585		562.3585	
	Speed (rpm)	190.5769		190.5769	
GLD B	Dosage (g/L)	3.3491	8.138708	3.3491	3.015734
	Time (Min)	964.4118		964.4118	
	Speed (rpm)	16.1765		16.1765	

4.4.2.4. Characterisation of the neutralised AMD

The interaction of carbonic materials with AMD would generally dissolve/disintegrate the carbonic structure. However, this disintegration occurs at different rates. This difference in dissolution rates could be due to the type of the mineral phase that makes up the carbonate material and the pH range of the AMD. This means that some minerals will dissolve readily at any pH, whereas some would dissolve at a preferential pH, as explained in our previous paper [14].

Eqns. 13 & 25 are generally used to explain the mechanism of carbonic effect on the AMD. In the equations, the sulphate precipitate in the form of calcium sulphate ($CaSO_4$). However, this may not be appreciably realised at pH values below 12 and thus remaining metastable in the solution. In addition to the pH of 12, the AMD should be fed with the $CaSO_4$ seed, which will facilitate its efficient crystallisation process.

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \qquad \textbf{\textit{Eqn. 24}}$$

The pH, Ec, acidity, and SO_4^{2-} of the AMD changed dramatically as listed in Table 21. The increment in pH was due to the dissolution of carbonate materials. This increment lowered the SO_4^{2-} in the reference materials. Although these findings may be contrary to the conditions of SO_4^{2-} reduction, similar results have been reported elsewhere [97], [106]. Unlike the findings of our previous study, the SO_4^{2-} concentrations found in the case of AMD neutralisation with $CaCO_3$ may have been influenced by the possible simultaneous dissolution of the carbonic phases found in this sample. The AMD used in this study case had a pH value which is best for dissolving most of the calcite in the sample, meaning that this simultaneous dissolution may have encouraged a slight reduction of SO_4^{2-} in the solution through precipitation. The SO_4^{2-} concentration, however, increased in the GLD treated samples because GLDs originate from a sulphate process. The Ec of all the neutralised samples increased with an increasing dosage of the reagents.

Table 21: *Chemical characteristics of AMD*

Factor	AMD	$Ca(OH)_2$ 1g/L	$CaCO_3$ 1g/L	GLD A 1g/L	GLD B 1g/L
pH	3.8	9.75	8.44	8.27	8.19
Ec (mS/cm)	2.603	2.602	2.618	2.998	2.730
SO_4^{2-} (mg/L)	1706	1662	1689	1930	1910
Acidity (mg/L $CaCO_3$)	2 843.50	6.50	58.10	96.40	81.00
Fe removal efficiency (%)		99.77	99.96	99.81	99.68
Al removal efficiency (%)		99.89	99.71	99.71	91.92
Mn removal efficiency (%)		99.81	40.00	3.85	28.46

Also, this change has also altered the composition of the neutralised AMD, as shown in Table 22. The increased pH that resulted from reagents addition of reagents created an environment for different species within the AMD to precipitate and/or to co-precipitate. This precipitation has led to a decrease in all elements that contribute towards AMD formation. Thus, more than a 91% decrease in Fe and Al was realised in all neutralised AMD samples. Only the $Ca(OH)_2$ neutralised AMD was found to have a high Mn reduction. This is because Mn precipitates proficiently as pH levels approach 10. Although this significant change was observed in the chemistry of the AMD, some metal ions such as Na, Co, Mg, and Ni leached from the neutralising reagents into the AMD. However, these ions could be easily removed through a post-treatment step, e.g., using $CaO/Ca(OH)_2$, as used in the limestone-$CaO/Ca(OH)_2$ AMD treatment process.

Table 22: ICP-AES/ICP-MS of AMD and the neutralised filtrates μg/L

Element	Accuracy (%)	AMD	$Ca(OH)_2$ 1g/L	$CaCO_3$ 1g/L	GLD A 1g/L	GLD B 1g/L
Sb	*98.3*	0.03	0.03	0.02	0.04	0.03
B	*95.4*	48.0	30.1	38.0	46.1	59.3
Sn	97.1	0.03	0.02	0.01	0.02	0.02
V	*98.9*	0.11	0.07	0.02	0.07	0.02
Cr	*99.2*	10.18	0.74	0.71	8.77	2.14
Co	*98.9*	1558.9	1.9	47.3	141.2	124.70
Ni	*97.7*	1738.9	3.5	28.8	82.8	128.20
Cu	*93.7*	96.2	20.6	18.3	23.1	12.1
***Zn**	*99.9*	*22.0*	0.64	0.02	0.03	0.5
As	*95.4*	4.62	0.11	0.10	0.11	0.20
Se	*96.9*	0.20	0.17	0.12	0.30	0.32
Mo	*98.8*	0.06	0.33	0.23	0.70	0.13
Cd	*97.3*	2.27	0.56	0.45	0.66	0.45
Ba	*98.1*	21.2	29.8	28.0	27.7	32.1
Hg	*97.4*	0.25	0.25	0.25	0.25	0.25
Pb	*96.7*	2.24	0.11	0.05	0.08	0.05
***Al**	*96.0*	10.4	0.011	0.03	0.03	0.84
***Ca**	*97.0*	401.3	655.3	492.6	393.9	427.2
***Fe**	*97.5*	1496.4	3.5	0.6	2.9	4.8
***K**	*96.9*	BLD	5.133	1.405	6.247	4.55
***Mg**	*95.5*	143.3	27.19	148.4	152.5	152.4
***Mn**	*97.3*	52.00	0.10	31.2	50.0	37.2
***Na**	*99.8*	10.78	6.263	6.902	150.6	45.38
***P**	*98.7*	BLD	BLD	BLD	0.2154	BLD
***Si**	*96.5*	2.753	0.6258	0.7329	1.144	1.916
***Sr**	*96.1*	0.57	0.61	0.75	0.84	0.64

*mg/L

4.4.2.5. Characterisation of the Sludge

The sludge that resulted from the AMD neutralisation process was analysed using SEM/EDX, XRF, ICP-AES/ICP-MS, and XRD. Figure 33 shows the morphological evidence that the reaction between the AMD and the calcitic structures had taken place. This is illustrated by the granulated assemblies that are evident in the SEM pictures. The spherical granules generally indicate that metals from the AMD had been displaced by precipitation, co-precipitation or adsorption onto GLD [29]. The EDX graphs alongside the SEM micrographs and the mapped SEM inserts show the distribution of various elements that were present in the sludge from the neutralised reactants.

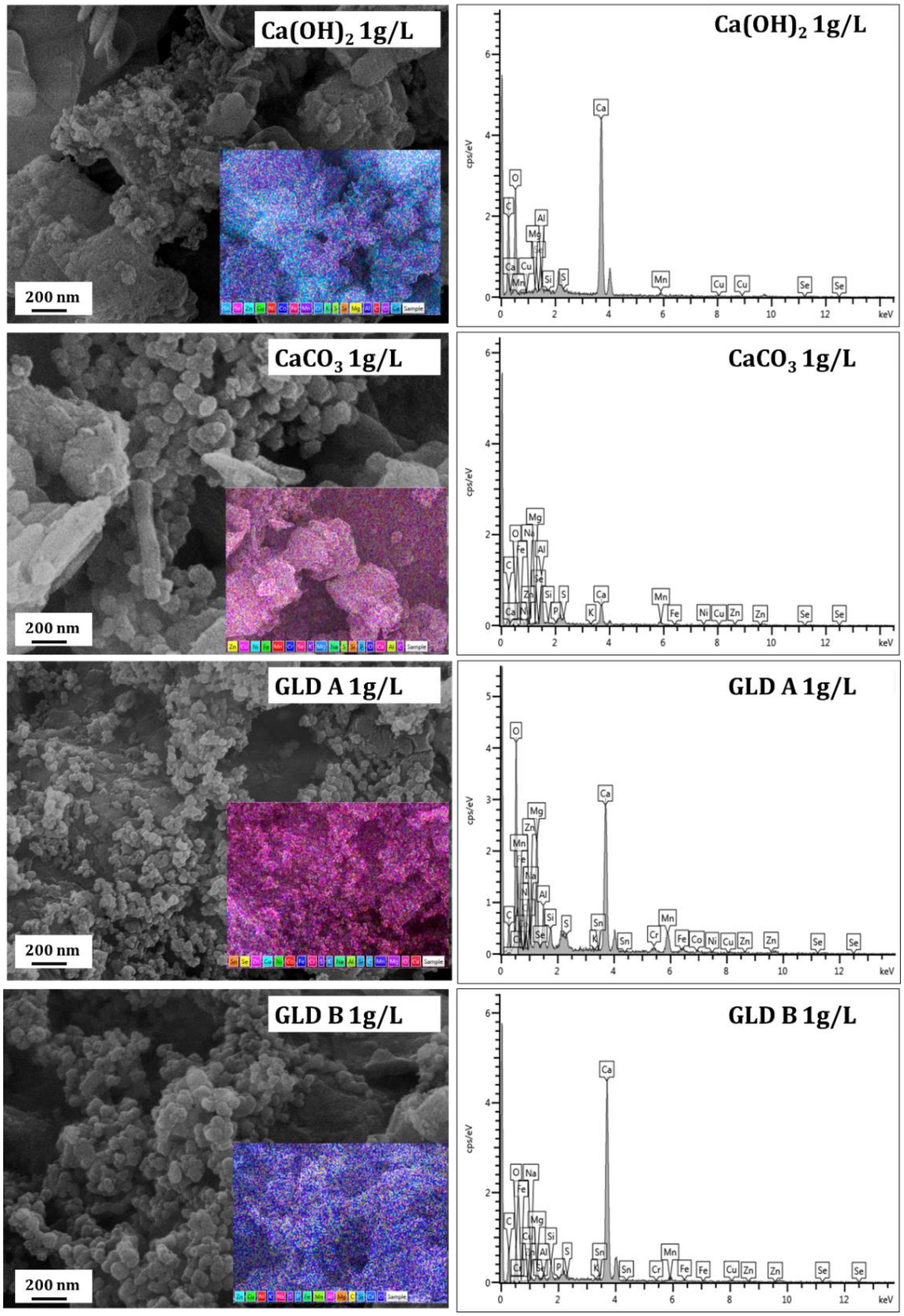

Figure 33: *SEM/EDX of precipitates from neutralisation of AMD.*

The XRF and ICP-AES/ICP-MS results in Tables 23 & 24, respectively further showed that there had been a change in the concentration of elements that were initially composed in the raw neutralising reagents, hence an increase in either an oxide or elemental concentration further affirms the possible precipitation of that element from the AMD.

Table 23: *XRF results of neutralising reagents and their sludge*

Parameter Wt %	**$Ca(OH)_2$**	**$CaCO_3$**	**GLD A**	**GLD B**	**$Ca(OH)_2$ 1 g/L**	**$CaCO_3$ 1g/L**	**GLD A 1g/L**	**GLD B 1g/L**
Al_2O_3	0.24	19.99	0.98	0.57	2.31	21.68	3.96	3.17
CaO	56.72	42.42	14.61	31.24	38.60	29.47	25.77	40.69
Cr_2O_3	BLD	-	0.72	0.04	BLD	BLD	1.22	0.06
FeO_3	BLD	0.13	0.66	0.57	BLD	BLD	BLD	0.07
K_2O	0.01	0.02	0.61	0.63	0.02	0.03	0.04	0.07
MgO	1.28	0.56	6.13	3.02	9.28	2.25	9.60	3.22
MnO	0.68	0.50	0.99	1.34	3.55	2.60	6.30	1.65
Na_2O	0.01	0.02	14.38	7.28	0.02	0.08	0.36	0.50
P_2O_5	0.01	0.04	0.29	0.26	0.01	0.04	0.50	0.26
SiO_2	1.20	0.81	1.18	2.97	1.54	1.78	2.55	3.94
TiO_2	0.02	0.03	0.04	0.04	0.01	0.03	0.05	0.03
Loi %	38,81	35.07	33.10	39.37	37.99	37.46	41.19	42.38
Summation of parameters	99.16	99.09	73.70	87.37	93.35	95.40	91.56	96.03

BLD= below detection

__Table 24:__ ICP-AES/ICP-MS results of neutralising reagents and their sludge mg/L

Element	**Accuracy (%)**	**$Ca(OH)_2$**	**$CaCO_3$**	**GLD A**	**GLD B**	**$Ca(OH)_2$ 1g/L**	**$CaCO_3$ 1g/L**	**GLD A 1g/L**	**GLD B 1g/L**
B	95.4	338.00	9.74	67.64	55.01	301.70	259.67	408.0	478.65
V	98.9	2.00	4.45	3.23	2.34	2.00	4.00	6.00	3.00
Cr	99.2	5.00	10.73	5565	255.03	9.00	9.00	4780	235
Co	98.9	12.00	0.88	11.32	13.63	1141	1527	2435	446
Ni	97.7	168.00	4.68	82.59	37.73	1589	2081	3346	776
Cu	93.7	4.00	30.25	156.94	161.75	37.00	33.00	315	246
Zn	99.9	159828	11.11	308.80	259.27	287313	89103	148244	197222
As	95.4	1.00	0.81	0.54	2.25	6.00	6.00	7.00	8.00
Se	96.9	0.59	0.57	2.99	1.35	1.05	1.10	1.35	0.85
Mo	98.8	0.28	0.38	1.17	0.72	0.81	0.49	0.61	0.35
Cd	97.3	14.00	0.02	0.39	0.18	11.50	9.40	17.40	19.4
Ba	98.1	8.03	10.65	668.62	438.86	16.00	18.02	929	521.3
Hg	97.4	BLD	0.03	0.02	0.04	*33.01	*104.1	*54.00	*93.00
Pb	96.7	0.49	2.72	12.38	11.73	2.40	5.13	22.08	17.30
Al	96,0	1116.4	92380.32	3759.43	2266.22	10925.4	105829.6	19156.1	14245.2
Ca	97.0	434065	268600.8	101030	198049	288756	232915	193024	306582
Fe	97.5	1811.5	870.48	4648.97	3528.13	3287.1	2194.2	9258.5	5850.8
K	96.9	BLD	259.71	5431.67	5419.11	BLD	BLD	BLD	BLD
Mg	95.5	7085	3354.04	36928.39	16381.3	55174	13076	53463	18219
Mn	97.3	5959.0	13.37	7762.37	9547.72	30318.4	21502.2	50536.6	14136.5
Na	99.8	2743	306.58	153011.4	71143.6	1876	1728	5673	7216
P	98.7	154	153.16	1251.82	760.96	150.00	271	2266	1306
Si	96.5	1994	2517.37	6321.21	6247.69	2502	2283	1159	1295
Sr	96.1	64.0	943.74	639.08	520.48	53.10	774.9	534.1	576.8

*μg/L

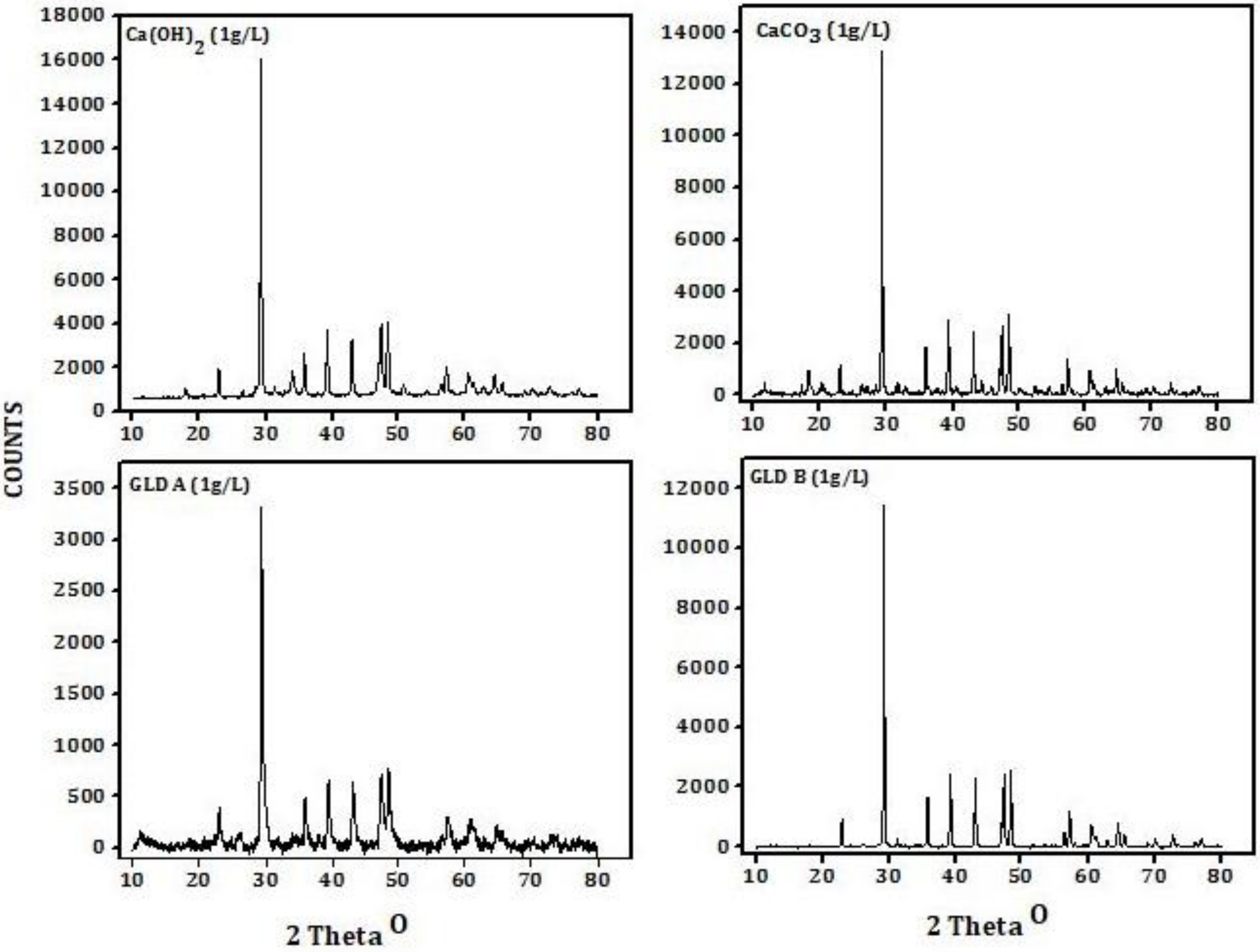

Figure 34: XRD pattern of the reacted neutralising reagents.

XRD graphs in Figure 34 were further used to quantify the mineralogical phases of the sludge. This mineralogical phase quantification and analysis showed that $CaCO_3$ was still the chief constituent found in all sludge. Other crystalline phases that were detected in the samples were;

$Ca(OH)_2$: calcite, quartz, periclase, zinc aluminium carbonate hydroxide-hydrate, sodium zinc oxide, natrita, and hematite.

$CaCO_3$: calcite, katoite, hydrogarnet, gibbite, zinc aluminium carbonate hydroxide-hydrate, and bayerite.

GLD A: calcite, graphite, natrite, and magnesium calcite.

GLD B: calcite, magnesium calcite, and graphite

A disadvantage of using this technology is that it is only able to detect the crystalline phases; that is, SO_4^{2-} is said to precipitate in the form of $CaSO_4$, according to Eqns. 13 &25. However, the XRD patterns do not indicate the presence $CaSO_4$. SO_4^{2-} anion may have precipitated as an amorphous phase (instead of a crystalline phase) that could not be detected by XRD.

4.4.2.6. Conclusions

The use of RSM has conclusively showed how the different independent variables could affect pH and Ec upon neutralisation of AMD with GLD. Dosage of the neutralising reagent was the most significant variable in this regard. The decreasing order of the significance of the variables was; GLD dosage > contact time > mixing speed. Although the critical values that were obtained from the DOE software were not evaluated for their effect on the response because they would exponentially raised the Ec, as shown on Table 20, of the treated AMD from leaching of nutrients from the GLD, the developed model can be used to predict the desired pH and Ec when neutralising AMD with GLD. Future work on this study will include the evaluation of neutralisation of AMD with GLD on a pilot scale, determination of the techno-economics of the process, and post-treatment of the GLD neutralised AMD.

CHAPTER 5: PRELIMINARY COST-BENEFIT ANALYSIS

5.1. Introduction

The above chapter (four) has shown that GLDs could be used as a material of choice in the place of $CaCO_3$ and its derivative $Ca(OH)_2$. However, costs associated with using them may not always be cost-effective. Thus, chapter five seeks to address the costs that could be associated with using GLDs for AMD neutralisation.

5.2. COST-BENEFIT ANALYSIS: LIMESTONE VS. GLDS

To ascertain potential benefits that may be achieved by replacing limestone with GLDs, we performed a simple cost-benefit analysis, see Table 25. Available GLDs at the reference local mills is about 100,000 tons/year. Based on our experimental data, the optimum GLD dosage is 1 g/l. The volume of AMD treat was at 25 (m^3/day), as at the local reference AMD treatment plant. This translates to approximately 7.5 tons/year of GLDs. Therefore, enough amount of GLDs available may be sufficient to run at least 1000 AMD plant with the same capacity as the reference plant. The process cost (labour, utility, and maintenance excluded) is almost 17% less than that of the limestone-based neutralisation process. The distance from the Kraft pulp to the AMD plant, however, should be limited to 20 km.

Using GLDs as discussed in this thesis represents a good starting point for future commercial applications of GLDS. Cost-benefit analysis favours the use of GLD against limestone. However, the distance from the Kraft pulp to the AMD plant should be limited to 20 km. It is also worth noting that characteristics of the dregs, differ significantly and are mill specific. This implies that there is no single solution for all dregs, and it is imperative that dregs produced at each mill be evaluated so that potential applications can be determined. The overall process economics GLDs/lime process vs. limestone/lime process, pilot trials, and detailed process design and economic analyses.

Another option, depending on the quantities of the AMD that is being treated, may be to adopt the recently developed macro-algae (sea-weed) facilitated aerobic wetland to polish the GLD treated AMD [165], [166]. This inventory is based on the competitive advantage that the macro-algae that were explored do not suffer from having low metabolic activity during the cold season as compared to the traditionally used macrophytes and microbials. Furthermore, the effectiveness of the macro-algae species (*Oedogonium crassum, Klebsormidium acidophilum,* and *Microspora quadrata*) is based on the fact that their metal content need increases with the increasing metal concentrations of their surrounding environment. Generally, the species were used to absorb Al, Fe, Mg, Mn, and ZN from AMD at varying pH levels viz.; 3, 5, and 7. The outcome of the study showed that *O. crassum* was the most effective species, followed by *K.klebsii* and *M. Tumudula.* In addition, pH levels seemed to affect the rate of these metals' bio-accumulation, i.e. metal accumulation increased with increasing pH levels [167].

In 2018, Oberhoslter *et al*. took this study further by conducting a pilot study on using the same macro-algae species for removal of S, Mg, Ca, and P on a pilot scale. In this study, the macro-algae species were subjected to the AMD with different pH levels (3, 5, 6.4, and 7). The study showed that *M. tumudula* was the most effective species to absorb S and P. This was most efficient at pH 5 and 7, respectively. High bioaccumulation of metals (Ca and Mg) by *O. crassum* that was reported in the previous study was also confirmed in this study. The effectiveness of these species to absorb S and dissolved metals together with the added advantage that they absorb better at higher pH values make the inventory to be a good post-treatment for GLD treated AMD [166].

Table 25: AMD treatment costs: limestone vs. GLD

Neutralising agent	Dosage rate (g/L)	AMD flow rate (m^3/day)	Volume of AMD treated (m^3/year)	Limestone consumed (ton/year)	Cost of neutralising agent ($/year)	Process cost ($/$m^3$)	Remarks
Limestone -S	4	25	7 500	30	1 177.07	0.16	Reference plant
GLD -S	4	25	7500	30	935.77	0.13*	
	4	25	7500	30	2 336.44	0.32**	
Limestone -E	1	25	7 500	7.5	293.89	0.04	
GLD - E	1	25	7500	7.5	233.55	0.0.03*	
	1	25	7500	7.5	584.13	0.08**	
	1	25	7500	7.5	1 168.25	0.16***	

- The price of limestone is $ 39.19 per ton (pricing, 2016).
- Price of GLD (refer to transport cost only: $ 1.56 /km/ton, 2016 pricing)
- The plant is operating 300 days per annum.
- The AMD flow rate is 25 m^3/day (as the reference plant).
- Limestone – E denotes that cost estimation is based on experimental data
- Limestone – S & GLD – S denotes that cost estimation is based on a reference plant, but the AMD characteristics differ from the one used in this study.
- **Note**: *refers to 20 Km distance from the pulp mill to the AMD plant,

  ** refers to 50 Km distance from the pulp mill to the AMD plant,

*** refers to100 Km distance from the pulp mill to the AMD plant.

CHAPTER 6: CONCLUSIONS AND RECOMMENDATIONS

6.1. CONCLUSIONS

The primary motivation of this study was to characterise the properties of GLDs produced in two of the South African Kraft pulp mills and evaluate if these properties could qualify them to be used as alternatives for limestone in the treatment of AMD. After their evaluation, they were to be used in pre-treating the AMD. An array of analytical instruments was used to characterise both the GLDs and AMD samples before and after treatment and the results were compared to those obtained from treating the AMD samples with conventional additives ($CaCO_3$ and $Ca(OH)_2$) as reference materials.

GLDs samples displayed neutralising potential that was comparable to that of $CaCO_3$ but lower than that of $Ca(OH)_2$. This comparable neutralising potential was due to the presence of calcite, which was revealed by the array of analytical instruments that were used. Furthermore, sample characterisation also showed that GLDs composition is mill specific. Thus, indicating that there could never be one solution of handling them and that critical characterisation needs to be done before each use. This is because the different carbonate mineral phases found in these GLDs react or behave differently, hence requiring caution in handling them. Nevertheless, the comparable neutralising potential, which is due to the diverse carbonic structures in GLDs, qualified them as the competent candidates to be used as an alternative for $CaCO_3$ and or $Ca(OH)_2$ in the pre-treatment of AMD.

Different types of AMD originating from gold and coal mines were used in this study. However, their treatment with GLDs yielded consistent increment in pH and Ec of the AMD samples due to dissolution of the carbonic structure in the GLDs. Dosage and contact time of the reactions were contributing significant effects in impacting the pH and Ec of the AMDs. Thus, the higher the dosage of GLDs and the longer the reaction time, the higher the pH and Ec. However, the mineralogy of the GLDs was a limiting factor on how far can this change be effected In that the GLD B could not raise the pH of the AMD beyond 9 whereas GLD A could.

Nevertheless, GLDs significantly reduced the concentrations of most ions present in AMD samples. The downfall of using GLDs was observed to be the SO_4^{2-} and Na, which contributed tremendously to the increment of Ec. Additionally, the settling properties of the GLDs sludge were comparable to those of $Ca(OH)_2$, giving them an added advantage over $CaCO_3$.

It has been demonstrated that GLDs are effective additives for use in neutralisation of AMDs. This implies that they can be effectively used for beneficiation of GLDs waste from Kraft pulp mills. The end results is symbiotic relationship that results in beneficiation of wastes from chemical pulp and mining industries.

6.2. RECOMMENDATIONS FOR FUTURE WORK

The main aim and objective of this study were achieved. The observed results showcased the potential for GLDs to be one of the good circular economy material for AMD treatment. However, further research in their use in AMD treatment is needed to adopt their use on an industrial scale.

Thus, it is recommended that the following should be investigated in the future:

- Conduct a post-treatment study.
- Pilot the method, i.e., both the pre- and post-treatment stages.
- Conduct a techno-economical study which includes both the treatment of AMD with GLDs and the post-treatment of the GLDs pre-treated AMD.
- Collect and characterise GLDs at the same mills but at different times because of the variation that may be caused by different factors such as the upset time during the pulping process.
- Collect and characterise GLDs from the landfills; check if their exposure to the environment can play a role in altering their character.

REFERENCES

[1] N. National Environmental Management: Waste Act, *Government Gazette*, vol. 525, no. 3. South Africa, 2009.

[2] U. Nations, 'General Assembley 70 session:Transforming our world: the 2030 Agenda for Sustainable Development', *General Assembley 70 session*, vol. 16301, no. October. pp. 1–35, 2015, doi: 10.1007/s13398-014-0173-7.2.

[3] J. Johakimu, T. Bush, and L. A. Lucia, 'Green liquor impregnation and kraft pulping of South African Pinus Patula- A practical approach to provide cost savings in a kraft mill's pulping operation', *Tappsa J.*, vol. 2, p. 6, 2011.

[4] C. Biermann, *Handbook of Pulping and Papermaking*, Second. Sand Dieogo, California: Elsevier, 1996.

[5] P. Bajpai, *Biotechnology for Pulp and Paper Processing*. Singapore: Springer Singapore, 2018.

[6] V. Ribeiro dos Santos, M. Dezena Cabrelon, E. de Sousa Trichês, and E. Quinteiro, 'Green liquor dregs and slaker grits residues characterization of a pulp and paper mill for future application on ceramic products', *J. Clean. Prod.*, vol. 240, 2019, doi: 10.1016/j.jclepro.2019.118220.

[7] M. Mäkitalo, J. Mácsik, C. Maurice, and B. Öhlander, 'Improving Till by Adding Green Liquor Dregs in Sealing Layers to Control AMD–A Pilot Study', in *mwen.info*, 2015, p. 7.

[8] H. Tran and E. K. Vakkilainnen, 'The Kraft Chemical Recovery Process', *TAPPI Kraft Recover. Course*, pp. 1–8, 2008.

[9] Department of environmental Affairs (DEA), *National Pricing Strategy for Waste Management (NPSWM)*, vol. 904, no. 40200. 2016, p. 48.

[10] M. Mäkitalo, C. Maurice, Y. Jia, and B. Öhlander, 'Characterization of Green Liquor Dregs, Potentially Useful for Prevention of the Formation of Acid Rock Drainage', *Minerals*, vol. 4, no. 2, pp. 330–344, 2014, doi: 10.3390/min4020330.

[11] P. Farage, A. Augusta, and P. Rezende, 'Intermediate covering of municipal solid

waste land fills with alkaline grits , dregs and lime mud by-products of kraft pulp production', *J. Clean. Prod.*, vol. 239, pp. 1–8, 2019, doi: 10.1016/j.jclepro.2019.117985.

[12] C. M. Torres, C. M. Silva, L. G. Pedroti, W. E. Fernandes, F. C. . Ballotin, and J. C. Zanuncio, 'Cement Portland production with dregs and grits from kraft pulp mills incorporated to clinker', *6th Int. Work. | Adv. Clean. Prod.*, 2017.

[13] H. Nurmesniemi, R. Pöykiö, P. Perämäki, and T. Kuokkanen, 'The use of a sequential leaching procedure for heavy metal fractionation in green liquor dregs from a causticizing process at a pulp mill', *Chemosphere*, vol. 61, no. 10, pp. 1475–1484, 2005, doi: 10.1016/j.chemosphere.2005.04.114.

[14] K. R. Sebogodi, J. K. Johakimu, and B. B. Sithole, 'Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa', *J. Clean. Prod.*, vol. 246, p. 118979, Oct. 2020, doi: 10.1016/j.jclepro.2019.118979.

[15] R. Modolo, A. Benta, V. M. Ferreira, and L. M. Machado, 'Pulp and paper plant wastes valorisation in bituminous mixes', *Waste Manag.*, vol. 30, no. 4, pp. 685–696, 2010, doi: 10.1016/j.wasman.2009.11.005.

[16] D. Ragnvaldsson *et al.*, 'A novel method for reducing acid mine drainage using green liquor dregs', *Environ. Chem. Lett.*, vol. 12, no. 3, pp. 443–447, 2014, doi: 10.1007/s10311-014-0469-z.

[17] K. K. Kefeni, T. A. M. Msagati, and B. B. Mamba, 'Acid mine drainage: Prevention, treatment options, and resource recovery: A review', *J. Clean. Prod.*, vol. 151, pp. 475–493, 2017, doi: 10.1016/j.jclepro.2017.03.082.

[18] I. Park *et al.*, 'A review of recent strategies for acid mine drainage prevention and mine tailings recycling', *Chemosphere*, vol. 219, pp. 588–606, 2019, doi: 10.1016/j.chemosphere.2018.11.053.

[19] S. Trope, 'An in depth look back at South Africa's mining history', *Living Lifestyle*, 2016. http://www.living-lifestyle.co.za/an-in-depth-look-back-at-south-africas-mining-history/ (accessed May 14, 2020).

[20] S. Matsumoto, H. Shimada, and T. Sasaoka, 'The Key Factor of Acid Mine Drainage (AMD) in the History of the Contribution of Mining Industry to the Prosperity of the United States and South Africa: A Review', *Nat. Resour.*, vol. 07, no. 07, pp. 445–460, 2016, doi: 10.4236/nr.2016.77039.

[21] Mineral Council, 'Mining in SA - Minerals Council South Africa', *Mineral Council South Africa*, 2020. https://www.mineralscouncil.org.za/sa-mining (accessed May 14, 2020).

[22] V. Munnik, G. Hochmann, M. Hlabane, and Stephen Law, 'The Social and Environmental Consequences of Coal Mining in South Africa: A Case Study', Cape Town, 2010.

[23] N. Mokonyane, 'Disused mines: what's being done? | SAnews', *South African Government News Agency*, 2015. https://www.sanews.gov.za/south-africa/disused-mines-what's-being-done (accessed May 14, 2020).

[24] D. B. Johnson and K. B. Hallberg, 'Acid mine drainage remediation options: A review', *Sci. Total Environ.*, vol. 338, no. 1-2 SPEC. ISS., pp. 3–14, 2005, doi: 10.1016/j.scitotenv.2004.09.002.

[25] T. S. McCarthy, 'The impact of acid mine drainage in South Africa', *S. Afr. J. Sci.*, vol. 107, no. 5/6, pp. 1–7, 2011, doi: 10.4102/sajs.v107i5/6.712.

[26] P. C. Singer and W. Stumm, 'Acidic Mine Drainage: The Rate-Determining Step', *Science (80-.).*, vol. 167, no. 3921, pp. 1121–1123, Feb. 1970, doi: 10.1126/science.167.3921.1121.

[27] V. Masindi, M. S. Osman, and A. M. Abu-Mahfouz, 'Integrated treatment of acid mine drainage using BOF slag, lime/soda ash and reverse osmosis (RO): Implication for the production of drinking water', *Desalination*, vol. 424, no. September, pp. 45–52, 2017, doi: 10.1016/j.desal.2017.10.002.

[28] A. G. Udayabhanu and B. Prasad, 'Studies on environmental impact of acid mine drainage generation and its treatment: an appraisal', *Indian J. Environ. Prot.*, vol. 30, no. 11, p. 15, 2010.

[29] V. Masindi, V. Akinwekomi, J. P. Maree, and K. L. Muedi, 'Comparison of mine

water neutralisation efficiencies of different alkaline generating agents', *J. Environ. Chem. Eng.*, vol. 5, no. 4, pp. 3903–3913, 2017, doi: 10.1016/j.jece.2017.07.062.

[30] E. Fosso-Kankeu, A. Manyatshe, and F. Waanders, 'Mobility potential of metals in acid mine drainage occurring in the Highveld area of Mpumalanga Province in South Africa: Implication of sediments and efflorescent crusts', *Int. Biodeterior. Biodegrad.*, vol. 119, pp. 661–670, 2017, doi: 10.1016/j.ibiod.2016.09.018.

[31] H. Tutu, T. S. McCarthy, and E. Cukrowska, 'The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study', *Appl. Geochemistry*, vol. 23, no. 12, pp. 3666–3684, 2008, doi: 10.1016/j.apgeochem.2008.09.002.

[32] G. A. Jones, S. E. Brierly, S. J. J. Geldenhuis, and J. R. Howard, 'Research on the Contribution of Mine Dumps to the Mineral Pollution Load at the Vaal Barrage', *Water Res. Comm. Rep.*, no. 136/1, p. 89, 1988.

[33] K. Naicker, E. Cukrowska, and T. S. McCarthy, 'Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs', *Environ. Pollut.*, vol. 122, no. 1, pp. 29–40, 2003, doi: 10.1016/s0269-7491(02)00281-6.

[34] Gardguide, 'Chapter 2 - GARDGuide', *The International Network for Acid Prevention INAP*, 2012. http://www.gardguide.com/index.php/Chapter_2 (accessed Apr. 27, 2020).

[35] J. Pope, N. Newman, D. Craw, D. Trumm, and R. Rait, 'Factors that influence coal mine drainage chemistry West Coast, South Island, New Zealand', *New Zeal. J. Geol. Geophys.*, vol. 53, no. 2–3, pp. 115–128, 2010, doi: 10.1080/00288306.2010.498405.

[36] T. I. Ojonimi, F. Asuke, M. A. Onimisi, and Y. Onuh, 'Acid Mine Drainage (AMD): an environmental concern generated by coal mining Acid', *J. Degrad. Min. Lands Manag.*, vol. 6, no. 4, pp. 1875–1881, 2019, doi: 10.15243/jdmlm.2019.064.1875.

[37] N. Belzile, Y.-W. Chen, M.-F. Cai, and Y. Li, 'A review on pyrrhotite oxidation', *J. Geochemical Explor.*, vol. 84, no. 2, pp. 65–76, Sep. 2004, doi: 10.1016/J.GEXPLO.2004.03.003.

[38] N. F. Gray, ‘Environmental impact and remediation of acid mine drainage: A management problem’, *Environ. Geol.*, 1997, doi: 10.1007/s002540050133.

[39] G. Street, ‘Impact of Temperature on the Rate of Formation of Sulfuric Acid in Mine Tailings’, vol. 32, no. 4, pp. 1155–1157, 2013, doi: 10.1002/ep.

[40] Y. Yunmei, Z. Yongxuan, A. E. Williams-jones, and G. Zhenmin, ‘A kinetic study of the oxidation of arsenopyrite in acidic solutions : implications for the environment’, vol. 19, pp. 435–444, 2004, doi: 10.1016/S0883-2927(03)00133-1.

[41] H. Anawar, ‘Impact of climate change on acid mine drainage generation and contaminant transport in water ecosystems of semi-arid and arid mining areas’, *Phys. Chem. Earth*, vol. 58–60, pp. 13–21, 2013, doi: 10.1016/j.pce.2013.04.002.

[42] C. L. Corkhill and D. J. Vaughan, ‘Applied Geochemistry Arsenopyrite oxidation – A review’, *Appl. Geochemistry*, vol. 24, no. 12, pp. 2342–2361, 2009, doi: 10.1016/j.apgeochem.2009.09.008.

[43] S. A. Waksman, ‘Microörganisms Concerned in the Oxidation of Sulfur in the Soil: IV. A Solid Medium for the Isolation and Cultivation of Thiobacillus thiooxidans.’, *J. Bacteriol.*, 1922.

[44] W. W. LEATHEN, S. A. BRALEY, and L. D. MCINTYRE, ‘The role of bacteria in the formation of acid from certain sulfuritic constituents associated with bituminous coal. II. Ferrous iron oxidizing bacteria.’, *Appl. Microbiol.*, 1953.

[45] J. F. Durand, J. Meeuvis, and M. Fourie, ‘The threat of mine effluent to the UNESCO status of the Cradle of Humankind World Heritage Site’, *J. Transdiscipl. Res. South. Africa*, vol. 6, no. 1, pp. 73–92, 2010, doi: 10.4102/td.v6i1.125.

[46] S. Naidoo, *Acid Mine Drainage in South Africa: Development Actors, Policy Impacts, and Broader Implications*. 2017.

[47] Havard Law School International Human Rights Clinic, *The Cost of Gold: Environmental, Health, and Human Rights Consequences of Gold Mining in South Africa’s West and Central Rand*. 2016.

[48] J. L. Gardea-Torresdey, J. R. Peralta-Videa, G. de la Rosa, and J. G. Parsons, ‘Phytoremediation of heavy metals and study of the metal coordination by X-ray

absorption spectroscopy', *Coord. Chem. Rev.*, vol. 249, no. 17–18, pp. 1797–1810, Sep. 2005, doi: 10.1016/J.CCR.2005.01.001.

[49] S. K. Sethy and S. Ghosh, 'Effect of heavy metals on germination of seeds.', *J. Nat. Sci. Biol. Med.*, vol. 4, no. 2, pp. 272–5, Jul. 2013, doi: 10.4103/0976-9668.116964.

[50] T. Medinski, 'SOIL CHEMICAL AND PHYSICAL PROPERTIES AND THEIR INFLUENCE ON THE PLANT SPECIES RICHNESS OF ARID SOUTH-WEST AFRICA', no. March, 2007.

[51] P. Singh and A. Nel, 'A comparison between *Daphnia pulex* and *Hydra vulgaris* as possible test organisms for agricultural run-off and acid mine drainage toxicity assessments', *Water SA*, vol. 43, no. 2, p. 323, 2017, doi: 10.4314/wsa.v43i2.15.

[52] J. Dabrowski, P. J. Oberholster, J. M. Dabrowski, J. Le Brasseur, and J. Gieskes, 'Chemical characteristics and limnology of Loskop Dam on the Olifants River (South Africa), in light of recent fish and crocodile mortalities', *Water SA*, vol. 39, no. 5, p. 675, 2013, doi: 10.4314/wsa.v39i5.12.

[53] J. Holman, 'Coal giant recognises water management responsibility', *Creamer Engineering News*, 2008. .

[54] P. J. Oberholster, J. G. Myburgh, P. J. Ashton, and A. M. Botha, 'Responses of phytoplankton upon exposure to a mixture of acid mine drainage and high levels of nutrient pollution in Lake Loskop, South Africa', *Ecotoxicol. Environ. Saf.*, 2010, doi: 10.1016/j.ecoenv.2009.08.011.

[55] F. Solomon, 'Impacts of metals on aquatic ecosystems and human health', 2008.

[56] R. Singh, N. Gautam, A. Mishra, and R. Gupta, 'Heavy metals and living systems: An overview', *Indian J. Pharmacol.*, vol. 43, no. 3, p. 246, 2011, doi: 10.4103/0253-7613.81505.

[57] M. Monachese, J. P. Burton, and G. Reid, 'Bioremediation and Tolerance of Humans to Heavy Metals through Microbial Processes: a Potential Role for Probiotics?', *Appl. Environ. Microbiol.*, vol. 78, no. 18, pp. 6397–6404, 2012, doi: 10.1128/aem.01665-12.

[58] W. E. Sharpe and R. S. Adams, 'HR502686 AR502687', 1998.

[59] J. F. Durand, 'The impact of gold mining on the Witwatersrand on the rivers and karst system of Gauteng and North West Province, South Africa', *J. African Earth Sci.*, vol. 68, pp. 24–43, 2012, doi: 10.1016/j.jafrearsci.2012.03.013.

[60] V. P. (Bill) Evangelou and Y. L. Zhang, 'A review: Pyrite oxidation mechanisms and acid mine drainage prevention', *Crit. Rev. Environ. Sci. Technol.*, vol. 25, no. 2, pp. 141–199, May 1995, doi: 10.1080/10643389509388477.

[61] B. G. Lottermoser, *Mine Wastes: Characterization, Treatment and Environmental Impacts*. Springer Berlin Heidelberg, 2010.

[62] M. Zhang and H. Wang, 'Utilization of Bactericide Technology for Pollution Control of Acidic Coal Mine Waste', *Adv. Eng. Res.*, vol. 129, no. Iceesd, pp. 667–670, 2017, doi: 10.2991/iceesd-17.2017.120.

[63] M. F. Cai, Z. Dang, Y. W. Chen, and N. Belzile, 'The passivation of pyrrhotite by surface coating', *Chemosphere*, vol. 61, no. 5, pp. 659–667, 2005, doi: 10.1016/j.chemosphere.2005.03.032.

[64] Y. W. Chen, Y. Li, M. F. Cai, N. Belzile, and Z. Dang, 'Preventing oxidation of iron sulfide minerals by polyethylene polyamines', *Miner. Eng.*, vol. 19, no. 1, pp. 19–27, 2006, doi: 10.1016/j.mineng.2005.04.007.

[65] P. Ačai, E. Sorrenti, T. Gorner, M. Polakovič, M. Kongolo, and P. de Donato, 'Pyrite passivation by humic acid investigated by inverse liquid chromatography', *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 337, no. 1–3, pp. 39–46, 2009, doi: 10.1016/j.colsurfa.2008.11.052.

[66] R. Pérez-López, J. Cama, J. M. Nieto, and C. Ayora, 'The iron-coating role on the oxidation kinetics of a pyritic sludge doped with fly ash', *Geochim. Cosmochim. Acta*, vol. 71, no. 8, pp. 1921–1934, 2007, doi: 10.1016/j.gca.2007.01.019.

[67] R. Fan *et al.*, 'The Formation of Silicate-Stabilized Passivating Layers on Pyrite for Reduced Acid Rock Drainage', *Environ. Sci. Technol.*, vol. 51, no. 19, pp. 11317–11325, 2017, doi: 10.1021/acs.est.7b03232.

[68] Z. Diao *et al.*, 'Silane-based coatings on the pyrite for remediation of acid mine drainage', *Water Res.*, vol. 47, no. 13, pp. 4391–4402, 2013, doi:

10.1016/j.watres.2013.05.006.

[69] Y. Ouyang *et al.*, ‘Pyrite oxidation inhibition by organosilane coatings for acid mine drainage control’, *Miner. Eng.*, vol. 72, pp. 57–64, 2015, doi: 10.1016/j.mineng.2014.12.020.

[70] J. Liu, L. Zhou, F. Dong, and K. A. Hudson-Edwards, ‘Enhancing As(V) adsorption and passivation using biologically formed nano-sized FeS coatings on limestone: Implications for acid mine drainage treatment and neutralization’, *Chemosphere*, vol. 168, pp. 529–538, 2017, doi: 10.1016/j.chemosphere.2016.11.037.

[71] I. Park, C. B. Tabelin, K. Seno, S. Jeon, M. Ito, and N. Hiroyoshi, ‘Simultaneous suppression of acid mine drainage formation and arsenic release by Carrier-microencapsulation using aluminum-catecholate complexes’, *Chemosphere*, vol. 205, pp. 414–425, 2018, doi: 10.1016/j.chemosphere.2018.04.088.

[72] I. Park, C. Baltazar, K. Magaribuchi, and K. Seno, ‘Suppression of the release of arsenic from arsenopyrite by carrier-microencapsulation using Ti-catechol complex’, *J. Hazard. Mater.*, vol. 344, pp. 322–332, 2018, doi: 10.1016/j.jhazmat.2017.10.025.

[73] X. Li, N. Hiroyoshi, C. B. Tabelin, K. Naruwa, C. Harada, and M. Ito, ‘Suppressive effects of ferric-catecholate complexes on pyrite oxidation’, *Chemosphere*, vol. 214, pp. 70–78, 2019, doi: 10.1016/j.chemosphere.2018.09.086.

[74] M. Mbonimpa, M. Aubertin, M. Aachib, and B. Bussière, ‘Diffusion and consumption of oxygen in unsaturated cover materials’, *Can. Geotech. J.*, vol. 40, no. 5, pp. 916–932, 2003, doi: 10.1139/t03-040.

[75] B. Bussière, M. Benzaazoua, M. Aubertin, and M. Mbonimpa, ‘A laboratory study of covers made of low-sulphide tailings to prevent acid mine drainage’, *Environ. Geol.*, vol. 45, no. 5, pp. 609–622, 2004, doi: 10.1007/s00254-003-0919-6.

[76] E. Mylona, A. Xenidis, and I. Paspaliaris, ‘Inhibition of acid generation from sulphidic wastes by the addition of small amounts of limestone’, *Miner. Eng.*, vol. 13, no. 10, pp. 1161–1175, 2000, doi: 10.1016/S0892-6875(00)00099-6.

[77] S. Miller, Y. Rusdinar, R. Smart, J. Andrina, and D. Richards, ‘Design and

Construction of Limestone Blended Waste Rock Dumps - Lessons Learned From a 10-Year Study At Grasberg', vol. 2006, no. 2, pp. 1287–1301, 2006, doi: 10.21000/jasmr06021287.

[78] C. B. Tabelin *et al.*, 'Arsenic, selenium, boron, lead, cadmium, copper, and zinc in naturally contaminated rocks: A review of their sources, modes of enrichment, mechanisms of release, and mitigation strategies', *Sci. Total Environ.*, vol. 645, pp. 1522–1553, 2018, doi: 10.1016/j.scitotenv.2018.07.103.

[79] J. Skousen *et al.*, 'Review of Passive Systems for Acid Mine Drainage Treatment', *Mine Water Environ.*, vol. 36, no. 1, pp. 133–153, Mar. 2017, doi: 10.1007/s10230-016-0417-1.

[80] J. G. Skousen, P. F. Ziemkiewicz, and L. M. McDonald, 'Acid mine drainage formation, control and treatment: Approaches and strategies', *Extr. Ind. Soc.*, vol. 6, no. 1, pp. 241–249, 2019, doi: 10.1016/j.exis.2018.09.008.

[81] J. Taylor, S. Pape, and N. Murphy, 'A Summary of Passive and Active Treatment Technologies for Acid and Metalliferous Drainage (AMD)', *Proc. 5th Aust. Work. Acid Drain.*, no. 29, pp. 1–49, 2005.

[82] B. Gazea, K. Adam, and A. Kontopoulos, 'A review of passive systems for the treatment of acid mine drainage', *Miner. Eng.*, vol. 9, no. 1, pp. 23–42, Jan. 1996, doi: 10.1016/0892-6875(95)00129-8.

[83] P. L. Younger, S. A. Banwart, and R. S. Hedin, 'Mine Water Hydrology', *Mine Water*. Springer Netherlands, pp. 127–270, 2002, doi: 10.1007/978-94-010-0610-1_3.

[84] C. Zipper and J. Skousen, 'Passive Treatment of Acid Mine Drainage', *Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils*. John Wiley & Sons, Inc., pp. 339–353, 2014, doi: 10.1002/9781118749197.ch30.

[85] J. J. Schoeman and A. Steyn, 'Investigation into alternative water treatment technologies for the treatment of underground mine water discharged by Grootvlei Proprietary Mines Ltd into the Blesbokspruit in South Africa', *Desalination*, vol. 133, no. 1, pp. 13–30, 2001, doi: 10.1016/s0011-9164(01)00079-0.

[86] C. Wolkersdorfer and R. Bowell, ‘Contemporary Reviews of Mine Water Studies in Europe, Part 1’, *Mine Water Environ.*, vol. 23, no. 4, pp. 162–182, 2004, doi: 10.1007/s10230-004-0060-0.

[87] D. . Everett, J. Du Plesis, and H. W. Gussman, ‘THE TREATMENT OF UNDERGROUND MINE WATERS FOR THE REMOVAL OF CALCIUM AND SULPHATES BY A GYP-CIX PROCESS ABSTRACT’, in *International Mine Water Association Symposium 1993*, 1993, no. 1, p. 29.

[88] D. Howard, C. Grobler, R. E. G. Robinson, and P. M. Cole, ‘SUSTAINABLE PURIFICATION OF MINE WATER USING ION EXCHANGE TECHNOLOGY’, no. October, pp. 447–453, 2009.

[89] Ö. Yavuz, Y. Altunkaynak, and F. Güzel, ‘Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite’, *Water Res.*, vol. 37, no. 4, pp. 948–952, 2003, doi: 10.1016/s0043-1354(02)00409-8.

[90] F. Rouquerol, J. Rouquerol, K. S. W. Sing, G. Maurin, and P. Llewellyn, ‘Introduction’, *Adsorption by Powders and Porous Solids*. Elsevier, pp. 1–24, 2014, doi: 10.1016/b978-0-08-097035-6.00001-2.

[91] T. Motsi, N. A. Rowson, and M. J. H. Simmons, ‘Adsorption of heavy metals from acid mine drainage by natural zeolite’, *Int. J. Miner. Process.*, vol. 92, no. 1–2, pp. 42–48, Jul. 2009, doi: 10.1016/J.MINPRO.2009.02.005.

[92] C. A. Cravotta III and C. S. Kirby, ‘ACIDITY AND ALKALINITY IN MINE DRAINAGE: PRACTICAL CONSIDERATIONS’, *J. Am. Soc. Min. Reclam.*, vol. 2004, no. 1, pp. 334–365, 2004, doi: 10.21000/jasmr04010334.

[93] T. Ramontja *et al.*, ‘Mine Water Management in the Witwatersrand Gold Fields With Special Emphasis on Acid Mine Drainage’, Jan. 2011.

[94] D. B. Johnson, ‘Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines’, *Water, Air, Soil Pollut. Focus*, vol. 3, no. 1, pp. 47–66, 2003, doi: 10.1023/A:1022107520836.

[95] V. R. K. Vadapalli, J. N. Zvimba, M. Mathye, H. Fischer, and L. Bologo, ‘Acid mine drainage neutralization in a pilot sequencing batch reactor using limestone from a

paper and pulp industry', *Environ. Technol. (United Kingdom)*, vol. 36, no. 19, pp. 2515–2523, 2015, doi: 10.1080/09593330.2015.1036786.

[96] G. Madzivire, L. F. Petrik, W. M. Gitari, G. Balfour, V. R. K. Vadapalli, and T. V Ojumu, 'Role of Ph on Sulphate Removal From Circumneutral Mine Water Using Coal Fly Ash', in *International Mine Water Conference*, 2009, no. 19-23 October, pp. 462–471.

[97] S. S. Potgieter-Vermaak, J. H. Potgieter, P. Monama, and R. Van Grieken, 'Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage', *Miner. Eng.*, vol. 19, no. 5, pp. 454–462, 2006, doi: 10.1016/j.mineng.2005.07.009.

[98] D. G. McDonald and A. F. Grandt, 'Limestone-Lime Treatment of Acid Mine Drainage- Full Scale', 1981. doi: EPA-600/S7-81-033.

[99] J. P. Maree, M. de Beer, W. F. Strydom, A. D. M. Christie, and F. B. Waanders, 'Neutralizing Coal Mine Effluent with Limestone to Decrease Metals and Sulphate Concentrations', *Mine Water Environ.*, vol. 23, no. 2, pp. 81–86, 2004, doi: 10.1007/s10230-004-0043-1.

[100] A. J. Geldenhuys, J. P. Maree, M. De Beer, and P. Hlabela, 'An integrated limestone / lime process for partial sulphate removal', no. May 2002, pp. 345–354, 2003.

[101] R. C. Wilmoth, 'Combination limestone-lime neutralization of ferrous iron acid mine drainage', US Environmental Protection Agency, Cincinnati, Ohio, 1978.

[102] V. Masindi, W. M. Gitari, H. Tutu, M. De Beer, and N. Nekhwevha, 'Neutralization and Attenuation of Metal Species in Acid Mine Drainage and Mine Leachates Using Magnesite: a Batch Experimental Approach', *An Interdiscip. Response to Mine Water Challenges*, 2014.

[103] J. P. Maree, M. Mujuru, V. Bologo, N. Daniels, and D. Mpholoane, 'Neutralisation treatment of AMD at affordable cost', *Water SA*, vol. 39, no. 2, 2013, doi: 10.4314/wsa.v39i2.7.

[104] V. R. K. Vadapalli, J. N. Zvimba, M. Mathye, H. Fischer, and L. Bologo, 'Acid mine drainage neutralization in a pilot sequencing batch reactor using limestone from a

paper and pulp industry', *Environ. Technol.*, vol. 36, no. 19, pp. 2515–2523, 2015, doi: 10.1080/09593330.2015.1036786.

[105] M. W. Gitari, L. F. Petrik, O. Etchebers, D. L. Key, E. Iwuoha, and C. Okujeni, 'Treatment of Acid Mine Drainage with Fly Ash: Removal of Major Contaminants and Trace Elements', *J. Environ. Sci. Heal. Part A*, vol. 41, no. 8, pp. 1729–1747, 2006, doi: 10.1080/10934520600754425.

[106] Kumar V.R. Vadapalli *et al.*, 'Neutralization of acid mine drainage using fly ash, and strength development of the resulting solid residues', *S. Afr. J. Sci.*, vol. 104, no. 7–8, pp. 317–322, 2008.

[107] L. F. Petrik, R. A. White, M. J. Klink, S. Vernon, C. L. Burgers, and M. V Fey, 'Utilization of South African Fly Ash to Treat Acid Coal Mine Drainage , and Production of High Quality Zeolites from the Residual Solids', vol. 2, 2003.

[108] R. Pérez-López, D. Quispe, J. Castillo, and J. M. Nieto, 'Acid neutralization by dissolution of alkaline paper mill wastes and implications for treatment of sulfide-mine drainage', *Am. Mineral.*, vol. 96, no. 5–6, pp. 781–791, 2011, doi: 10.2138/am.2011.3685.

[109] T. Motsi, N. A. Rowson, and M. J. H. Simmons, 'Adsorption of heavy metals from acid mine drainage by natural zeolite', *Int. J. Miner. Process.*, vol. 92, no. 1–2, pp. 42–48, 2009, doi: 10.1016/j.minpro.2009.02.005.

[110] X. Querol *et al.*, 'Synthesis of zeolites from coal fly ash: an overview', *Int. J. Coal Geol.*, vol. 50, no. 1–4, pp. 413–423, 2002, doi: 10.1016/s0166-5162(02)00124-6.

[111] M. De Beer, J. P. Maree, J. Wilsenach, S. Motaung, L. Bologo, and V. Radebe, 'Acid Mine Water Reclamation using the ABC Process', 2010.

[112] V. Bologo, J. P. Maree, and F. Carlsson, 'Application of magnesium hydroxide and barium hydroxide for the removal of metals and sulphate from mine water', *Water SA*, vol. 38, no. 1, 2012, doi: 10.4314/wsa.v38i1.4.

[113] J. P. Smit, 'THE TREATMENT OF POLLUTED MINE', in *International Mine Water Association 1999*, 1999, pp. 467–471.

[114] A. Neba, 'THE RHODES BioSURE PROCESS AND THE USE OF SUSTAINABILITY

INDICATORS IN THE DEVELOPMENT OF BIOLOGICAL MINE WATER TREATMENT', 2006.

[115] Aveng, 'Aveng Water Blueprint for Treatment of AMD', 2009. http://www.avengwater.co.za/news-room/press-releases/emalahleni-blueprint-treatment-amd. (accessed May 15, 2017).

[116] C. J. M. Macdonald, 'Water usage in the South African pulp and paper industry', 2004.

[117] PAMSA, 'Industry Progress Report: Paper in Perspective', Johannesburg, 2016.

[118] PAMSA, 'South African Pulp and Paper Industry: Annual summary 2019 statistics', Johannesburg, 2019.

[119] Safiri, 'Eastern Cape Freight Databank-Forestry', *Eastern Cape Freight Databank-Forestry*, 2011. https://www.safiri.co.za/ec/forestry.html (accessed May 01, 2018).

[120] F. M. Martins, J. M. Martins, L. C. Ferracin, and C. J. da Cunha, 'Mineral phases of green liquor dregs, slaker grits, lime mud and wood ash of a Kraft pulp and paper mill', *J. Hazard. Mater.*, vol. 147, no. 1–2, pp. 610–617, 2007, doi: 10.1016/j.jhazmat.2007.01.057.

[121] M. J. Quina and C. T. Pinheiro, 'Inorganic waste generated in kraft pulp mills: The transition from landfill to industrial applications', *Appl. Sci.*, vol. 10, no. 7, 2020, doi: 10.3390/app10072317.

[122] M. Naqvi, J. Yan, and E. Dahlquist, 'Black liquor gasification integrated in pulp and paper mills: A critical review', *Bioresour. Technol.*, vol. 101, no. 21, pp. 8001–8015, 2010, doi: 10.1016/j.biortech.2010.05.013.

[123] M. Cardoso, É. D. de Oliveira, and M. L. Passos, 'Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills', *Fuel*, vol. 88, no. 4, pp. 756–763, 2009, doi: 10.1016/j.fuel.2008.10.016.

[124] Y. Sewsynker-sukai, A. Naomi, and E. B. G. Kana, 'Recent developments in the application of Kraft pulping alkaline chemicals for lignocellulosic pretreatment:

potential beneficiation of green liquor dregs waste', *Bioresour. Technol.*, no. March, p. 123225, 2020, doi: 10.1016/j.biortech.2020.123225.

[125] K. Manskinen, H. Nurmesniemi, and R. Pöykiö, 'Total and extractable non-process elements in green liquor dregs from the chemical recovery circuit of a semi-chemical pulp mill', *Chem. Eng. J.*, vol. 166, no. 3, pp. 954–961, 2011, doi: 10.1016/j.cej.2010.11.082.

[126] D. Sanchez and H. Tran, 'Treatment of lime slaker grit and green liquor dregs - Current practice', in *2005 TAPPI Engineering, Pulping, Environmental Conference - Conference Proceedings*, 2005, p. 9.

[127] P. (Pratima) Bajpai, *Environmentally friendly production of pulp and paper*. Wiley, 2013.

[128] A. Shrinath and B. Chris, 'A review of issues related to green liquor quality, and approaches towards improved clarification', in *Pulp and Paper International Congress*, pp. 1–10.

[129] M. Golmaei, T. Kinnarinen, E. Jernström, and A. Häkkinen, 'Study on the filtration characteristics of green liquor dregs', *Chem. Eng. J.*, vol. 317, pp. 471–480, 2017, doi: 10.1016/j.cej.2017.02.104.

[130] I. Moodley, C. M. Sheridan, U. Kappelmeyer, and A. Akcil, 'Environmentally sustainable acid mine drainage remediation: Research developments with a focus on waste/by-products', *Miner. Eng.*, vol. 126, no. August 2017, pp. 207–220, 2018, doi: 10.1016/j.mineng.2017.08.008.

[131] Komline-Sanderson, 'Rotary Drum Vacuum Filter | Komline-Sanderson'. http://www.komline.com/products/rotary-drum-vacuum-filter/ (accessed Jul. 18, 2019).

[132] M. C. Monte, E. Fuente, A. Blanco, and C. Negro, 'Waste management from pulp and paper production in the European Union', *Waste Manag.*, vol. 29, no. 1, pp. 293–308, Jan. 2009, doi: 10.1016/J.WASMAN.2008.02.002.

[133] K. Taylor and B. Mcguffie, 'Investigation of non-process element chemistry at Elk Falls mill - Green liquor clarifier and lime cycle', *Pulp Pap. Canada*, vol. 108, no. 2,

pp. 27–32, 2007.

[134] R. Pöykö, H. Nurmesniemi, T. Kuokkanen, and P. Perämäki, ‘Green liquor dregs as an alternative neutralizing agent at a pulp mill’, *Environ. Chem. Lett.*, vol. 4, no. 1, pp. 37–40, 2006, doi: 10.1007/s10311-005-0031-0.

[135] L. Sartz, ‘Alkaline by-products as amendments for remediation of historic mine sites’, 2010.

[136] M. Mäkitalo, J. Mácsik, C. Maurice, and B. Öhlander, ‘Improving Properties of Sealing Layers Made of Till by Adding Green Liquor Dregs to Reduce Oxidation of Sulfidic Mine Waste’, *Geotech. Geol. Eng.*, vol. 33, no. 4, pp. 1047–1054, 2015, doi: 10.1007/s10706-015-9886-4.

[137] I. Martínez-Lage *et al.*, ‘Concretes and mortars with waste paper industry: Biomass ash and dregs’, *J. Environ. Manage.*, vol. 181, pp. 863–873, Oct. 2016, doi: 10.1016/j.jenvman.2016.06.052.

[138] R. M. Novais, J. Carvalheiras, L. Senff, and J. A. A. Labrincha, ‘Upcycling unexplored dregs and biomass fly ash from the paper and pulp industry in the production of eco-friendly geopolymer mortars: A preliminary assessment’, *Constr. Build. Mater.*, vol. 184, pp. 464–472, Sep. 2018, doi: 10.1016/j.conbuildmat.2018.07.017.

[139] T. Kinnarinen, M. Golmaei, E. Jernström, and A. Häkkinen, ‘Separation, treatment and utilization of inorganic residues of chemical pulp mills’, *J. Clean. Prod.*, vol. 133, pp. 953–964, 2016, doi: 10.1016/j.jclepro.2016.06.024.

[140] Y. Jia, C. Maurice, and B. Öhlander, ‘Effect of the alkaline industrial residues fly ash, green liquor dregs, and lime mud on mine tailings oxidation when used as covering material’, *Environ. Earth Sci.*, vol. 72, no. 2, pp. 319–334, Jul. 2014, doi: 10.1007/s12665-013-2953-3.

[141] A. H. Österås, I. Sunnerdahl, and M. Greger, ‘The impact of wood ash and green liquor dregs application on Ca, Cu, Zn and Cd contents in bark and wood of Norway spruce’, *Water. Air. Soil Pollut.*, vol. 166, no. 1–4, pp. 17–29, 2005, doi: 10.1007/s11270-005-7747-0.

[142] R. Modolo, A. Benta, V. M. Ferreira, and L. M. Machado, ‘Pulp and paper plant

wastes valorisation in bituminous mixes', *Waste Manag.*, vol. 30, no. 4, pp. 685–696, 2010, doi: 10.1016/j.wasman.2009.11.005.

[143] Y. Jia, C. Maurice, and B. Öhlander, 'Mobility of as, Cu, Cr, and Zn from tailings covered with sealing materials using alkaline industrial residues: a comparison between two leaching methods', *Environ. Sci. Pollut. Res.*, 2016, doi: 10.1007/s11356-015-5300-2.

[144] L. Alakangas, E. Andersson, and S. Mueller, 'Neutralization/prevention of acid rock drainage using mixtures of alkaline by-products and sulfidic mine wastes', *Environ. Sci. Pollut. Res.*, 2013, doi: 10.1007/s11356-013-1838-z.

[145] C. Maurice, L. Villain, and K. Hargelius, 'Green liquor dregs for the remediation of abandoned mine tailings – opportunities and limitations', *8th Int. Conf. Acid Rock Drain.*, pp. 1–6, 2009.

[146] Y. Jia, D. Stenman, M. Mäkitalo, C. Maurice, and B. Öhlander, 'Use of Amended Tailings as Mine Waste Cover', *Waste and Biomass Valorization*, vol. 4, no. 4, pp. 709–718, 2013, doi: 10.1007/s12649-013-9232-0.

[147] Y. Jia, C. Maurice, and B. Öhlander, 'Metal Mobilization in Tailings Covered with Alkaline Residue Products: Results from a Leaching Test Using Fly Ash, Green Liquor Dregs, and Lime MudMobilisierung von Metallen in Abraumhalden die mit alkalischen Rückständen abgedeckt wurden: Ergebnisse von ', *Mine Water Environ.*, vol. 34, no. 3, pp. 270–287, 2015, doi: 10.1007/s10230-014-0317-1.

[148] S. Sirén, C. Maurice, L. A.-12th I. M. Water, and U. 2016, 'Green liquor dregs in mine waste remediation, from laboratory investigations to field application', 2016.

[149] R. Pérez-López, J. Castillo, D. Quispe, and J. M. Nieto, 'Neutralization of acid mine drainage using the final product from CO2 emissions capture with alkaline paper mill waste', *J. Hazard. Mater.*, vol. 177, no. 1–3, pp. 762–772, 2010, doi: 10.1016/j.jhazmat.2009.12.097.

[150] N. T. (Nigel T. . Faithfull, *Methods in agricultural chemical analysis : a practical handbook*. Cabi Pub, 2002.

[151] F. Cabral, H. M. Ribeiro, L. Hilário, L. Machado, and E. Vasconcelos, 'Use of pulp mill inorganic wastes as alternative liming materials', *Bioresour. Technol.*, vol. 99, no. 17, pp. 8294–8298, 2008, doi: 10.1016/j.biortech.2008.03.001.

[152] R. Pöykiö, H. Nurmesniemi, T. Kuokkanen, and P. Perämäki, 'Green liquor dregs as an alternative neutralizing agent at a pulp mill', *Environ. Chem. Lett.*, vol. 4, no. 1, pp. 37–40, 2006, doi: 10.1007/s10311-005-0031-0.

[153] R. Pöykiö, H. Nurmesniemi, T. Kuokkanen, and P. Perämäki, 'The use of a sequential leaching procedure for assessing the heavy metal leachability in lime waste from the lime kiln at a caustizicing process of a pulp mill', *Chemosphere*, vol. 65, no. 11, pp. 2122–2129, 2006, doi: 10.1016/j.chemosphere.2006.06.018.

[154] T. Zakir, 'Evaluation and Control of Pirssonite Scale Formation in Green Liquor Systems of the Kraft Process', University of Toronto, 2011.

[155] T. Zakir, H. Tran, and V. G. Papangelakis, 'Formed in the Kraft Mill Green Liquor', vol. 12, no. 1, pp. 53–59, 2013.

[156] U. Y. Stambulska, M. M. Bayliak, and V. I. Lushchak, 'Chromium(VI) toxicity in legume plants: Modulation effects of rhizobial symbiosis', *Biomed Res. Int.*, vol. 2018, no. Table 1, 2018, doi: 10.1155/2018/8031213.

[157] R. Jobby, P. Jha, A. K. Yadav, and N. Desai, 'Biosorption and biotransformation of hexavalent chromium [Cr(VI)]: A comprehensive review', *Chemosphere*, vol. 207, pp. 255–266, 2018, doi: 10.1016/j.chemosphere.2018.05.050.

[158] F. MARTINS, J. MARTINS, L. FERRACIN, and C. DACUNHA, 'Mineral phases of green liquor dregs, slaker grits, lime mud and wood ash of a Kraft pulp and paper mill', *J. Hazard. Mater.*, vol. 147, no. 1–2, pp. 610–617, 2007, doi: 10.1016/j.jhazmat.2007.01.057.

[159] M. Chaplin, 'Ice III (ice-three)', *Water structure and science*, 2011. http://www1.lsbu.ac.uk/water/ice_iii.html (accessed Jan. 13, 2017).

[160] F. Bouchelaghem, 'A numerical and analytical study on calcite dissolution and gypsum precipitation', *Appl. Math. Model.*, vol. 34, no. 2, pp. 467–480, 2010, doi: 10.1016/j.apm.2009.06.004.

[161] A. N. Zaitsev, J. Keller, J. Spratt, E. N. Perova, and A. Kearsley, ‘Nyerereite-pirssonite-calcite-shortite relationships in altered natrocarbonatites, Oldoinyo Lengai, Tanzania’, *Can. Mineral.*, vol. 46, no. 4, pp. 843–860, 2008, doi: 10.3749/canmin.46.4.843.

[162] D. Feng, C. Aldrich, and H. Tan, ‘Treatment of acid mine water by use of heavy metal precipitation and ion exchange’, *Miner. Eng.*, vol. 13, no. 6, pp. 623–642, Jun. 2000, doi: 10.1016/S0892-6875(00)00045-5.

[163] CSIR, ‘Characterising the risk of human exposure and health impacts from acid mine drainage in South Africa’, no. March, pp. 1–183, 2013.

[164] J. P. Maree, G. J. Van Tonder, A. M. Van Niekerk, and C. Naidoo, ‘The collection , treatment and utilization of water accumulated in the coal mines located in the Upper Olifants River catchment’, no. March 2000. COALTECH 2020, 2000.

[165] P. J. Oberholster, P. H. Cheng, A. M. Botha, and B. Genthe, ‘The potential of selected macroalgal species for treatment of AMD at different pH rangesin temperate regions’, *Water Res.*, vol. 60, no. 21, pp. 82–92, 2014, doi: 10.1016/j.watres.2014.04.031.

[166] P. J. Oberholster, P. H. Cheng, A. M. Botha, P. Hobbs, and L. Hill, ‘Assessment of selected macroalgae for use in a biological hybrid system for treating sulphur in acid mine drainage (AMD)’, *J. Appl. Phycol.*, vol. 30, no. 2, pp. 1361–1370, 2018, doi: 10.1007/s10811-017-1314-0.

[167] P. J. Oberholster, P.-H. Cheng, A.-M. Botha, and B. Genthe, ‘The potential of selected macroalgal species for treatment of AMD at different pH ranges in temperate regions’, *Water Res.*, vol. 60, pp. 82–92, 2014, doi: 10.1016/j.watres.2014.04.031.

[168] G. Walser, ‘Economic impact of world mining’, *Uranium Prod. Cycle Environ.*, vol. 2, p. 86, 2000.

[169] V. Masindi, M. S. Osman, and R. Shingwenyana, ‘Valorization of acid mine drainage (AMD): A simplified approach to reclaim drinking water and synthesize valuable minerals-Pilot study’, *J. Environ. Chem. Eng.*, vol. 7, no. 3, p. 103082, 2019, doi: 10.1016/j.jece.2019.103082.

[170] G. S. Simate and S. Ndlovu, 'Acid mine drainage: Challenges and opportunities', *J. Environ. Chem. Eng.*, vol. 2, no. 3, pp. 1785–1803, 2014, doi: 10.1016/j.jece.2014.07.021.

[171] J. Skousen, A. Rose, G. Geidel, J. Foreman, R. Evans, and W. A. Hellier, 'Handbook of technologies for avoidance and remediation of acid mine drainage national mine land reclamation center', *West Virginia Univ. Morgat. WV*, vol. 132, 1998.

[172] S. E. Pratt, 'All that glitters...Acid Mine Drainage: The Toxic Legacy of Gold Mining in South Africa', *Earth*, vol. 56, no. 10, p. 30, 2011.

[173] R. Johnston, 'Arsenic and the 2030 Agenda for Sustainable Development', pp. 12–14, 2016, doi: 10.1201/b20466-7.

[174] A. C. Żołnowski, W. Sądej, M. S. Suski, A. Wyrwas, and D. Skrocki, 'Impact of Paper Mill Waste on Physicochemical Properties of Soil, Crop Yield, and Chemical Composition of Plants', *Clean - Soil, Air, Water*, vol. 1900080, pp. 1–8, 2019, doi: 10.1002/clen.201900080.

[175] M. S. Thopil, R. C. Bansal, L. Zhang, and G. Sharma, 'A review of grid connected distributed generation using renewable energy sources in South Africa', *Energy Strateg. Rev.*, vol. 21, no. August 2017, pp. 88–97, 2018, doi: 10.1016/j.esr.2018.05.001.

[176] V. Masindi, E. Chatzisymeon, I. Kortidis, and S. Foteinis, 'Assessing the sustainability of acid mine drainage (AMD) treatment in South Africa', *Sci. Total Environ.*, vol. 635, pp. 793–802, 2018, doi: 10.1016/j.scitotenv.2018.04.108.

[177] V. Masindi, M. S. Osman, R. N. Mbhele, and R. Rikhotso, 'Fate of pollutants post treatment of acid mine drainage with basic oxygen furnace slag: Validation of experimental results with a geochemical model', *J. Clean. Prod.*, vol. 172, pp. 2899–2909, Jan. 2018, doi: 10.1016/J.JCLEPRO.2017.11.124.

[178] S. Motaung *et al.*, 'Recovery of Drinking Water and By-products from Gold Mine Effluents', *Int. J. Water Resour. Dev.*, vol. 24, no. 3, pp. 433–450, Sep. 2008, doi: 10.1080/07900620802150475.

[179] G. M. Ochieng, E. S. Seanego, and O. I. Nkwonta, 'Impacts of mining on water

resources in South Africa: A review', *Scientific Research and Essays*. 2010.

[180] D. B. Johnson and K. B. Hallberg, 'Acid mine drainage remediation options: a review', *Sci. Total Environ.*, vol. 338, no. 1–2, pp. 3–14, 2005, doi: 10.1016/j.scitotenv.2004.09.002.

[181] R. Perez-Lopez, D. Quispe, J. Castillo, and J. M. Nieto, 'Acid neutralization by dissolution of alkaline paper mill wastes and implications for treatment of sulfide-mine drainage', *Am. Mineral.*, vol. 96, no. 5–6, pp. 781–791, 2011, doi: 10.2138/am.2011.3685.

[182] Y. Jia, C. Maurice, and B. Öhlander, 'Metal Mobilization in Tailings Covered with Alkaline Residue Products: Results from a Leaching Test Using Fly Ash, Green Liquor Dregs, and Lime Mud', *Mine Water Environ.*, vol. 34, no. 3, pp. 270–287, Sep. 2015, doi: 10.1007/s10230-014-0317-1.

[183] K. Manskinen, *Utilisation aspects of ashes and green liquor dregs from an integrated semichemical pulp and board mill*, no. June 2013. 2013.

APPENDIX A:

PEER-REVIEWED ARTICLES THAT EMANATED FROM THIS THESIS

Paper #1

Published in the Journal of Cleaner production

ARTICLE IN PRESS

Journal of Cleaner Production xxx (xxxx) xxx

Contents lists available at ScienceDirect

Journal of Cleaner Production

journal homepage: www.elsevier.com/locate/jclepro

Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa

Keolebogile R. Sebogodi [a, b, *], Jonas K. Johakimu [a], B. Bruce Sithole [a, b]

[a] *Biorefinery Industry Development Facility, Chemicals Cluster, Council for Scientific and Industrial Research, 359 King George Ave, Durban, 4001, South Africa*
[b] *Discipline of Chemical Engineering, University of KwaZulu-Natal, Howard College Campus, Durban, 4001, South Africa*

ARTICLE INFO

Article history:
Received 29 January 2019
Received in revised form
17 October 2019
Accepted 19 October 2019
Available online xxx

Handling editor: Cecilia Maria Villas Bôas de Almeida

Keywords:
Acid mine drainage
Green liquor dregs
Active acid mine drainage treatment
Landfills
Industrial wastes

ABSTRACT

Acid mine Drainage (AMD) is a low pH, sulphate and heavy metal rich leachate that is produced from oxidation of sulphide bearing minerals commonly found in the host rocks of some mineral ores. The pH augmentation, and sulphate and metal removal in AMD is often achieved by adding alkaline reagents in it. $CaCO_3$ and/or its derivatives are commonly used for this purpose due to their abundance and affordability as compared to other neutralizing reagents. The problems associated with the use of this naturally occurring reagent do not only include the emission of greenhouse gases and ecological disturbances but also include a disastrous implication of depleting their reserves. To avoid these predicaments, green liquor dregs (GLD) from two Kraft pulp manufactures in South Africa were used as alternative alkaline reagents to neutralize AMD originating from Witwatersrand goldfields in Johannesburg. These GLD samples were referred to as GLD A and B. $CaCO_3$ was used as a reference material. The GLD samples had neutralizing values that are comparable to that of $CaCO_3$. Thus, $CaCO_3$, GLD A, and GLD B had a neutralizing value of, 26.0, 21.2, and 21.0% CaO respectively. Different dosages 1, 2, 6, 10, and 20 g/L of these neutralizing reagents were used to neutralize the AMD. Results of this study showed that raising the pH of AMD was possible even at a low dosages of 1 g/L. At this dosage, the acidity of the AMD sample changed from 183.36 to 21.7, 36.4, and 48.72 mg/L $CaCO_3$, and changed the pH from 5.6 to 8.84, 8.21, and 8.0 respectively. However, the SO_4^{2-} and Ec had increased from 2093 to 2360, 2538, and 2407 mg/L and from 3.6 to 4.0, 4.3, 4.2 mS/cm respectively, indicating that caution should be taken to keep these values low by keeping the reagent dosage low and being cognizant of the carbonate mineral present in GLD. The x-ray diffraction patterns of the reacted samples confirmed the presence of metal oxides and Ca and Mg compounds that were depicted by SEM/EDX micrographs. In conclusion, the results from this study showed that the pH of AMD can be raised to optimum pH process value and reduce the acidity at a low dosage, a competitive advantage over commercial $CaCO_3$. The proposed concept can be adopted by both the mining and pulp and paper industries, for the upscaling of co-disposing GLD and AMD contaminants as an eco-friendly alternative for the $CaCO_3$.

1. Introduction

South Africa is one of the countries that are rich in mineral ores and has been reported to be among the major producers of gold and coal(Masindi et al., 2014; Masindi et al., 2017). However, gold and coal mine waste rocks and tailings have been characterized to have high concentrations of sulphide (S^{2-}) bearing minerals, such as pyrite (FeS_2). Unfortunately, this mineral gets oxidized when exposed to water, oxygen, and/or acidophile micro-organisms, resulting in the production of acid mine drainage (McCarthy, 2011; Kefeni et al., 2017; Masindi et al., 2018). This oxidation process could be better explained by Eqns. (1)–(4) below. Basically, the first equation depicts the FeS_2 dissociation and/or oxidation in the presence of oxygen and water. This reaction produces sulphate

---

* Corresponding author. Biorefinery Industry Development Facility, Chemicals Cluster, Council for Scientific and industrial Research, 359 King George Ave, Durban, 4001, South Africa.
E-mail address: sebogodirevelation@gmail.com (K.R. Sebogodi).

https://doi.org/10.1016/j.jclepro.2019.118979

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

(SO_4^{2-}) and acid, H^+. Under the acidic conditions created in Eqn. (1), together with excess oxygen and possibly microbial activity, the Fe^{2+} gets oxidized further into Fe^{3+} as shown in Eqn. (2). Near alkaline environment-from the surrounding alkaline soils, ($pH \geq 3.5$) may be formed as a result of H^+ ion consumption in Eqn. (2), and this environment makes it possible for the formation of ferric oxide-hydroxide ($Fe(OH)_3$) through a precipitation process in Eqn. (3). However, if the near alkalinity was not sufficient to precipitate all the Fe^{3+} ions, then this cation will further facilitate the oxidation of FeS_2 to produce more H^+ and SO_4^{2} as presented in Eqn. (4) (Kefeni et al., 2017).

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

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

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

$$FeS_2 + 15/2O_2 + 7/2\,H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \qquad 4$$

Johannesburg, the epicenter of the economic growth in South Africa, is one of the cities that grew exponentially during the gold rush years. Today, this town, which receives an average of only 750 mm of summer rainfalls, is estimated to be a home of between 4.4 and 4.9 residents (Naicker et al., 2003). Unfortunately, the demand of water, not only for domestic purpose but for industrial use, has also increased. This demand could be compromised because the little water that the city receives from annual rainfall is subject to contamination by the 3444 mega liters of the AMD that is produced daily from the Witwatersrand Goldfields (Motaung et al., 2008). The tragedy that comes along with such contamination may include the ceasing of all the activities associated with a contaminated water body and the endangerment of the ecosystems which are dependent on such streams are bound to suffer (Johnson and Hallberg, 2005; Motaung et al., 2008; Ochieng et al., 2010; Ramontja et al., 2011). For example, the AMD contaminated water cannot be used for; (i) agricultural activities due to low pH and heavy metals in it. This is because most plants may not be able to survive in acidic conditions, and if the plants may in any case survive the low pH, metals laden in them (through absorption) may end up either killing them or being distributed in the food chain (Oberholster et al., 2014); (ii) industrial activities may also suffer-corrosion of machinery and scale formation may result from the use of this water; (iii) tourism and educational centers such as the caves which are primarily made of the carbonate rocks may be dissolved by this acidic water and hence result in the formation of sinkhole (Durand et al., 2010); (iv) people may have diseases such as cancer when exposed to AMD and AMD contaminated food (Solomon, 2009).

The predicaments of the above-mentioned examples may impact negatively on the economy of the town and/or the country because without potable water, people will go out to places where there is water, job opportunities will be lost, there will be no food security, and the money that was accumulated through tourism and educational centers such as the Cradle of Humankind, will be lost. Therefore, to minimize the impact of AMD on the economy of the country, this water needs to be treated and then be released for the beneficiation of all the dependent activities and people.

Over the past few decades, scientists across the world have been focusing on developing the AMD treatment technologies. These technologies have been classified as either biotic or abiotic depending on the feedstock that is used to aid the treatment process. These are further categorized into passive and active treatment technologies. The passive technologies have been hauled for their minimal cost because they require less maintenance, material loading, and generally less labor once they have been erected. On the other hand, the active technologies are commended for their versatility, ability to treat enormous quantities of AMD, time efficiency, and the small surface area that they occupy (Johnson and Hallberg, 2005; Akcil and Koldas, 2006; Kefeni et al., 2017).

In addition, different mechanisms such as chelation, adsorption, oxidation-reduction (redox), and pH control processes are said to be the driving forces behind these technologies (Taylor et al., 2005). Detailed description of how these mechanisms work has been intensively covered on several papers including (Chartrand and Bunce, 2003; Falayi and Ntuli, 2014; Feng et al., 2000; Herrera, 2007; Matlock et al., 2002; Moodley, 2018; Motsi et al., 2009; Neculita and Rosa, 2019; Simate, 2016; Simate and Ndlovu, 2014; Skousen, 2017; Taylor et al., 2005; Zagury et al., 2006; Zhong, 2007). In most cases, these mechanisms work independently of one another for effective treatment. For example, the pH value of AMD determines the species and concentration present in it. That is, low pH AMD would lead to higher concentrations of most metals (depending also on the geochemical environment surrounding the AMD source) but a slight increase in pH would alter the metal load quantities. For example, Fe^{2+} hydrolyses into Fe^{3+} at low pH levels and the slight increase in pH values would precipitate the Fe^{3+} ions that were formed. Thus, such instances take advantage of the redox and pH control systems (Taylor et al., 2005; Kefeni et al., 2017; Skousen et al., 2017).

Additionally, some treatment mechanisms are highly dependent on the interaction between the AMD, pH and the material used for treatment. Such instances have been observed when mechanisms such as adsorption are used. For example Iakovleva et al. (2015) showed that the use of modified limestone as an adsorbent in AMD treatment did not only encourage adsorption but also precipitation, co-precipitation, and complexation must have encouraged the overall outcome of the treatment process. However, the modified limestones in this study were reported to have removed ions more effectively than their unmodified counterpartsdue to their improved surface area structure. Similarly, Barrera et al. (2017) reported that although the adsorbents could be of the same origin and be modified using the same ion of varying source, the outcome may not be the same. Thus, in their study, nanostructured calcium silicate hydrate (nanoCSH) was modified using Fe^{3+} from $FeCl_3$ and $FeOH_3$ highlighted that the $FeCl_3$ modified nano-CSH had a more stable structure than that of $FeOH_3$ modified nano-CSH. This would mean that the more stable structure would adsorb metal toxins and forming insoluble salts.

Although adsorption has been renowned to be the most economically and effective mechanism of treating AMD (Iakovleva et al., 2015; Barrera et al., 2017), pH control by addition of primary alkaline reagents such as lime (CaO), limestone ($CaCO_3$), hydrated lime ($Ca(OH)_2$), sodium hydroxide (NaOH), and ammonia (NH_3), is still widely used across the globe (Taylor et al., 2005; Skousen, 2014). $CaCO_3$ and/or its derivatives has been widely exploited in AMD treatment processes because of its abundance and low cost as compared to other AMD neutralizing reagents. Although the use of these carbonate materials may have been adequate in AMD treatment and/or prevention, researchers have now highlighted the need to preserve these resources by developing and exploring either other ecofriendly methods of AMD treatment or alternative and sustainable materials that could be used in place of $CaCO_3$ (Vadapalli et al., 2015).

On the other hand, pulp and paper industry has been playing a major role towards the economy of South Africa since its first establishment in the 1920s (Association of pulp paper and board manufacturers of South Africa, 1960; Macdonald, 2004). The Pulp and Paper Manufacturers Association (PAMSA) reported that this industry had contributed –R28 billion towards the South African

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

economy in 2015. This translates to 0.5% towards the country's manufacturing gross domestic product (PAMSA, 2016). Out of the four virgin pulping techniques viz; mechanical, semi-mechanical, chemical, thermo-chemical, and chemi-mechanical pulping techniques, Kraft pulping method, which is one of the chemical pulping techniques, has been regarded as the most widely used technique. This is due to its versatility to process both the hard and soft wood species, and to the superior properties of the pulp and/or paper that it produces as compared to other pulping methods (Johakimu et al., 2011; Alén, 2018).

Generally, the Kraft, also known as the sulphate pulping method produces cellulose pulp by employing a mixture of sodium hydroxide, NaOH, and sodium sulphide, Na_2S, known as the cooking/white liquor, to de-lignify the debarked wood chips. After cooking, the pulp and the liquor, now referred to as weak black liquor, are separated. The pulp would then be washed with water, and the resulting leachate, together with the weak black liquor are combined and sent into the chemical recovery chamber (Biermann, 1996; Bajpai, 2018).

In the chemical recovery chamber, the weak liquor which consist of ~15% solids, is first evaporated in multiple effect evaporators to increase its solid content to ≥65–75%. Due to high solid content, this liquor is then called concentrated black liquor. The concentrated black liquor will then be sent into a furnace where the organic content in it, mainly lignin, will be burnt to produce energy. Under this immense heat environment, sodium carbonate (Na_2CO_3) and Na_2S are formed. Burning these solids produces a smelt (Biermann, 1996; Bajpai, 2018).

The smelt from the furnace is then sent into a dissolving tank where it will be diluted with the weak white liquor (from the previous cycle) to produce green liquor. This liquor will be led into the clarifying tank to allow the non-process elements to settle down and then be removed from the liquor as green liquor dregs (GLD), see Fig. 1 below. These wastes are then disposed of in landfills. After this, the clarified green liquor would be sent into the causticizing chamber to produce NaOH which together with the Na_2S that is already in the liquor would form the white/cooking liquor which would then be used in the next pulping cycle (Biermann, 1996; Bajpai, 2018).

Fig. 1. Picture of fresh GLD sample.

GLDs are known as the non-process elements (NPEs) that come from different sources such as the wood itself, the impurities of the white liquor, and the metals that might come out from the walls of reaction/process tanks. These elements may include iron (Fe), copper (Cu), silicon (Si), sodium (Na), and calcium (Ca). The Ca and Na present in these wastes have been identified to be present in the form of $CaCO_3$ and Na_2CO_3. Their presence makes GLD to have an alkaline property with the pH value of ~10–12 (Sanchez and Tran, 2005; Pöykö et al., 2006; Cabral et al., 2008; Tran and Vakkilainnen, 2008; Manskinen et al., 2011; Mäkitalo et al., 2014).

Furthermore, GLD has been reported to be the major inorganic wastes that the Kraft mills produce. In South Africa, four of this type of mills are found located in four different provinces. Two of these mills are the largest and have been estimated to produce ~100 000 tons of GLD per annum. Disposing these wastes in landfills without any option of reusing is challenging because these wastes will continue to increase year in year out and there are costs involved in both disposing and maintaining the landfills, possible purchase of more landfills as the other ones get exhausted, and tax penalties.

In a pursuit to overcome these challenges, researchers together with the pulp and paper industry are constantly seeking for possible solutions towards either minimizing waste production and/or valorizing the ones that they cannot avoid producing. Thus, scientists around the world have been characterizing GLD to build its database and explore their possible use in various industries. These include using them in building and construction (Modolo et al., 2010), agricultural fertilizer (Österås et al., 2005), soil rehabilitation (Mäkelä et al., 2012), prevention of AMD formation (Jia, Maurice and Öhlander, 2014a, 2014b; Mäkitalo et al., 2014), and in acidic waste water treatment (Pöykö et al., 2006; Pérez-López et al., 2011). The basis of these exploitation was based on the calcite that is present in GLD.

On treating the acidic waste effluents from the Kraft pulp mill, Pöykö et al. (2006) endorsed the potential of using GLD as an alternative for $CaCO_3$. This is due to the GLD's high pH (~10) and $CaCO_3$ comparable liming effect of 39,6% Ca equivalent- $CaCO_3$'s liming effect was 38% Ca equivalent. Although they have endorsed the potential of using GLD as an economic and environmentally sustainably alternative for neutralizing these effluents, they had also reported the leeching of some of the NPEs into the effluents, albeit, at lower concentrations. Similarly, Pérez-López et al. (2011) had also reported and endorsed the use of GLD as the neutralizing reagent of choice. In their study, two AMD of different identities were neutralized using GLD. The GLD sample that was used had the net neutralizing potential of 830 kg H_2SO_4. This sample was able to raise the pH of these AMD samples from 3.6 to 2.61 to 6.60 and 6.01 respectively. The various metals in the AMD were reported to have reduced up to 100% after neutralization by GLD.

Though the studies indicate that the GLD could be used to treat AMD, it is well known that their nature and character may vary from one mill to another as shown in Table 1, and probably from one shift to another, hence implying that there could never be one solution for handling all GLD. Thus, caution need to be taken when using GLD, especially when it comes to the NPE load in them. Additionally, more alkalizing Kraft mill wastes such as lime mud could have been chosen for this study, but its annual production quantities are lower than that of GLD, meaning that its supply may be limited especially when considering the copious amounts of AMD that is produced daily in the Western Basin. Moreover, there is only one publication that addresses the use of GLD in AMD treatment, and according to the knowledge of this study's authors, none of the South African GLDs have been characterized and explored for this purpose. Therefore, based on the universal alkalinity property that GLD possesses, this study seeks to characterize and explore the feasibility of using GLD produced from the South African Kraft mills

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

Table 1
Differences in the character of GLD.

Parameter	References		
	Pöykö et al. (2006)	Cabral et al. (2008)	Mäkelä et al. (2016)
	Concentration(ppm)		
P	10	0,90–2,10	0,2
Ca	84500	118,2-347	0,175
Na	26100	29,8–144,4	0,0198
K	1700	0,90–6,60	1,4
Mg	29700	21,0–51,1	0,0959
S	10600	N/A	0,0312
Cu	110	2,60–5,40	0,33
Zn	1200	0,0488–0,258	6,49
Fe	4500	2,60–5,40	8,01
Mn	10300	1,6–7,8	0,0351
Cd	10	0,00407–0,00612	0,011
Cr	300	0,0474–0,0689	0,16
Ni	200	0,119–0,254	0,08
Al	N/A	0,3–4,10	0,0255
Pb	N/A	0,0311–0,0624	0,052
pH	10	12,1–12,3	N/A

in neutralizing AMD. The success of this study would help in establishing an eco-friendly way of co/disposing GLD with the toxic metals that emanates from the AMD.

2. Materials and methods

2.1. Materials

2.1.1. Chemicals

37% Hydrochloric (HCl) acid and sodium hydroxide (NaOH) used in this study were supplied by Sigma-Aldrich (Merck).

2.1.2. Samples

The GLD samples used in this study were acquired from two major South African Kraft pulp mills and were labelled GLD A and GLD B. These samples were collected from the green liquor processing plant at the dregs filter points. $CaCO_3$ which was purchased from Kulu Carbonates (Durban, South Africa) was used as a reference material in this study.

The AMD sample was collected at 18 Winze decant point of the Western basin in Randfontein, Johannesburg. Sampling was done during summer rainfall season in January 2016. The sample was collected in an airtight high-density polyethylene (HDPE) container which was pre-rinsed three times with AMD. The sample was then transported to the laboratory where it was kept at 4°C until analysis.

2.2. Methods

A vast range of instrumentation was used to characterize both the solid and liquid samples. The particle size of raw solids was determined by first sieving them through a 75 μm mesh and then they were further analyzed using a Shimadzu SALD-3101 (Wing-SALD II: version 3:4) flow cell. The surface morphology of the samples was studied using the ZEISS Field Emission Gun- Scanning Electron Microscope which was coupled with Oxford Energy Dispersive X-ray probe. The mineralogical and chemical composition of solid samples were obtained by X-ray diffraction analysis (XRD) and, X-ray fluorescence (XRF) and ICP-AES/ICP-MS respectively. The XRD analysis was performed with Panalytical Empyrean diffractometer using a Cobalt radiation generated at 40 mA and 40 kV. The scanning range was measured from 3-9°. A PANalytical Axios Wavelength Dispersive spectrometer which was fitted with a Rh tube was used for XRF analysis while Thermo ICap inductively coupled plasma atomic electron spectroscopy/Agilent 7900 inductively coupled plasma-mass spectroscopy was used for ICP-AES/ICP-MS analysis. A Malvern Panalytical X'Pert Highscore plus software (Almelo (the Netherlands), and Malvern (United Kingdom) was used to determine the XRD mineral phases and their relative weight percentages using the Rietveld method. The neutralizing value was determined using a titration method described by Faithfull (2002). The equation used in the determination of neutralizing value was:

$$\text{Neutralizing value} = [Y \times (0{,}01402/X)] \times 100\%\ CaO \qquad 5$$

Where:

Y is the sample mass in grams(g)
X is the titre volume in millilitre (ml)

The pH and electrical conductivity (Ec) measured in milliSiemens per cm (mS/cm), were measured using Hanna HI 98195 multiparameter. SO_4^{2-} was measured using turbidimetry. The pH, Ec, and ICP-AES/ICP-MS results were used to estimate the acidity level of the AMD. This was done by using both manual calculations-as per Eqn. (6) and the AMDTREAT version 5.02 + PHREEQC version 3.0 software-these software packages are used to estimate the cost of treating AMD, and to perform different aqueous geochemical

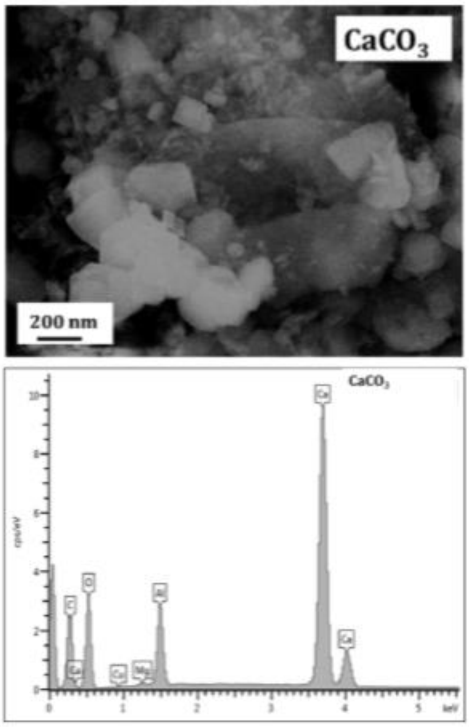

Fig. 2. SEM micrograph and EDX spectra of $CaCO_3$.

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

calculations respectively.

$$\text{Acidity (mg/L CaCO}_3) = 50\,(10^{(3-\text{pH})} + 2(C_{Fe}/55.8) + 2(C_{Mn}/54.9) + 3(C_{Al}/27.0)) \quad 6$$

Where C is the concentration of a specific metal in mg/L.

2.3. *AMD neutralization experiments*

1000 mL of AMD were charged into beakers and were conditioned by stirring at 250 rpm for 10 min using overhead stirrers prior to the neutralization process. Different dosages, 1.0, 2.0, 6.0,10 and 20 g/L, of neutralizing reagents were added into the AMD. After this, the AMD samples were stirred at 250 rpm for 6 h. During this time, both the Ec and pH of the solutions were measured at 30 min' intervals. At the end of the process, the treated samples were filtered and stored in a refrigerator at 4 °C until analysis. The sludge was dried in an oven at 105 °C until a constant mass was obtained and then stored in an airtight glass sample holder until analysis.

3. Results and discussions

3.1. *Characterization of raw neutralizing reagents*

3.1.1. *Particle size distribution and surface morphology*

GLD samples came in a form of a paste. These were first dried to remove the surface water and they were ground using a rod mill. The results from the particle size analyzer indicated that their median particle size(d_{50}) were 13.880, 19.597 and 17.528 for $CaCO_3$, GLD A, and GLD B, respectively. These results suggested that $CaCO_3$ had higher reaction surface which would be advantageous in facilitating an efficient reaction as compared to GLD A and B. However, GLD B may facilitate a better reaction than GLD A because it has higher fines (Vadapalli et al., 2015).

Figs. 2–4 show the SEM micrographs and the EDX spectra of the raw samples. The presence of the rhombohedral structures on the micrographs indicate that the samples were composed of calcite (Pöykö et al., 2006; Taylor and Mcguffie, 2007; Cabral et al., 2008; Tran and Vakkilainnen, 2008; Pérez-López et al., 2011; Mäkitalo et al., 2014). Orthorhombic structures were also visible on the micrograph of GLD A. This suggested the presence of another form of carbonate group which could possibly be pirssonite ($Na_2Ca(CO_3)_2.2H_2O$) (Zakir, 2011; Zakir et al., 2013). Other elements which could not be specified into mineral phases, were detected by the EDX. These included elements such as Cu, Fe, Mn, K, Cl, S, Si, Al, and Mg.

3.1.2. *Chemical properties*

The pH of GLD A and B were 13.4 and 12.5 respectively and the neutralizing value for $CaCO_3$, GLD A and GLD B were 26.0, 21.2, and 21.0% CaO. The high pH values could be mainly due to calcite. While

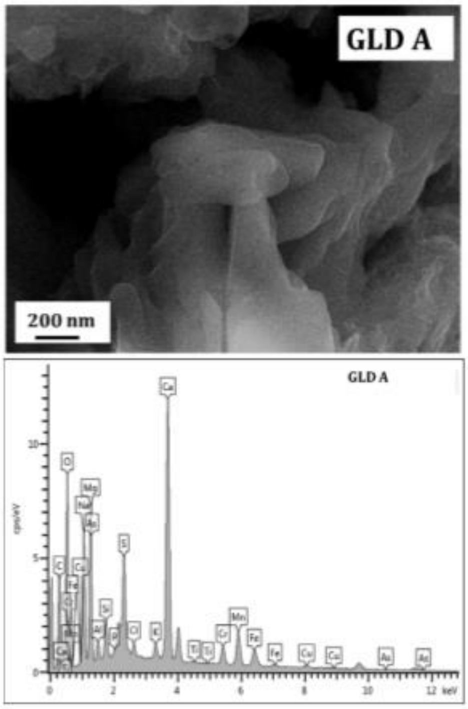

Fig. 3. SEM micrograph and EDX spectra GLD A.

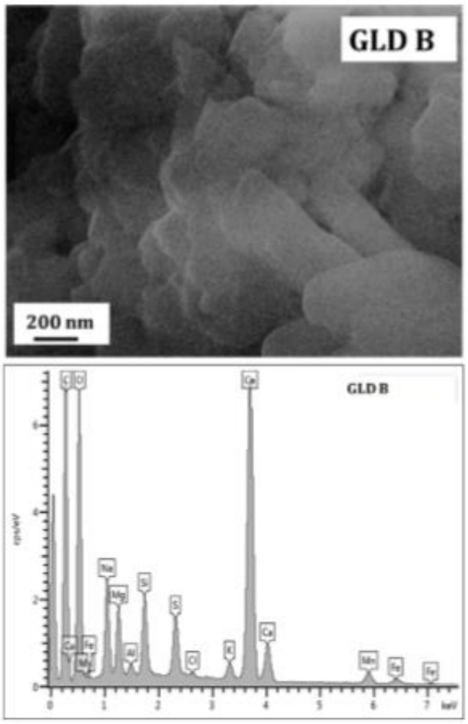

Fig. 4. SEM micrograph and EDX spectra GLD B.

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

this is true, it should be noted that GLD A had visible grains of NaOH. On the other hand, the neutralizing values of all the neutralizing reagents used in this study is lower than what is available in the literature. That is, (Manskinen et al., 2011 and Pöykö et al., 2006) reported the neutralizing values of 38.0 %Ca for $CaCO_3$ and 34.2 and 39.6 %Ca for GLD samples respectively.

The chemical composition of these neutralizing reagents, shown in Table 2, indicate that some metals such as Cu, Zn, Ba and Pb were present at trace concentrations in GLD samples. Hence their concentrations suggest that the respective metals may not pose any hazardous impacts towards the environment (Mäkitalo et al., 2014). Cr was rather detected at very high concentrations. These, depending on the oxidation state, may cause adverse effects on plants, animals, and humans. The adverse effects on humans and animals may include cancer, ulcers, and kidney dysfunction. Physiological and biochemical processes in plants may also be affected negatively (Jobby et al., 2018; Stambulska et al., 2018). The results also show that the concentration of Ca decreases from $CaCO_3$ through GLD B to GLD A, while the Na content decreases in the order of the exact opposite trend. The high concentration of Na, which is equivalent to the Ca in GLD A suggested the presence of $Na_2Ca(CO_3)_2.2H_2O$ (Zakir, 2011; Zakir et al., 2013). Na could have also been from the NaOH crystals. These results agree with the SEM results.

Furthermore, the abundant total concentration of elements within the samples was analyzed with XRF. Similarly, to ICP, this instrument determines the total element concentration within the samples. Table 3 shows different elements in terms of oxides. From this table, it is evident that $CaCO_3$ and GLD B had high amounts of Ca content whereas high amounts of both the Ca and Na were present in GLD A data. This equal amounts of Ca and Na are clear indication that the sample is composed mainly of pirrsonite, confirming the results of SEM and ICP-AES/ICP-MS (Taylor and Mcguffie, 2007; Zakir, 2011; Zakir et al., 2013).

3.1.3. *Mineralogical properties*

XRD was used to estimate the quantities of each element in each neutralizing solid. An X'Pert Highscore plus software identified

Table 2
The chemical composition of Neutralizing and sludge samples thereof as determined by ICP-AES/ICP-MS (mg/L).

Element	Accuracy (%)	$CaCO_3$	GLD A	GLD B	$CaCO_3$ (1 g/L)	GLD A (1 g/L)	GLD B (1 g/L)
Li	99.7	2.24	3.40	2.39	7.46	5,42	1,39
Be	98.3	0.18	0.18	0.47	<0.2	0,31	<0.2
B	95.4	9.74	67.64	55.01	25.64	48,45	36,40
Ti	–	100.29	187.42	135.22	66.29	230,97	104,53
V	98.9	4.45	3.23	2.34	2.74	3,76	1,51
Cr	99.2	10.73	5564.99	255.03	11.39	6269,09	214,00
Co	98.9	0.88	11.32	13.63	36,05	63,41	35,63
Ni	97.7	4.68	82.59	37.73	45,30	150,59	53,94
Cu	93.7	30.25	156.94	161.75	126,61	246,07	164,85
Zn	99.9	11.11	308.80	259.27	29,03	369,57	194,29
As	95.4	0.81	0.54	2.25	261,30	402,01	285,09
Se	96.9	0.57	2.99	1.35	0,08	0,58	0,09
Mo	98.8	0.38	1.17	0.72	1,37	2,92	1,47
Cd	97.3	0.02	0.39	0.18	0,03	0,47	0,13
Ba	98.1	10.65	668.62	438.86	58,91	812,69	392,95
Hg	97.4	0.03	0.02	0.04	0,06	0,08	0,04
Pb	96.7	2.72	12.38	11.73	3,82	19,05	12,43
Al	96.0	92380.32	3759.43	2266.22	77676,43	5149,72	2100,32
Ca	97.0	268600.88	101030.03	198049.76	197852,46	187656,40	251152,37
Fe	97.5	870.48	4648.97	3528.13	73570,18	113941,61	84317,42
K	96.9	259.71	5431.67	5419.11	123,17	173,26	255,85
Mg	95.5	3354.04	36928.39	16381.13	10813,11	42186,59	12889,90
Mn	97.3	13.37	7762.37	9547.72	11763,95	34930,84	10873,63
Na	99.8	306.58	153011.4	71143.63	508,83	3095,06	3246,01
P	98.7	153.16	1251.82	760.96	126,65	1770,85	741,22
S	96.7	2688.18	34488.36	18271.63	18970,84	9393,13	36399,09
Si	96.5	2517.37	6321.21	6247.69	6586,41	5099,52	6464,34
Sr	96.1	943.74	639.08	520.48	683,88	443,19	438,37

Table 3
The XRF analysis of the neutralizing reagents and resultant sludge.

Oxide Wt %	$CaCO_3$	GLD A	GLD B	$CaCO_3$ (1 g/L)		GLD A (1 g/L)	GLD B (1 g/L)
Al_2O_3	19.99	0.98	0.57	12,90	0,90		0,42
CaO	42.42	14.61	31.24	27,12	26,16		35,35
Cr_2O_3	–	0.72	0.04	0,00	0,83		0,03
FeO_3	0.13	0.66	0.57	8,87	12,26		8,74
K_2O	0.02	0.61	0.63	0,01	0,04		0,03
MgO	0.56	6.13	3.02	1,92	6,31		2,35
MnO	0.50	0.99	1.34	1,71	4,22		1,40
Na_2O	0.02	14.38	7.28	0,03	0,23		0,14
P_2O_5	0.04	0.29	0.26	0,03	0,38		0,20
SiO_2	0.81	1.18	2.97	1,61	2,32		2,87
TiO_2	0.03	0.04	0.04	0,01	0,03		0,05
Loi %	35.07	33.10	39.37	29,64	36,39		34,37
Sum of concentration	99.09	73.70	87.37	83,86	90,06		85,95

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

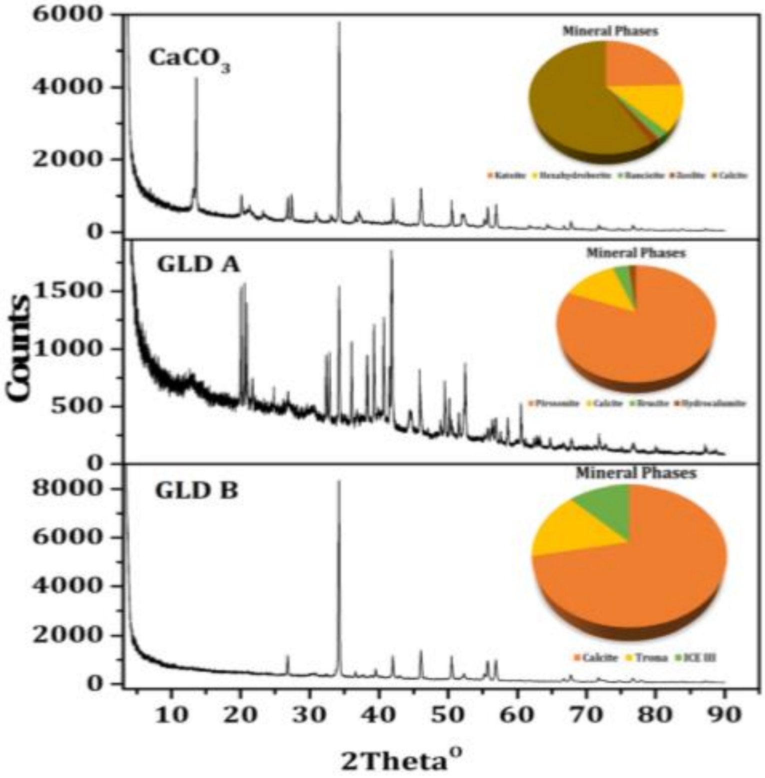

Fig. 5. XRD patterns and mineral mass percentages of raw neutralizing reagents.

mineral phases and calculated their relative percentages within each reagent. The XRD diffracto-grams of the $CaCO_3$ and GLD B are too similar as shown in Fig. 5. These graphs show that the samples are mainly composed of calcite, 58.30 and 75.4% respectively. However, $CaCO_3$ also constituted about 25% of gypsum which has a peak around 10 and 20 2 Theta^{0} (Hammarstrom et al., 2003). GLD B also constituted trona ($Na_2CO_3.NaHCO_3.2H_2O$) which is another form of the carbonate mineral. The samples also exhibited other minerals which are found in the pie chart insert in Fig. 5.

GLD A exhibited a diffracto-gram which was different from those of the other samples. This sample's mineralogical data indicated that the sample had higher concentration of minerals than its counterpart. Unlike $CaCO_3$ and GLD B, XRD pattern of GLD A showed that the huge percentage of Ca in the sample was not calcite but rather $Na_2Ca(CO_3)_2.2H_2O$.

Both the trona and $Na_2Ca(CO_3)_2.2H_2O$ minerals that were found in the GLD samples might have been formed during the "upset time". This is the time when the raw green liquor was supersaturated with total titratable alkali (TTA) and when the liquor had low temperatures (Zakir et al., 2013). It is also possible that trona might have originated from the soda ash which is sometimes used as a makeup chemical. However, the presence of Ice III assures us that the majority of trona that is present in the sample could have been caused by a rapid drop in temperature (from −1000 to 25 °C) (Chaplin, 2011).

On the other hand, $Na_2Ca(CO_3)_2.2H_2O$ formation might have also followed a direct reaction between Na_2CO_3 in the green liquor and the suspended $CaCO_3$ that came with the weak liquor or (b) the Ca^{2+} ions that became available in the liquor after the dissolution of $CaCO_3$, may react with the CO_3^{2-} and Na^{+} present in the medium (Zakir, 2011).

3.2. *Neutralization of AMD*

Naturally, carbonates dissolve in AMD, however, they dissolve at different rates depending on the carbonate type and the pH of the AMD. The interaction of these carbonates and AMD would lead to the dissociation of the carbonate material, as shown in Eqn. (7) below, and increment of pH would dramatically alter the character and composition of the AMD.

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

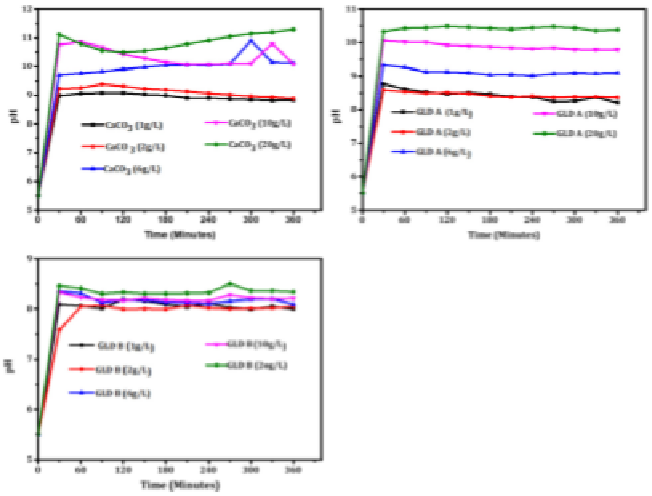

Fig. 6. Effect of neutralizing reagent dosage on pH as measured over time.

$$CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + CO_2 + H_2O \qquad 7$$

Similarly, the initial character of AMD used in this study changed after treatment different neutralizing reagents. Prior to alkalizing reagent dosage, the AMD had a pH of 5.6, Ec of 3.6 mS/cm, SO_4^{2-} of 2093 mg/L, and an acidity of 183 mg/L. Figs. 5 and 6 show that the pH and Ec of the AMD samples changed dramatically after the addition of the neutralizing reagents. This change could be attributed to the dissociation of the calcitic mineral found in both the $CaCO_3$ and GLD samples. However, the nature of Ca^{2+} sources of these neutralization reagents may have followed different mechanisms as described next:

$CaCO_3$: this reagent may have followed Eqn. (7), however, the XRD results show that this reagent also contained $CaSO_4.2H_2O$ in its matrix. Thus, Eqn. (8) may be used to better explain the neutralization mechanism. The preference associated with dissolution of $CaSO_4.2H_2O$ rather than $CaCO_3$, is that the later dissolves better in more acidic media than the former which can easily dissolve even in alkaline environment (Bouchelaghem, 2010).

$$CaCO_3 + CaSO_4 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + CaCO_3 + H_2O \qquad 8$$

GLD A: this neutralizing reagent's main Ca source was $Na_2Ca(CO_3)_2.2H_2O$ and small amounts of $CaCO_3$. Equally to $CaSO_4.2H_2O$, this mineral dissolves readily in neutral medium (Zaitsev et al., 2008). Thus, the $CaCO_3$ in it may have not undergone dissolution as described in Eqn. (9) below

$$CaCO_3 + Na_2Ca(CO_3)_2.2H_2O + H_2SO_4 \rightarrow$$
$$Ca^{2+} + SO_4^{2-} + Na^+ + CaCO_3 + H_2O \qquad 9$$

GLD B: of the three reagents used in the neutralization of AMD in this study, GLD B raised the pH value of AMD to values between 8 and 8.5 only. This is because this GLD had a sufficient $Na_2CO_3.NaHCO_3.2H_2O$ mineral to effectively raise the leachate pH and either wholly or partially impede the dissolution of $CaCO_3$ present in the reagent. The small quantities of Na_2CO_3-$NaHCO_3.2H_2O$ in GLD B in comparison to other Ca^{2+} sources in $CaCO_3$ and GLD A samples could be the reason why the pH of AMD never reached high levels despite the increase in dosages of the reagents. Consequently, Eqn. (10) below may be used to describe the neutralization process. Fig. 7

$$Na_2CO_3.NaHCO_3.2H_2O + CaCO_3 + H_2SO_4 \rightarrow$$
$$CO_3^- + SO_4^{2-} + Na^+ + CaCa_3 + H_2O \qquad 10$$

The ion activities presented by different cations such as Ca^{2+}, Na^+, Mg^{2+} and anions which include SO_4^{2-}, CO_3^{2-}, HCO_3^- play major roles in the neutralization. In this study, Ec was increased with increase in dosage. This is contrary to what other researchers have reported (Potgieter-Vermaak et al., 2006; Pérez-López et al., 2011). However, a different trend was observed on the AMD samples treated with 10 and 20 g/L of $CaCO_3$, whereby the Ec decreased. This decrease could be attributed to the precipitation of SO_4^{2-} in the form of $CaSO_4.H_2O$. This precipitation was only observed on these two samples because the $CaCO_3$ sample that was used contained $CaSO_4$ (which acted as a seed for precipitation) in its mineralogical make up and the pH values of the AMD were ≥10 (Madzivire et al., 2009). Although the pH of the 6 g/L $CaCO_3$ treated sample was high pH of 10, its Ec did not decrease and this could be due to insufficient gypsum seed to catalyze its precipitation in the medium and thus it remained meta-stable in the solution (Feng et al., 2000; Pérez-López et al., 2011).

Based on the scope of this study, which is to neutralize the AMD, the pH results showed that dosing the sample with 1 g/L of GLD was able to raise the pH to values above the neutral value. Thus, only these samples together with their corresponding $CaCO_3$ treated sample were analyzed.

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

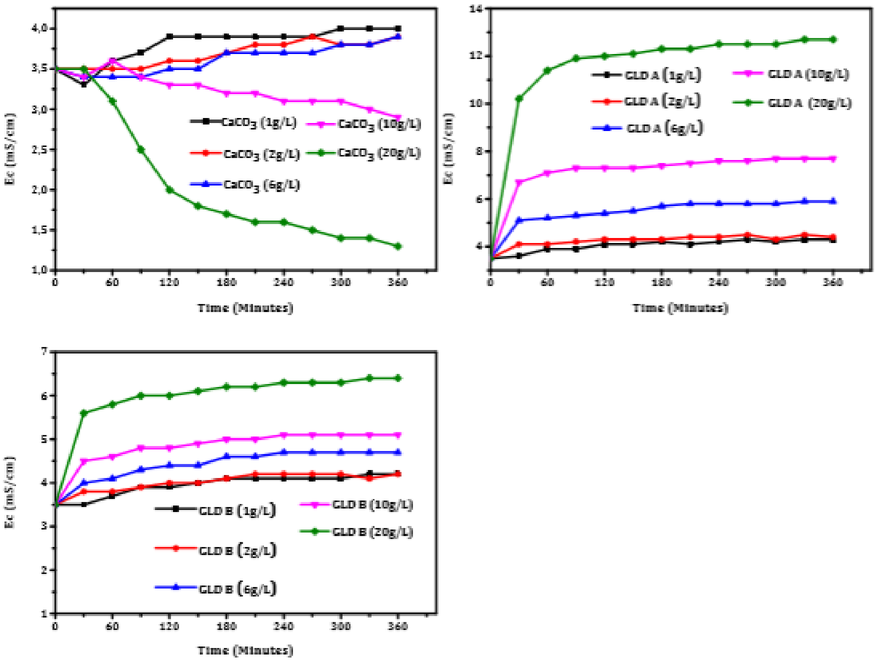

Fig. 7. Effect of neutralizing reagent dosage on Ec as measured over time.

Addition of alkalizing reagents on AMD does not only impart alkalinity into the sample but it also reduces its elemental load. For example, Table 4 shows that the concentration of three main critical elements that drive the AMD formation were reduced after the neutralization process. Thus, Fe concentrations were reduced by 99% for all samples, Mn by 66, 81, and 13%, while Al was reduced with −2.0, 76, and 96% for $CaCO_3$ (1 g/L), GLD A (1 g/L), and GLD B (1 g/L) respectively. The dissolution of carbonate minerals is confirmed the increment of Ca, Na, and Mg in the treated AMD. This reduction in metal concentration was due to precipitation of the metal constituents of AMD as hydroxides.

The overall outcome of this neutralization process is that acidity of the AMD dropped from 183 to 21.7, 36.4, and 48.72 mg/L $CaCO_3$, and changed the pH from 5.6 to 8.84, 8.21, and 8.0 respectively for $CaCO_3$, GLD A and GLD B treated samples. However, SO_4^{2-} and Ec had increased from 2093 to 2360, 2538, and 2407 mg/L and from 3.6 to 4.0, 4.3, 4.2 mS/cm respectively. These changes could be attributed to the, origin of the reagent and different carbonate mineral phases and their quantities thereof, that the samples were composed of. That is, GLD samples may have increased the SO_4^{2-} in the samples because they originate from a Na_2S driven process, while the presence and dissolution of gypsum in the $CaCO_3$ sample are the reason behind SO_4^{2-} increment in the $CaCO_3$ (1 g/L) treated sample. Additionally, the carbonate minerals other than calcite itself were responsible for the pH augmentation because of their ability to dissolve readily as compared to calcite which preferably dissolves in acidic medium. The quantities of these minerals were the ones that determined the overall attained pH values. That is,

Table 4
The chemical composition of the raw and optimum neutralized AMD samples.

Element	Accuracy (%)	AMD	$CaCO_3$ (1 g/L)	GLD A (1 g/L)	GLD B (1 g/L)
Li	99.7	0,08	0,05614	0,06324	0,06431
Be	98.3	0,00	0,00100	0,00100	0,00100
B	95.4	0,83	0,26442	0,24892	0,40104
Ti	-	0,04	0,00009	0,00010	0,00004
V	98.9	0,03	0,00011	0,00007	0,00006
Cr	99.2	0,06	0,00093	0,00233	0,00062
Co	98.9	0,07	0,04327	0,04382	0,06179
Ni	97.7	0,05	0,00057	0,01160	0,02993
Cu	93.7	4,01	0,00057	0,00547	0,00429
Zn	99.9	0,12	0,00042	0,01166	0,02252
As	95.4	0,20	0,00156	0,00164	0,00193
Se	96.9	0,02	0,00021	0,00026	0,00021
Mo	98.8	0,01	0,00010	0,00034	0,00022
Cd	97.3	0,00	0,00005	0,00019	0,00015
Ba	98.1	0,04	0,02506	0,03102	0,04906
Hg	97.4	0,001	<0.00005	<0.00005	<0.00005
Pb	96.7	0,01	<0.00001	0,00001	0,00014
Al	96.0	0,72	0,73138	0,17016	0,03037
Ca	97.0	578,41	595,400	491,600	531,700
Fe	97.5	68,94	0,00260	0,00133	0,00325
K	96.9	28,64	24,0100	22,8700	21,76000
Mg	95.5	135,85	138,30	145,60	146,10
Mn	97.3	30,65	9,681	5,986	26,74
Na	99.8	146,90	151,50	284,7	184,30
P	98.7	<0,02	<0.00005	<0.00005	<0.00005
Si	96.5	7,96	0,3881	4,17100	5,60600
Sr	96.1	0,51	0,7318	0,9174	0,55857

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

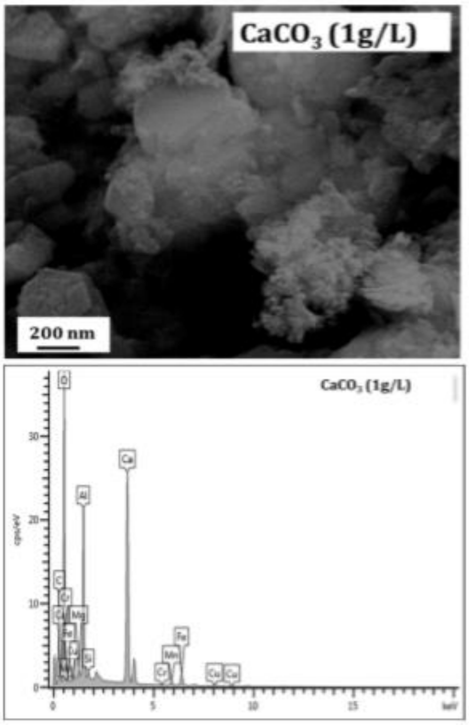

Fig. 8. SEM micrograph and EDX spectra of CaCO$_3$ (1 g/L).

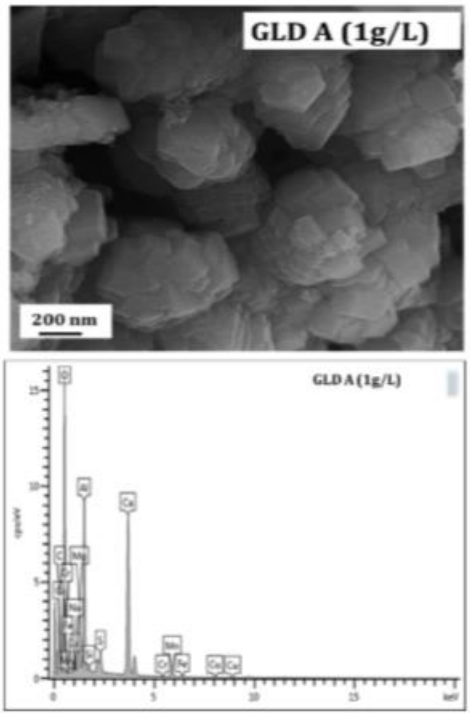

Fig. 9. SEM micrograph and EDX spectra of GLD A (1 g/L).

low quantities of trona in GLD B could have limited the dissolution of calcite that was in the sample and because its quantities were lower than its counterpart, pirrsonite in GLD B, GLD B treated samples only attained the pH values below 9. Thus, this study has therefore shown that the variable character of GLD composition is an important factor that should be considered when pursuing their valorization in AMD treatment. Furthermore, this study has also shown that the dosages of GLD should preferably be kept low (this will also be dependent on the pH of the AMD itself) to avoid introducing some ions into the AMD and destabilizing ions which precipitate at low pH values.

3.3. *Characterization of the resulting sludge*

Based on the results obtained in the lab during the measurements of both the pH and Ec, only the samples with the lowest neutralizing reagents dosages were analyzed. These precipitates were reddish. The dominance of this colour was excessively obvious for CaCO$_3$ sample while the GLD sludge were in a transition phase between black and red. The reddish colour could be associated with Fe rich compounds. CaCO$_3$ (1 g/L) had white colour further indicating that CaCO$_3$ may have not totally dissolved.

Figs. 8–10 bellow show the SEM micrographs together with their corresponding EDX spectra of the lowest dosage reacted neutralizing reagents. Based on the globular colonies that are evident on these SEM micrographs, it could be assumed that the concentration of elements that were present in the AMD sample could have been reduced through precipitation, co-precipitation, or absorption on the surface of other formed mineral phases. The prominent rhombohedral structures suggest the presence of calcite, which seem to have been armoured by other compounds as they were settling/precipitating on top of them. The evidence of the precipitated elements is confirmed by the EDX spectra.

These reacted neutralizing reagents were also analyzed using ICP-AES/ICP-MS and XRF as shown in Table 2 and 3 respectively. These results showed an increase in the concentration of most elements. This confirms that some of the AMD constituents had been reduced and formed part of the sludge.

Due to the limitations of the SEM, XRF, and ICP-AES/ICP-MS, of not being able to identify the mineral phases of the sludge, XRD was used to determine the possible precipitates that may have been formed during the AMD neutralization process. Thus, Fig. 11 show the show the XRD patterns and mineral phases quantities of the reacted neutralizing reagents. These confirmed the presence of CaCO$_3$ in all samples. These results support the assumption of

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

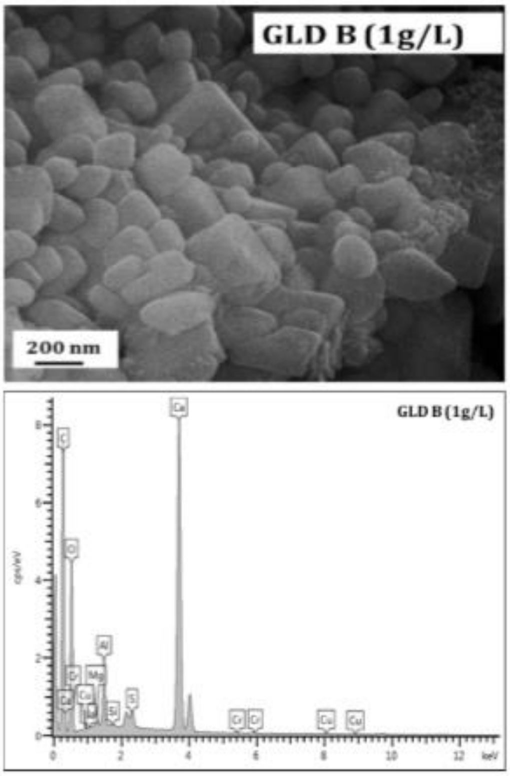

Fig. 10. SEM micrograph and EDX spectra of GLD B (1 g/L).

preferential carbonate mineral dissolution instead of the calcite. It should be noted that some of the precipitates that may have been during neutralization period may be amorphous and hence would not be detected using XRD technique. In addition, these XRD results confirm the co-precipitation of metals that was hypothesized on SEM results.

4. Conclusion

GLD, the inorganic wastes from chemical Kraft mills, can effectively neutralize the pH of AMD. This is due to their chemical properties, namely; high pH, carbonate mineral content, and liming factor, that are comparable to those of limestone. However, different GLD samples have different neutralizing capabilities that are attributed to the different carbonate mineral phases and their quantities thereof, present in the samples. Thus, this study has shown that GLD wastes from South African Kraft mills are effective in neutralization of AMD in agreement with studies reported in Finland and Huelva. This indicates that GLD wastes can be beneficiated as agents for neutralization of AMD thus leading to environmental benefits for the Kraft pulp and mining industries. Techno-economic, and pilot studies concerning the use of GLD in AMD neutralization process should be conducted.

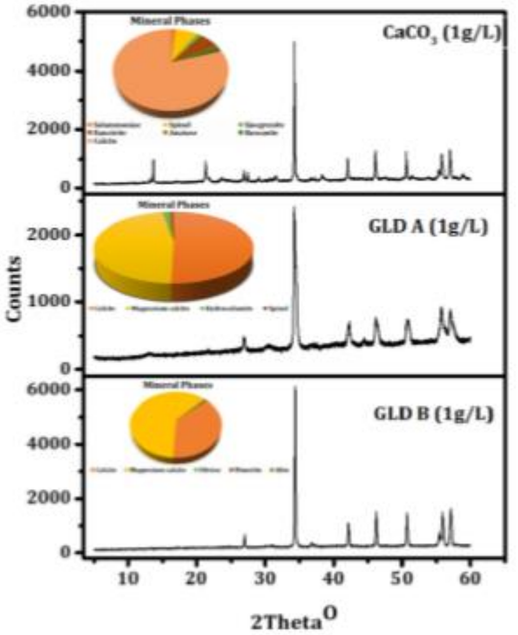

Fig. 11. XRD pattern and mineral mass percentages of the reacted 1 g/L neutralizing reagents.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

The authors of this article would like to thank the Council of Scientific and Industrial Research (CSIR), National Research Foundation (NRF), and University of KwaZulu-Natal (UKZN) for their financial support.

References

Akcil, A., Koldas, S., 2006. Acid Mine Drainage (AMD): causes, treatment and case studies. J. Clean. Prod. 14 (12), 1139–1145. https://doi.org/10.1016/j.jclepro.2004.09.006.

Alén, R., 2018. Characteristic testing of pulp and paper. In: Reference Module in Chemistry, Molecular Sciences and Chemical Engineering, third ed. Elsevier Inc. https://doi.org/10.1016/b978-0-12-409547-2.14014-4. 3rd edn.

Association of pulp paper and board manufacturers of South Africa, 1960. 'A survey of the pulp, paper and board industry IN South Africa', *Empire forestry review*. Commonw. For. Assoc. 39 (4), 437–442. Available at: http://www.jstor.org/stable/42601065.

Bajpai, P., 2018. Biotechnology for Pulp and Paper Processing. Springer Singapore, Singapore. https://doi.org/10.1007/978-981-10-7853-8.

Barrera, K., et al., 2017. 'Treatment of Acidic Mine Drainage in an Adsorption Process Using Calcium Silicate Modified with Fe(III)', *Hydrometallurgy*, vol. 172. Elsevier, pp. 19–29. https://doi.org/10.1016/J.HYDROMET.2017.06.016.

Biermann, C., 1996. Handbook of Pulping and Papermaking, second. Elsevier, Sand Dieogo, California. https://doi.org/10.1016/B978-0-12-097362-0.X5000-6.

Bouchelaghem, F., 2010. A numerical and analytical study on calcite dissolution and gypsum precipitation. Appl. Math. Model. 34 (2), 467–480. https://doi.org/

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

10.1016/j.apm.2009.06.004. Elsevier Inc.

Cabral, F., et al., 2008. Use of pulp mill inorganic wastes as alternative liming materials. Bioresour. Technol. 99 (17), 8294–8298. https://doi.org/10.1016/j.biortech.2008.03.001.

Chaplin, M., 2011. Ice III (ice-three), Water structure and science. Available at: http://www1.lsbu.ac.uk/water/ice_iii.html. Accessed: 13 January 2017.

Chartrand, M.M.G., Bunce, N.J., 2003. Electrochemical remediation of acid mine drainage. J. Appl. Electrochem. 33 (3/4), 259–264. https://doi.org/10.1023/A:1024139304342. Kluwer Academic Publishers.

Durand, J.F., Meeuvis, J., Fourie, M., 2010. The threat of mine effluent to the UNESCO status of the Cradle of Humankind world heritage site. J. Transdiscipl. Res. South. Afr. 6 (1), 73–92. https://doi.org/10.4102/td.v6i1.125.

Faithfull, N.T., Nigel, T., 2002. Methods in Agricultural Chemical Analysis : a Practical Handbook. Cabi Pub. Available at: https://books.google.co.za/books?id=S9EOngEACAAJ&dq=editions:ISBN0851997899. Accessed: 20 September 2019.

Falayi, T., Ntuli, F., 2014. Removal of heavy metals and neutralisation of acid mine drainage with un-activated attapulgite. J. Ind. Eng. Chem. 20 (4), 1285–1292. https://doi.org/10.1016/J.JIEC.2013.07.007. Elsevier.

Feng, D., Aldrich, C., Tan, H., 2000. 'Treatment of acid mine water by use of heavy metal precipitation and ion exchange', *Minerals Engineering*. Pergamon 13 (6), 623–642. https://doi.org/10.1016/S0892-6875(00)00045-5.

Hammarstrom, J.M., Sibrell, P.L., Belkin, H.E., 2003. Characterization of limestone reacted with acid-mine drainage in a pulsed limestone bed treatment system at the Friendship Hill National Historical Site, Pennsylvania, USA. Appl. Geochem. 18 (11), 1705–1721. https://doi.org/10.1016/S0883-2927(03)00105-7.

Herrera, P., et al., 2007. 'Treatment of acid mine drainage through a ferrite formation process in central Hokkaido, Japan: evaluation of dissolved silica and aluminium interference in ferrite formation', *Minerals Engineering*. Pergamon 20 (13), 1255–1260. https://doi.org/10.1016/J.MINENG.2007.06.007.

Iakovleva, E., et al., 2015. Acid mine drainage (AMD) treatment: neutralization and toxic elements removal with unmodified and modified limestone. Ecol. Eng. 81, 30–40. https://doi.org/10.1016/J.ECOLENG.2015.04.046. Elsevier.

Jia, Y., Maurice, C., Öhlander, B., 2014a. Effect of the Alkaline Industrial Residues Fly Ash, Green Liquor Dregs, and Lime Mud on Mine Tailings Oxidation when Used as Covering material Environmental Earth Sciences, vol. 72. Springer Berlin Heidelberg, pp. 319–334. https://doi.org/10.1007/s12665-013-2953-3, 2.

Jia, Y., Maurice, C., Öhlander, B., 2014b. Effect of the alkaline industrial residues fly ash, green liquor dregs, and lime mud on mine tailings oxidation when used as covering material. Environ. Earth Sci. 72 (2), 319–334. https://doi.org/10.1007/s12665-013-2953-3.

Jobby, R., et al., 2018. Biosorption and biotransformation of hexavalent chromium [Cr(VI)]: a comprehensive review. Chemosphere 207, 255–266. https://doi.org/10.1016/j.chemosphere.2018.05.050. Elsevier Ltd.

Johakimu, J., Bush, T., Lucia, L.A., 2011. 'Green liquor impregnation and kraft pulping of South African Pinus Patula- A practical approach to provide cost savings in a kraft mill's pulping operation'. Tappsa Journal 2, 6.

Johnson, D.B., Hallberg, K.B., 2005. Acid mine drainage remediation options: a review. Sci. Total Environ. 338 (1), 3–14. https://doi.org/10.1016/j.scitotenv.2004.09.002.

Kefeni, K.K., Msagati, T.A.M., Mamba, B.B., 2017. Acid mine drainage: prevention, treatment options, and resource recovery: a review. J. Clean. Prod. 151, 475–493. https://doi.org/10.1016/j.jclepro.2017.03.082. Elsevier Ltd.

Macdonald, C.J.M., 2004. 'Water usage in the South African pulp and paper industry', (December). Available at: http://citeseerx.ist.psu.edu/viewdoc/download?doi=10.1.1.727.7670&rep=rep1&type=pdf.

Madzivire, G., et al., 2009. Role of Ph on sulphate removal from circumneutral mine water using coal fly ash. In: International Mine Water Conference. Pretoria, South Africa, pp. 462–471. Available at: http://hdl.handle.net/11189/3379.

Mäkelä, M., et al., 2012. Utilization of steel, pulp and paper industry solid residues in forest soil amendment: relevant physicochemical properties and heavy metal availability. J. Hazard Mater. https://doi.org/10.1016/j.jhazmat.2011.02.015.

Mäkelä, M., et al., 2016. Cyclone processing of green liquor dregs (GLD) with results measured and interpreted by ICP-OES and NIR spectroscopy. Chem. Eng. J. 304, 448–453. https://doi.org/10.1016/J.CEJ.2016.06.107. Elsevier.

Mäkitalo, M., et al., 2014. Characterization of green liquor dregs, potentially useful for prevention of the formation of acid rock drainage. Minerals 4 (2), 330–344. https://doi.org/10.3390/min4020330.

Manskinen, K., Nurmesniemi, H., Pöykiö, R., 2011. Total and extractable non-process elements in green liquor dregs from the chemical recovery circuit of a semichemical pulp mill. Chem. Eng. J. 166 (3), 954–961. https://doi.org/10.1016/j.cej.2010.11.082. Elsevier B.V.

Masindi, V., et al., 2014. 'Neutralization and Attenuation of Metal Species in Acid Mine Drainage and Mine Leachates Using Magnesite: a Batch Experimental Approach', *an Interdisciplinary Response To Mine Water Challenges*.

Masindi, V., et al., 2018. Fate of pollutants post treatment of acid mine drainage with basic oxygen furnace slag: validation of experimental results with a geochemical model. J. Clean. Prod. 172, 2899–2909. https://doi.org/10.1016/J.JCLEPRO.2017.11.124. Elsevier.

Masindi, V., Osman, M.S., Abu-Mahfouz, A.M., 2017. Integrated treatment of acid mine drainage using BOF slag, lime/soda ash and reverse osmosis (RO): implication for the production of drinking water. Desalination 424 (September), 45–52. https://doi.org/10.1016/j.desal.2017.10.002. Elsevier.

Matlock, M.M., Howerton, B.S., Atwood, D.A., 2002. Chemical precipitation of heavy metals from acid mine drainage. Water Res. 36 (19), 4757–4764. https://doi.org/10.1016/S0043-1354(02)00149-5.

McCarthy, T.S., 2011. The impact of acid mine drainage in South Africa. South Afr. J. Sci. 107 (5/6), 1–7. https://doi.org/10.4102/sajs.v107i5/6.712.

Modolo, R., et al., 2010. Pulp and Paper Plant Wastes Valorisation in Bituminous mixes Waste Management, vol. 30. Elsevier Ltd, pp. 685–696. https://doi.org/10.1016/j.wasman.2009.11.005, 4.

Moodley, I., et al., 2018. Environmentally Sustainable Acid Mine Drainage Remediation: Research Developments with a Focus on waste/by-products Minerals Engineering, vol. 126. Elsevier, pp. 207–220. https://doi.org/10.1016/j.mineng.2017.08.008. August 2017.

Motaung, S., et al., 2008. Recovery of drinking water and by-products from gold mine effluents. Int. J. Water Resour. Dev. 24 (3), 433–450. https://doi.org/10.1080/07900620802150475. Taylor & Francis Group.

Motsi, T., Rowson, N.A., Simmons, M.J.H., 2009. Adsorption of heavy metals from acid mine drainage by natural zeolite. Int. J. Miner. Process. 92 (1–2), 42–48. https://doi.org/10.1016/J.MINPRO.2009.02.005. Elsevier.

Naicker, K., Cukrowska, E., McCarthy, T.S., 2003. Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs. Environ. Pollut. 122 (1), 29–40. https://doi.org/10.1016/S0269-7491(02)00281-6.

Neculita, C.M., Rosa, E., 2019. A review of the implications and challenges of manganese removal from mine drainage. Chemosphere 214, 491–510. https://doi.org/10.1016/J.CHEMOSPHERE.2018.09.106. Pergamon.

Oberholster, P.J., et al., 2014. The potential of selected macroalgal species for treatment of AMD at different pH rangesin temperate regions. Water Res. 60 (21), 82–92. https://doi.org/10.1016/j.watres.2014.04.031. Elsevier.

Ochieng, G.M., Seanego, E.S., Nkwonta, O.I., 2010. Impacts of Mining on Water Resources in South Africa: A Review. Scientific Research and Essays.

Österås, A.H., Sunnerdahl, I., Greger, M., 2005. The impact of wood ash and green liquor dregs application on Ca, Cu, Zn and Cd contents in bark and wood of Norway spruce. Water Air Soil Pollut. 166 (1–4), 17–29. https://doi.org/10.1007/s11270-005-7747-0.

PAMSA, 2016. Industry progress report: paper in perspective, paper manufactures association of South Africa. Johannesburg. Available at: http://www.thepaperstory.co.za/wp-content/uploads/2017/01/LBS29-PAMSA-Report_low-res.pdf.

Pérez-López, R., et al., 2011. Acid neutralization by dissolution of alkaline paper mill wastes and implications for treatment of sulfide-mine drainage. Am. Mineral. 96 (5–6), 781–791. https://doi.org/10.2138/am.2011.3685.

Potgieter-Vermaak, S.S., et al., 2006. Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage. Miner. Eng. 19 (5), 454–462. https://doi.org/10.1016/j.mineng.2005.07.009.

Pöykiö, R., et al., 2006. Green liquor dregs as an alternative neutralizing agent at a pulp mill. Environ. Chem. Lett. 4 (1), 37–40. https://doi.org/10.1007/s10311-005-0031-0.

Ramontja, T., et al., 2011. Mine water management in the Witwatersrand gold fields with special emphasis on acid mine drainage. Available at: https://www.researchgate.net/publication/263067382_Mine_Water_Management_in_the_Witwatersrand_Gold_Fields_With_Special_Emphasis_on_Acid_Mine_Drainage/link/02e7e53aa956484267000000/download.

Sanchez, D., Tran, H., 2005. Treatment of lime slaker grit and green liquor dregs - current practice. In: 2005 TAPPI Engineering, Pulping, Environmental Conference - Conference Proceedings. Philadelphia: TAPPI Engineering, Pulping & Environmental Conference, p. 9. Available at: https://www.researchgate.net/profile/Honghi_Tran/publication/294738547_Treatment_of_Lime_Slaker_Grit_and_Green_Liquor_Dregs_-_Current_Practice/links/56c3c2c008ae60234250b6fd.pdf. Accessed: 18 July 2019.

Simate, G.S., et al., 2016. Coal-based adsorbents for water and wastewater treatment. J. Environ. Chem. Eng. 4 (2), 2291–2312. https://doi.org/10.1016/J.JECE.2016.03.051. Elsevier.

Simate, G.S., Ndlovu, S., 2014. Acid mine drainage: challenges and opportunities. J. Environ. Chem. Eng. 2 (3), 1785–1803. https://doi.org/10.1016/j.jece.2014.07.021. Elsevier B.V.

Skousen, J., 2014. Overview of acid mine drainage treatment with chemicals. In: Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils: Causes, Assessment, *Prediction, Prevention, and Remediation*. https://doi.org/10.1002/9781118749197.ch29.

Skousen, J., et al., 2017. Review of passive systems for acid mine drainage treatment. Mine Water Environ. 36 (1), 133–153. https://doi.org/10.1007/s10230-016-0417-1.

Solomon, F., 2009. Impacts of Copper on Aquatic Ecosystems and Human Health. Environment & Communities, January, p. 4. Available at: http://www.ushydrotech.com/files/6714/1409/9604/Impacts_of_Copper_on_Aquatic_Ecosystems_and_human_Health.pdf.

Stambulska, U.Y., Bayliak, M.M., Lushchak, V.I., 2018. Chromium(VI) toxicity in legume plants: modulation effects of rhizobial symbiosis. BioMed Res. Int. https://doi.org/10.1155/2018/8031213, 2018(Table 1).

Taylor, J., Pape, S., Murphy, N., 2005. A summary of passive and active treatment technologies for acid and metalliferous drainage (AMD). Proc. 5th Aust. Workshop. Acid Drain. (29), 1–49.

Taylor, K., Mcguffie, B., 2007. Investigation of non-process element chemistry at Elk Falls mill - green liquor clarifier and lime cycle. Pulp and Paper Canada 108 (2), 27–32.

Tran, H., Vakkilainnen, E.K., 2008. The Kraft Chemical Recovery Process. TAPPI Kraft Recovery Course, pp. 1–8.

Vadapalli, V.R.K., et al., 2015. Acid mine drainage neutralization in a pilot

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

sequencing batch reactor using limestone from a paper and pulp industry. Environ. Technol. 36 (19), 2515–2523. https://doi.org/10.1080/09593330.2015.1036786.

Zagury, G.J., Kulnieks, V.I., Neculita, C.M., 2006. Characterization and reactivity assessment of organic substrates for sulphate-reducing bacteria in acid mine drainage treatment. Chemosphere 64 (6), 944–954. https://doi.org/10.1016/J.CHEMOSPHERE.2006.01.001. Pergamon.

Zaitsev, A.N., et al., 2008. Nyerereite-pirssonite-calcite-shortite relationships in altered natrocarbonatites, Oldoinyo Lengai, Tanzania. Can. Mineral. 46 (4), 843–860. https://doi.org/10.3749/canmin.46.4.843.

Zakir, T., 2011. Evaluation and Control of Pirssonite Scale Formation in Green Liquor Systems of the Kraft Process. University of Toronto. Available at: http://hdl.handle.net/1807/33786.

Zakir, T., Tran, H., Papangelakis, V.G., 2013. Formed in the Kraft Mill Green Liquor 12 (1), 53–59.

Zhong, C.-M., et al., 2007. Treatment of acid mine drainage (AMD) by ultra-low-pressure reverse osmosis and nanofiltration. Environ. Eng. Sci. 24 (9), 1297–1306. https://doi.org/10.1089/ees.2006.0245.

Please cite this article as: Sebogodi, K.R et al., Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa, Journal of Cleaner Production, https://doi.org/10.1016/j.jclepro.2019.118979

Paper #2

Accepted for publication in The Journal of Solid Waste Technology and Management

A Review of Technologies Used in Handling the Acid Mine Drainage Challenge: Perspectives on Using Green Liquor Dregs as a Sustainable Option for Treatment of Acid Mine Drainage

Keolebogile R. Sebogodi*, **, Jonas K. Johakimu* and B. Bruce Sithole*,**

**Biorefinery Industry Development Facility, Chemicals Cluster, Council for Scientific and Industrial Research (CSIR), 359 Mazisi Kunene Road, Durban, 4001.*

***Discipline of Chemical Engineering, University of KwaZulu-Natal (UKZN), Howard College Campus, Durban, 4001*

Corresponding author: sebogodirevelation@gmail.com; sitholeb1@ukzn.c.za

Abstract

Acid mine drainage (AMD) is one of the repercussions that result from earth-moving activities around the sulfide-bearing mineral hosts. The detrimental effects associated with this AMD are driven by its characteristics, which include low pH and high concentrations of sulfate and toxic dissolved metals. Traditionally, the prevention and treatment of AMD are achieved by using technologies that use, amongst other, naturally occurring soils and carbonates. However, the continual use of these materials may eventually lead to their depletion. On the other hand, industrial by-products have been proven to occupying land that could have otherwise been used for profitable businesses. Additionally, the handling and maintenance of landfills are costly. In this current trend of a circular economy that is driven by industrial symbiosis, scientists are concerned with valorising industrial by-products. One such by-product is the green liquor dregs (GLDs) from Kraft mills. The neutralising and geotechnical properties of these wastes have prompted the research pioneers to seek their potential use in handling the challenges associated with AMD. In this review, the formation AMD, trends in technologies for treatment and prevention of AMD are critically analysed. This includes the feasibility of using GLD as an alternative, promising sustainable material.

Keywords: Acid mine drainage; green liquor dregs; landfills; passive and active treatment; industrial waste; waste management.

1.0. Introduction

The mining industry has been an integral part of global economic abruptness for decades [168]. However, its earth-moving activities around the sulfide (S^{2-}) bearing mineral deposits may come with repercussions that may peril the environment and the livelihood in the area or country where these activities may be taking place. Such challenges/ problems may be observed because of the effects of the sulfate (SO_4^{2-}) and toxic mineral-rich, low pH leachate, known as acid mine drainage (AMD), that is formed upon the interaction between the S^{2-}, water (H_2O), oxygen (O_2), and micro-organisms [17], [18], [25], [27]. Pyrite (FeS_2), the most commonly understood and probably most abundant S^{2-} bearing mineral which is mostly found in gold and coal deposits, is used below in Equations 1-4 to illustrate the interaction between S^{2-} with H_2O, O_2, and /or micro-organisms [17], [18], [169]. Thus, the initial reaction takes place when FeS_2 is exposed to oxidising conditions, i.e., under excess H_2O, O_2, at a neutral pH level to produce Fe^{2+}, SO_4^{2-} and acid, H^+ [17], [31].

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

In the absence of alkalinity, the reaction in Equation 1 moves forward. At pH levels below 7, Fe^{2+} will be oxidised into Fe^{3+} as illustrated in Equation 2. The rate of this reaction may be accelerated by the presence of acidophilic micro-organisms [17], [18], [31].

$$Fe^{2+} + \tfrac{1}{4}\ O_2 + H^+ \rightarrow Fe^{3+} + \tfrac{1}{2}\ H_2O \qquad \textit{Equation 2}$$

At pH ≥ 3.5, Fe^{3+} may precipitate as hydrated ferric oxide-hydroxide, ($Fe(OH)_3$) as shown in Equation 3 [17], [31].

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

In cases where the alkalinity in the leachate is not sufficient to precipitate Fe^{3+} in Equation 3, further oxidation of FeS_2 will occur. At this stage, Fe^{3+} would be acting as an oxidising agent. This reaction, Equation 4, proceeds at pH levels below those that would precipitate Fe^{3+} [17], [31].

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

The overall H^+ produced during the FeS_2 oxidation is strong enough to dissolve the surrounding rocks that often contain toxic heavy metals such as aluminium (Al), uranium (U), radium (Ra), thorium (Th) and, nickel (Ni). As these rocks dissolve, the metals bound to them dissolve and become part of the acidic leachate [33]

In most cases, this leachate end-up being washed into waterbodies such as rivers, dams, and underground water, and this is where tremendous disaster may arise. For example, the world's largest gold reserves, Witwatersrand, are found in Johannesburg, South Africa. Unfortunately, these reserves are laying at a very critical location where its AMD can be distributed across the whole country. This is made possible by the Vaal and Orange rivers which flow from Johannesburg to the Atlantic Ocean while the Limpopo-Olifant river system flows into the Indian Ocean. Some challenges posed by the decanting of the Witwatersrand into the water bodies could be illustrated by the decanting of the Western basin, which decants into the Tweelopiespruit. This watercourse/stream runs through Krugersdorp Game Reserve's Hippo Dam, Figure 1, and off into the Cradle of Humankind World Heritage Site [25], [45].

On its way to, and in the Hippo Dam, this leachate would be able to peril the integrity of the living species that it may be in contact with. Thus, the fish, crocodiles, hippos, vegetation (including dependent farms) may suffer from the low pH and intolerable concentrations of dissolved metals and SO_4^{2-}. Ingestion by animals and humans of such contaminated water may cause chronic ailments such as cancer, and reduced reproductive performance, and seed germination, growth, and homeostasis in plants [130], [170]. When AMD finds its way into carbonic strata, such as the dolomite that makes the walls of The Cradle of Humankind World Heritage Site, it dissolves them, and this may, in long-term, results in the formation of sinkholes [25], [45].

Conventional methods of handling AMD are to either prevent its formation or mitigate it once it has been produced. Natural resources such as limestone($CaCO_3$) and clays are usually used to achieve this [79], [81], [171]. Unfortunately, the utilisation of these raw resources has negative environmental and economic impacts. These include greenhouse gases involved in mining and/or calcining and transporting $CaCO_3$ and/or its derivatives, ecological disturbances and, most importantly, depletion of these resources. One alternative to avoid these is to use industrial wastes and by-products of similar characteristics. The use of these by-products may not only help in curbing the factors associated with the use of the naturally occurring resources used in AMD treatment and/or prevention but also help in reducing the costs associated with the disposal of wastes in the landfills.

Figure 1: AMD from Western basin contaminated Hippo Dam at the Krugersdorp Game Reserve, South Africa [172]

Although scientists around the globe have been conducting research pertaining to the use of second generational materials for AMD treatment and prevention, green liquor dregs (GLDs) has only gained attention for such purpose over the past decade. Thousand tons of these Kraft mills' most abundant inorganic waste stream are hopelessly disposed of in landfills. However, this practice has proven to be not cost-effective due to disposal and management-related costs. In attempts to minimise and valorise these wastes from being landfilled, scientists have characterised and explored them (GLDs) in various fields such as in building and construction [142], agricultural [141], and water industry[108], [134]. The bases of GLD use in the water industry have been about their ability to neutralise acidic media since they have high concentrations of calcite and to be used as a sealing layer/cover on top of mine tailings due to their excellent geotechnical properties. Thus, this review seeks to highlight a brief overview of AMD treatment and prevention using conventional methods, background on the origin of GLD, and most importantly how GLDs' properties have been taken advantage of in AMD prevention and treatment.

2.0. ACID MINE DRAINAGE

2.1. Prevention of AMD

As highlighted in the introduction section, AMD is formed when S^{2-} bearing minerals, mine waste rock or tailings react with water and oxygen. Thus, keeping the ingress of either one of the reagents out of the system offers an opportunity of retarding/prohibiting the formation of AMD. Thus, several techniques such as bactericides [60]–[62], organic coating [63]–[65], micro-encapsulation [60], [66], [67], silane-based coating [18], [68]–[70] and carrier-micro-encapsulation [71]–[73] have been studied and explored in preventing the formation of AMD. The basis of these technologies is discussed in Table 1. However, other methods such as sealing layer (barriers) application on top of mine wastes and blending mine wastes with alkaline sources are discussed below.

Barriers

Barriers are described as materials that protect the mine tailings from being in contact with either of the factors that induce their oxidation. These barriers are classified as water or soil barriers [16], [74], [75].

Water barrier: Although not widely practised, water can be used to prevent the formation of acid mine drainage. This is made possible by the relatively low amount of oxygen present in water (30 times less than that found in the atmosphere). Thus, the limited amounts of dissolved oxygen in water barriers retard the reaction rate and possibly inhibit it once all oxygen is exhausted [74].

Soil barrier: One of the most effective ways of ensuring that mine waste or tailings do not undergo oxidation processes is to use a cover that serves as either a water or an oxygen barrier. The covers are typically single or multi-layered (in 3-5 layers). These may include (but not limited to) the tailings/waste rocks containing sulfide-bearing minerals, sealing layers, protective layers, and topsoil, as illustrated in Figure 2 [74], [75].

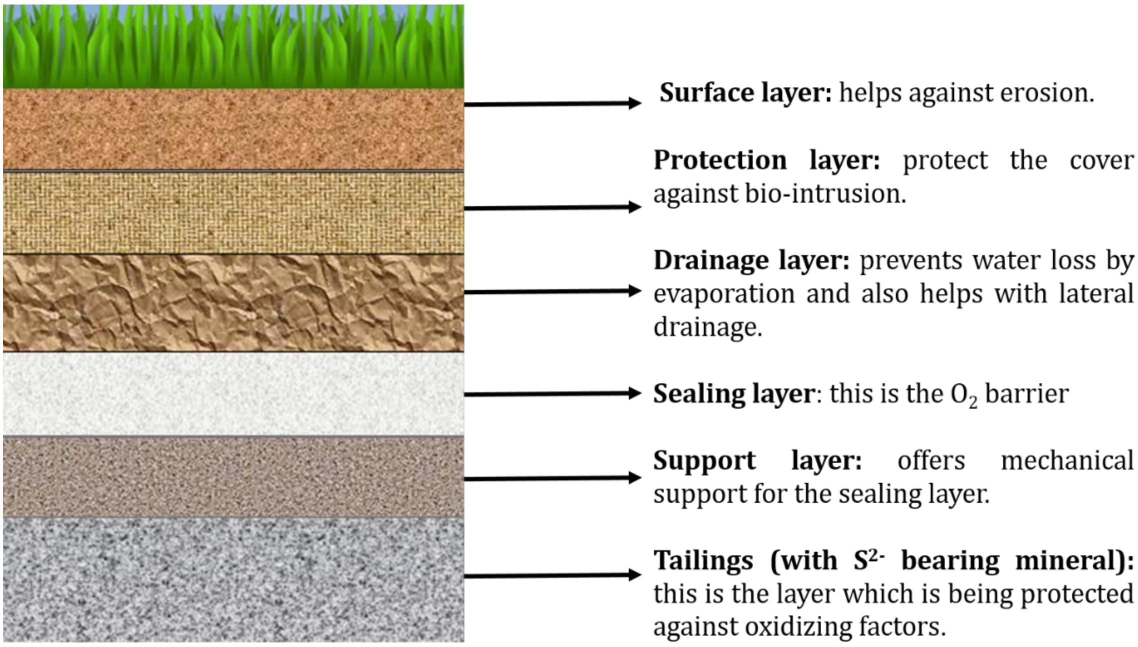

Figure 2: AMD soil cover (adapted from [24])

Blending and co-disposal of tailings and alkaline materials.

Blending the reactive mine tailings with alkaline materials such as limestone, dolomite, and lime could be considered as one of the promising methods of reducing low pH mine leachate, especially where backfilling the mine voids is desired. However, the homogeneity and stoichiometry between the S^{2-} source and the buffering material should be considered as the wrong combination may result in disastrous consequences [76], [77]. For instance, low quantities of the alkaline source may lead to the formation of AMD whereas the high amounts may lead to the production of highly alkaline (pH ~10, suitable for Mn and SO_4^{2-} precipitation) leachate which may be rich in toxic metals that precipitate at slightly lower pH levels [78]. When done correctly, this method's effectiveness will not only aid in neutralising the AMD that may be formed but would also immobilise the toxic metals through precipitation, reduce the rate of AMD formation by disengaging the acidophiles with the alkaline environment, and in the long run, the formation of gypsum hardpan may reduce the ingress of O_2 into the S^{2-} source [76].

Table 1: Methods of preventing /and or minimising the AMD formation [18].

Prevention Method	Materials used	Features	Advantages	Limitations
Oxygen barrier	•AMD treatment sludge, ash, clay, industrial alkaline wastes, low sulfide tailings, natural till/soil, non-reactive mine residue, organic materials	•Placing the covers composed of fine-grained materials, basic materials, and organic substrate over-reactive mine wastes. •Submerging mine tailings underwater.	•Dry and water covers suppressed the formation of AMD by limiting water and/or O_2 availability to mine wastes.	•The alkaline cover may enhance the solubility of some heavy metals and toxic metalloids. •Organic cover can cause a reductive dissolution of iron (Fe) precipitates. •Water cover is not applicable to arid and semi-arid regions.
Bactericide	•Acetic acid, lactic acid, sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, sodium lauryl sulfate	•Reduction of biological activity or extermination of bacteria present in mine wastes.	•Bactericides effectively inhibit the growth of micro-organisms, thereby suppressing AMD formation.	•It cannot permanently inhibit microbial activity, so repetitive addition is required.
Organic coating	•DETA, DTC-TETA, humic substance, phospholipids, sodium oleate, TETA, 8-hydroxyquinoline	•Formation of hydrophobic coatings on sulfide minerals.	•Organic compounds render sulfide minerals hydrophobic, which inhibits mineral-water interactions.	•The long-term stability of these organic coatings, which could be degraded by some micro-organisms, is unknown.

Microencapsulation	•Coating agents: Apatite, cement, MgO, $KMnO_4$, manganite, phosphate, sodium metasilicate •Oxidants: H_2O_2, NaClO •Buffer: Sodium acetate	•Formation of inorganic coatings like iron-oxyhydroxide, iron-phosphate, and iron-hydroxide/silica.	•Iron-oxyhydroxide, iron-phosphate, and iron-oxyhydroxide/silica coatings were effective in suppressing AMD formation by preventing mineral contact with oxidants like O_2 and Fe^{3+}.	•Excessive use of phosphate may cause eutrophication of water bodies. •H_2O_2 is difficult to handle and store. •The techniques are non-selective.
Silane-based coating	AAPS, APS, MTMOS, NPS, PropS-SH, PropS-SH/SiO_2, TEOS, TMOS, VTMS	•Formation of coatings composed of both inorganic and organic components.	•Silane-based coatings combine the advantages of both inorganic (i.e., durability and superior adhesion) and organic components (i.e., flexibility, crack-resistance, and compatibility). •Do not require any pre-oxidation step using H_2O_2.	•It has little selectivity for sulfide minerals.
Carrier micro-encapsulation	•Metal(loid) ions: Al^{3+}, Fe^{3+},Ti^{4+}, Si^{4+} •Organic carrier: Catechol	•Selective formation of metal(loid)-oxyhydroxide coatings on sulfide minerals	•Redox-sensitive metal(loid)-catecholate complexes were able to target sulfide minerals to	•The effects of coexisting minerals and the long-term stability of the coating remain unclear.

form surface protective coatings specifically.

2.2. Treatment of AMD

AMD treatment has been proven to be a costly practice as compared to AMD prevention. This is because the production of AMD may last for decades or even centuries before the S^{2-} embedded in the mine tailings could be consumed. Moreover, the continual exposure of S^{2-} through the ongoing mining of precious minerals assures that both the current and the future generations are bound to suffer the devastating challenges associated with AMD. Nevertheless, scientists have developed biotic and abiotic methods that are further classified as either passive or active AMD treatment technologies [17], [24].

The fundamental choice between these two technologies is based on the amount and characteristics of AMD, the material used for treatment, labour, management, the objectives of AMD treatment (protection of the site infrastructure, downstream aquatic ecosystems or agricultural activities, or human consumption), and the overall cost. Between the two, passive technologies have been reported to be cost-effective as they require no/low maintenance, management, labour, material (chemical) addition. However, their employment may, unfortunately, be limited by various factors such as prolonged time (~12 h) necessary for effective treatment, not applicable to all types of AMD, is designed to treat low volumes of AMD per day, and require large surface areas [24], [92], [93]. The methods categorised in this technology include aerobic and anaerobic wetlands, compost bioreactors, anoxic $CaCO_3$ drains, open $CaCO_3$ ponds, and permeable reactive barriers [92], [94].

Table 2: Summary of advantages and disadvantages of AMD treatment technologies [17]

Treatment technology	Principle/Mechanism	Conventional material used	Advantages	Disadvantages
Alkaline addition	•The most common approach for the treatment of AMD •Involves neutralising the pH with one or more alkaline materials, after which the metals are insolubilised and removed •Metals are precipitated according to as (oxy) hydroxides, sulfides, and carbonates •Sulfate is removed as gypsum, but removal efficiency is low	•Limestone, quicklime, hydrated lime, dolomite, kiln dust, sodium bicarbonate, ammonia, potassium hydroxide, barium carbonate, barium hydroxide, magnesite, calcium peroxide	•Neutralizing agents can be applied to any form of AMD treatment, i.e. ponds, pits, streams •Is a quick temporary solution for AMD treatment	•Conventional substrates are prone to armouring •Lime cannot raise the pH above 8 resulting in some metals not being removed •Sludge produced is voluminous, has a low solid content and is difficult to settle •Metals in the sludge are sensitive to pH
Desalination (sulfate removal)	•Involves the use of multiple alkaline agents sequentially to remove sulfate •There are various processes some of which include the ettringite process, barium sulfate process, and nanofiltration	•Lime, aluminium hydroxide, barium sulfate	•Ettringite process can lower sulfate to below 200 ppm •Nanofiltration can remove more than 99% of sulfate •Hybrids of desalination processes eliminate most of the disadvantages	•Produces large amounts of sludge that is difficult to settle •Treatment reaction times are too long •Unpractical for large-scale treatment •Barium sulfate process produces toxic barium salt, poisonous hydrogen sulfide gas and is expensive

				•Nanofiltration requires a pre-treatment step and produces large amounts of waste brine
Adsorption	•Involves the use of adsorbent materials to selectively adsorb metals from AMD while releasing oxides and hydroxides to neutralise the pH	•Dead biomass, clay, tree bark, tea leaves, blast furnace slag, fly ash, natural zeolite, commercial chemical oxides and hydroxides	•Simple to operate •Efficient •Low volume of sludge produced •Does not require the use of chemicals	•The adsorption capacity of conventional materials is low •Cannot treat AMD containing suspended solids •Some commercial adsorbents are expensive •Regeneration of adsorbent is costly, and significant amounts of material are lost with each cycle •Conventional adsorbents have a limited lifespan
Anaerobic (sub-surface flow) constructed wetlands	•Forms the basis of passive treatment of AMD •Are natural wetlands that are engineered to naturally and biologically produce alkalinity •Treat AMD primarily through DSR by *Desulfovibrio* bacteria •Other mechanisms include dilution; filtration; sedimentation; hydrolysis;	•Wetlands typically comprise of a bedrock (limestone/gravel), soil, plants and an organic substrate (compost, manure, hay bales, peat, wood chips, leaf mulch, sewage sludge, cellulose, ethanol, acetate, lactate)	•Natural treatment for AMD •Environmentally friendly •Can be used for land and habitat rehabilitation •Removes both metals and sulfate •Metal precipitates are stable in the wetland and need not be removed	•Long retention times •Difficult to remove high concentrations of metals •Requires vast land space •Chemical substrates are expensive •Organic substrates can be costly for treatment in remote areas

	ion exchange by plants, soil and organic matter; other microbial redox reactions		•Low volume of sludge is produced •High long-term performance •Low maintenance •Cost-effective	•Gravel can be steep in some countries
Sulphidogenic bioreactors	•Treats AMD through DSR in batch, continuous or semi-continuous reactors •Dependent on an organic carbon source •Continuously stirred reactors are most common •Other types include fluidised bed reactor, up-flow anaerobic granular sludge bed (UASB) bioreactor and submerged membrane bioreactor (MBR)	•Animal manure, compost, sawdust, wood chips, spent mushroom compost, cellulose waste, limestone, bark Installation is simple	•Easy to install •Low cost •Removes high concentrations of metals and sulfate well •Performance is predictable •Allows for differential removal of metals	•Long-term performance is not understood due to complex biogeochemical processes •Lifetime is limited •Mn metal removal is poor •Requires continuous additions of organic substrates
Anoxic limestone drains	•Used to improve the efficiency of wetlands •Usually serve as a pre-treatment step by passing the AMD through a bed of limestone under reducing conditions	•Consists of a sealed trench buried in the ground which is filled with limestone and covered with an impermeable substrate such as clay	•Requires little land space •Cheaper than CWs •Requires lower maintenance than CWs •Good short-term performance	•Anoxic conditions are challenging to maintain •Prone to clogging of limestone •Conventionally known to fail in the long-term run

	and raising its pH, while metals are still in their reduced form •This allows a higher concentration of metals to be removed when sent to a CW/ settling pond			•Cannot handle high metal concentrations •Can only remove metals in their reduced states, e.g. Fe (III) and Al •Removes sulfate in low concentrations
Permeable reactive barriers	•Recent and emerging technology •Is an in-situ passive treatment •Are underground trenches filled with porous reactive materials, through which an AMD plume passes through •Similar to sub-surface flow wetlands in that DSR is used to remove metals and sulfate •Contaminants can also be immobilised in the reactive material through adsorption, ion exchange, and precipitation processes	•Granular iron, zero-valent iron, limestone, dolomite, quick lime, zeolite, compost, sewage sludge, wood chips, bone char, apatite, bauxite, activated alumina, fly ash, peat moss, ferric oxyhydroxides	•Low-cost in-situ treatment •Prevents cross-contamination with surface waters •Prevents loss of large amounts of groundwater •No land space required •Does not require any waste disposal	•Needs multiple substrates for effective treatment •Capital and implementation costs can be high if substantial barriers are needed •Mine site must be well characterised and modelled before treatment, which is time-consuming •PRBs are site-specific and are limited to AMD plumes that are less than 20 m below the ground •Long-term performance is unknown

AAPS→N-(2- aminoethyl)-3-aminopropyltrimethoxysilane ;APS→γ-amino-propyltrimethoxysilane ,DETA→diethylenetriamine ; DTC-TETA→sodium triethylenetetramine- bisdithiocarbamate ;MTMOS→methyltrimethoxysilane; NPS→n-propyltrimethoxysilane; PropS-SH→γ-mercaptopropyltrimethoxysilane;TEOS→tetraethoxysilane ;TETA →triethylenetetramine ;TMOS→ tetramethoxysilane; VTMS→vinyltrimethoxysilane

On the other hand, active treatment technologies are the most versatile of these technologies because they could be used to treat all types and volumes. This versatility is made possible by their ability to be custom designed/modified to achieve effective treatment for a specific AMD character. Also, these technologies require less operating space as compared to the passive ones. However, active technologies suffer from not being cost-effective because they are labour, material, and energy-intensive, produce large quantities of toxic sludge that is mainly landfilled and may cause ecological disturbances [24]. These technologies include off-line sulfidogenic bioreactors, the addition of alkaline reagents (neutralisation), flocculants/coagulants, ion exchange resins, electrodialysis, zeolites, and membrane technologies. Their advantages and disadvantages are listed in Table 2 above.

The addition of alkaline reagents to the AMD has been popularly adopted across the globe. The traditional chemicals that have been used for the past decades are sodium hydroxide (NaOH), $CaCO_3$, CaO, hydrated lime ($Ca(OH)_2$), dolomite ($CaMg(CO_3)_2$), magnesite ($MgCO_3$), and ammonia (NH_3). The selection of these chemicals is, however, dependent on several factors, e.g. pH, acidity level, and volume of AMD to be treated. Amongst these, $CaCO_3$ and its derivatives are widely used because of the copiousness $CaCO_3$ and/or its derivatives, and low cost as compared to other chemicals [14], [95]. In most cases, $CaCO_3$ is used to raise the pH of AMD to values between 6 and 8. This step will then be followed by the post-treatment step, which, uses $Ca(OH)_2$ to raise the pH of the neutralised AMD to values around 12 [96], [97]. Thus, the initial step of $CaCO_3$ addition is used to precipitates all the metals which need not higher pH levels to precipitate, e.g., Fe^{3+} and Al, precipitates at pH values of 3-4 and 7 respectively. This step is crucial as it ensures that some of the metals which may be amphoteric do not re-enter the AMD through dissolution (if the pH were to be allowed to rise to values around 12). The subsequent step (post-treatment) is designed to precipitate ions such as Mn and SO_4^{2-} [97], [98].

3.0. GREEN LIQUOR DREGS (GLDs)

3.1. Origin of GLDs

One of the 2030 Agenda for Sustainable Development (ASD) goals is to protect the planet from degradation through sustainable consumption and production, sustainably managing natural resources and taking urgent action on climate change, so that the earth can support the needs of the present and the future generation [2], [173]. This means that conventional mitigation and remediation technologies that utilise unsustainable materials need to be assessed and “new sustainable and/or ecofriendly materials” should be used instead. In the context of this review, utilising industrial wastes in addressing the challenges that the world is faced with regards to AMD would not only help in moving closer towards achieving the 2030 ASD goal of protecting the planet but also help in cutting the costs of materials used in handling the AMD challenges and minimises landfilling. Thus, GLDs, a by-product in a Kraft pulping process, has been proven to be one of the wonder materials of this century that could be used as an alternative for some of the traditional, non-sustainable AMD preventative and treatment materials [108], [135], [143], [174].

The pulping process is divided into two parts viz; pulp manufacturing and recovery system, which represent a closed-loop overall system as discussed below and illustrated in Figure 3 [120].

Pulping: The Kraft pulping method produces pulp from wood by cooking the debarked, chipped wood in a hot mixture of NaOH and Na_2S, known as cooking/white liquor. This liquor liberates the cellulose fibres from the lignin matrix that binds the fibres together. After cooking, the fibres and the resultant black liquor are separated in the pulp washing process step. The pulp fibres are then sent to the papermaking process or exported. The spent “black liquor” recovered during pulp washing are then sent to the recovery system where the white liquor components will be recovered and recycled back into the next pulping cycle [5], [8], [122], [123].

Kraft Recovery system: The Kraft recovery system has been referred to as the kidney of the Kraft pulping process. This is due to the different vital processes that ensure the overall well-being and sustainability of the pulping plant/equipment. These are discussed below.

Energy regeneration: the black liquor that enters the recovery system is composed of about 15 % solids/organics (e.g., lignin, the source of carbon) and NPEs. To optimise the energy recovery efficiency from this liquor, the liquor is evaporated in multi-stage effect evaporators to about 60-75% of solids. This is now referred to as concentrated black liquor. The concentrated liquor is then released into the bottom of an elevated temperature furnace, where the organic matter in the liquor is burnt to generate green, sustainable energy. Under these stringent conditions, inorganic salts, Na_2S, and sodium carbonate, Na_2CO_3, are formed [5], [123].

Causticisation: the smelt that results from the deoxygenated recovery boiler is then sent into the dissolving tank where it is dissolved with weak white liquor to form the green liquor. The green liquor is then transferred into the green liquor clarifier where all the non-process elements will be removed (using different technologies) from the liquor, washed and discarded in landfills as GLDs [5], [125].

The clarified green liquor will then be sent into the slacker where CaO will be added. CaO will react with water to form calcium hydroxide ($Ca(OH)_2$). Another form of solid waste is removed from the process at this stage and is disposed of in landfills as slaker grits. The produced liquor is then directed into the causticising reactor, where Na_2CO_3 in the liquor will react with $Ca(OH)_2$ to form NaOH and $CaCO_3$. At this stage, the liquor now consists of white liquor (NaOH and Na_2S) and $CaCO_3$. From here, the slurry is fed into a white liquor clarifying tank where $CaCO_3$ will be allowed to settle at the bottom. This settled $CaCO_3$ is now referred to as lime mud. The clarified white liquor is then sent back to the pulping cycle. The lime mud is washed (producing weak white liquor), filtered with a pre-coat, sent into a kiln for drying and calcination, and will be used in another causticising process. The weak white liquor will be used to wash GLDs in the next pulping cycle [5], [125].

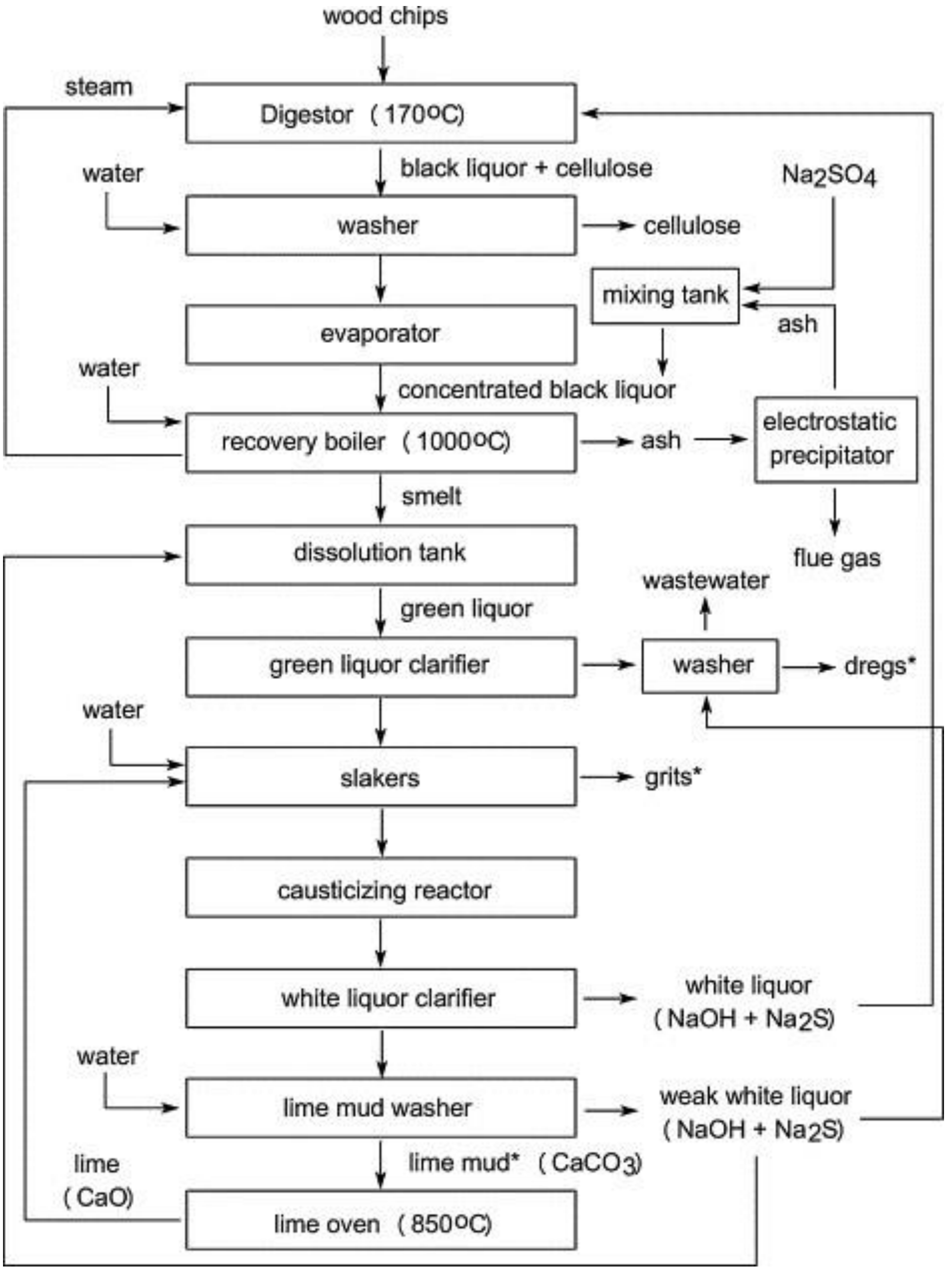

Figure 3: Kraft pulp manufacturing process [120].

3.1.1. Removal of GLDs from the system

GLDs are found in the green liquor system and contribute significantly to the NPEs found in the chemical recovery operations. They mainly constitute inorganic contaminants such as; potassium, calcium, silica, manganese, barium, iron, copper, nickel, chromium, and zinc. Their carryover to the downstream processes has a negative effect on the quality of the cooking liquor produced as well as the operation of the kiln. This carryover has to do with poor dregs' filtration efficiency in the cooking liquor and mud lime systems, respectively. Therefore, it is necessary that dregs be purged out of the process through a liquid-solid separation process. Green liquor clarifying technologies that are used are either sedimentation or filtration processes. The common principle among them is that the pH of dregs should be below the maximum recommended value of 13. Thus, depending on the method used for separating dregs from the liquor, a washing step may be necessary to reduce the pH of dregs to recommended values [5], [126].

3.1.1.1. Sedimentation of GLDs

The dregs separation through sedimentation processes is dependent on the settling properties of the solid particulates in the liquor. The sedimentation technologies which have been invented and used by various Kraft mills across the globe include the green liquor clarifying tank and the centrifuge system[126], [127]. These inventions differ in the efficiency of the liquor clarification, the settling rate, as well as the time needed to sediment the solids [4].

Green liquor clarifying tank: this technology uses the rake system to remove the dregs from the liquor. Essentially, the process starts by allowing the insoluble particulates to settle at the bottom of the clarifying tank - this process could take ~12 hours. Some mills use flocculants to enhance the sedimentation process. This is achieved by decreasing the surface area of the particulates and hence accelerating the settling rate by increasing the density of the conglomerates. After settling, the clarified liquor is then transferred into the causticising plant where it will be reacted with $Ca(OH)_2$ while a rake system is used to take the sediment slurry out of the tank. The dregs will then be sent to the washer where they will be diluted with freshwater, and the resulting slurry is then transferred into a washer. The overflow liquor, also known as the weak white liquor, will be transferred into the weak wash liquor tank while the underflow will be sent to the effluent treatment plant. The washed GLDs are then disposed of in landfills [4], [5], [126].

3.1.1.2. Filtration of GLDs

Several green liquor dregs filtration processes including the crossflow, cassette, tube, pressure disk, and pre-coat vacuum filters, are commonly used. The filtration processes are facilitated by membrane processes whereby semi-permeable membranes are used as filters to separate the solid particulates from the liquor. The methods may be driven by internal pressure (from the liquor feed pump), or external/introduced air pressure [127], [128]. This paper will only cover the use of the pre-coat vacuum filter which is widely used in the Kraft mills.

Green liquor pre-coat vacuum filter: the most used green liquor vacuum filter is known as a pre-coat vacuum filter, Figure 4A. This filter is equipped with a slurry feed vat, filter drum, filtrate pipe, and knife blade. The sediment slurry is collected in a vat that has an agitator, which prevents the insoluble solids from settling. The filter, which is pre-coated with lime mud, rotates and picks up the slurry from the vat, the liquid is sucked into the hollow filter drum and the solid particulate forms a cake on the outside surface of the filter and, finally, the cake is scrubbed out of the mesh by a knife blade. This cycle keeps on repeating until all the liquor has been filtered out and the cake is then sent for disposal as GLDs, as shown in Figure 4B. The lime mud used to enhance the filtration process ends up increasing the quantities of dregs that are being landfilled. Typically, 1-1.5 Kg of lime mud is used to aid the filtration process of 1Kg dregs [126], [129], [130].

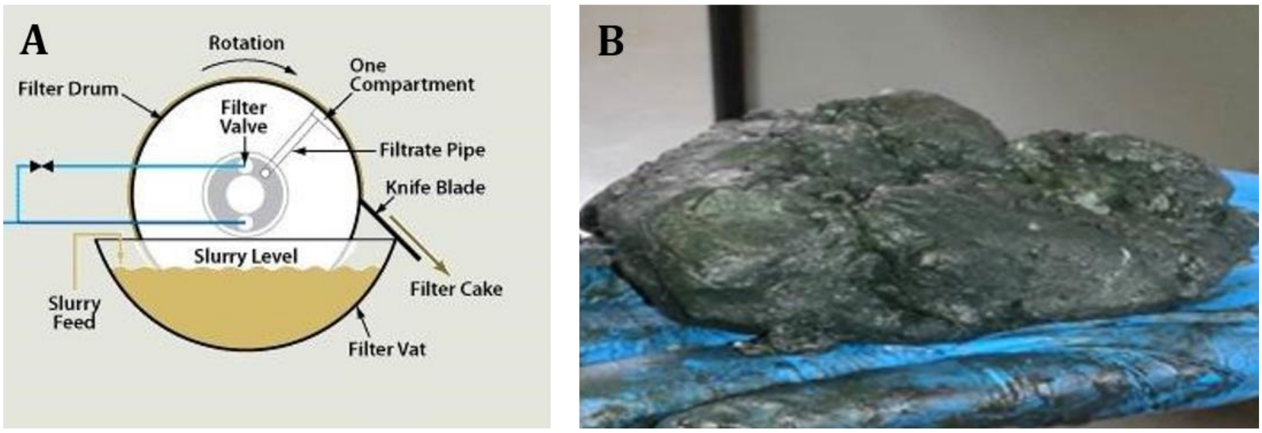

Figure 4: (A) A rotary pre-coat vacuum filter [131] and (B) fresh GLDs

3.2. Properties and applications of GLDs

Chemical and mineralogical composition: GLDs are generally characterised by having high quantities of $CaCO_3$, sodium carbonate (Na_2CO_3), carbon, and non-process elements (NPEs). The $CaCO_3$ present in the GLDs are mainly introduced when the GLDs are filtered with a lime mud-coated vacuum filter while the traces of carbon may be the leftovers of lignin that was not burnt during the energy regeneration step, and the NPEs may have either came through the process through the wood, chemicals used, or the corrosion of pulping equipment [125], [132]–[134]. The NPEs may include magnesium (Mg), iron (Fe), silicon (Si), potassium (K), copper (Cu), and zinc (Zn) and these together with their concentrations may differ from one mill to another. Similar to the NPE composition, the mineralogical composition of GLDs differs from one mill to another. This difference in elemental and mineralogical composition is shown in Tables 3 and 4, respectively. [16], [108], [125], [133], [135], [136].

Table 3: Elemental composition of GLDs [14]

Character	**Concentration(ppm)**			
P	10	0,90-2,10	0,2	98-78
Ca	84500	118,2-347	0,175	18,500-20,700
Na	26100	29,8-144,4	0,0198	311,000-267,00
K	1700	0,90-6,60	1,4	9,830-11,600
Mg	29700	21,0-51,1	0,0959	8,030-12,100
S	10600	N/A	0,0312	N/A
Cu	110	2,60-5,40	0,33	N/A
Zn	1200	0,0488-0,258	6,49	269-313
Fe	4500	2,60-5,40	8,01	6,590-10,600
Mn	10300	1,6-7,8	0,0351	3,980-5,950
Cd	10	0,00407-0,00612	0,011	N/A
Cr	300	0,0474-0,0689	0,16	33-42
Ni	200	0,119-0,254	0,08	32-38
Al	N/A	0,3-4,10	0,0255	1,670-2,050
Pb	N/A	0,0311-0,0624	0,052	N/A
pH	**10**	**12,1-12,3**	**N/A**	**N/A**

Table 4: Mineralogical composition of GLDs

Mineral Name	Formula	Reference
Pirssonite	$Na_2CO_3. CaCO_3. 2H_2O$	[14], [120], [125], [133]
Calcite	$CaCO_3$	[10], [14], [16], [108], [120], [133], [137]–[140]
Portlandite	$Ca(OH)_2$	[120], [133]
Thermonatrite	$Na_2CO_3. H_2O$	[125], [133]
Natrite	Na_2CO_3	[16], [133]
Sjögrenite	$Mg6Fe_2^{3+}(CO_3)(OH)_{16}. 4H_2O$	[133]
Anhydrite	$CaSO_4$	[14], [133]
Quartz	SiO_2	[133]
Graphite	C	[16], [126], [133]
Halite	NaCI	[133]
Diopside	$CaMgSi_2O_6$	[133]
Pargasite	$NaCa_2Mg_3Fe^{2+}Si_6AI_3O_{22}(OH)_2$	[133]
Vermiculite	$Mg_{1.8}Fe_{0.9}^{2+}AI_{4.3}SiO_{10}(OH)_2.4(H_2O)$	[133]
Dolomite	$CaMg(CO_3)_2$	[137]
Thenerdite	Na_2SO_4	[137]
Cesanite	$Ca_2Na_3(SO_4)_3OH$	[137]

pH and neutralising potential: the presence of carbonic mineral phases together with the fact that the Kraft pulping process virtually an alkaline process, efficiency of filtration, and/or NaOH that may sometimes be carried over from the liquor play a significant role in the pH level of GLDs equipment [125], [132]–[134]. Also, the neutralising potential of GLDs were determined to be comparable to that of limestone [134]. This could be taken advantage of in replacing the use of limestone in specific industries.

Geotechnical properties: a study that was carried out by Mäkitalo *et al.* (2014) showed that GLDs have excellent geotechnical properties such as high porosity and water retention ability, the small particle size of ~12μm, the large surface area of ~18 m^2/g, and very low hydraulic conductivity. However, GLDs were reported to have low shear strength.

3.3. Exploitation of GLDs

The properties that GLDs possess had enabled researchers across the globe to explore them to beneficiate various fields/industries such as in agriculture [141], building and construction [12], [137], [142], and mining, pulp and paper, and water industries [7], [10], [16], [108], [134], [143]. In this review, we will be looking only into the beneficiation of GLDs in the mining industry and particularly in remediation and amelioration of AMD.

3.3.1. Remediation of AMD formation

Blending and Co-disposal of GLDs

Alakangas, Andersson and Mueller (2013) expropriated the GLDs' neutralising power in blending them with S^{2-} rich mine tailings as an initiative of reducing their landfilling and preserving natural carbonate materials. In their study, different ratios of GLDs were mixed with tailings and exposed to the oxidising environment for stipulated periods. At the end of their experiments, GLDs were proven to be effective in buffering the AMD that would have otherwise been formed had it not been the presence of the alkalising effect produced by GLDs. In other words, the presence of GLDs assured the production of leachate with pH values that were above 7 and had low metal concentration as compared to the leachate that was produced from the tailings that were not blended. Nevertheless, the authors also outlined that the actual particle size of mine rocks/tailings may negatively impact blend ratios and that the longevity of using GLDs as the alternative for traditional unsustainable carbonates needs to be investigated. The other problem that was not highlighted by the authors of this study is that the versatility of NPE and their concentration thereof must be carefully studied before using GLDs for this purpose and that further treatment may be required to turn the neutralised AMD into potable water. Additionally, high $CaCO_3$ content may be a preferred mineral phase composition of the GLDs as this phase is not prone to fast depletion as compared to other phases such as $Na_2CO_3.CaCO_3.2H_2O$. On the other hand, the gradual formation and accumulation of precipitates, especially the $CaSO_4$, use of this technology may, in a long-term turn into a non-porous surface that may inhibit the proliferation leachate.

Sealing layer using GLD

The characterisation of GLDs for use in sealing layers

Mäkitalo *et al.*, (2014) studied GLDs for possible use as a sulfidic rock sealing layer and concluded that GLDs could effectively prevent or reduce AMD formation due to several properties they have. These include high porosity, water retention ability, the small particle size of ~12μm, the large surface area of ~18 m^2/g, and very low hydraulic conductivity. The high porosity allows water to flux through the cover. Due to the large surface area (which results from the small particle size), the water that enters GLDs is imbibed through chemical interactions by GLDs particles. This results in high water saturation of ≥85% that inhibits or limits the permeation of O_2 into AMD tailings. High water saturation also helps to keep the sealing layer intact as it prevents shrinkage and cracking of the layer that could occur due to seasonal changes.

However, it was also determined that GLDs' effectiveness and/or durability might be affected by various factors. Other studies in which GLDs were used as sealing layers evaluated factors that could impact the efficacy and/or durability of the layers. These factors included weather conditions, CaO quantities, pH, and topography of the area However, Maurice, Villain and Hargelius (2009); Jia *et al.* (2013); Jia, Maurice and Öhlander (2014)b; Mäkitalo *et al.* (2014) had also reported that the that GLDs' effectiveness and/or durability may be affected by various factors such as the CaO content, pH, and weather conditions as shown below.

High CaO content: The high amounts of CaO in GLDs may increase the hydraulic conductivity of the layers and negative impact on the efficiency of the sealing layers. This means that water and O_2 may infiltrate through the till and induce oxidation [140], [146].

pH: batch leaching tests conducted by Jia, Maurice and Öhlander (2015)showed that GLDs could immobilise different metals such as cadmium, lead (Pb), copper (Cu), nickel (Ni), and zinc (Zn). This is achieved when high pH levels are reached in the presence of calcite, and the stabilised forms of metals were either carbonate salts or metal hydroxides. Unfortunately, the high pH levels mobilise As by lowering the stability of its hydroxide. The same situation also occurs with Cr wherein the alkalinity above the neutral value encourages the conversion of Cr^{3+} to the Cr^{4+} thus facilitating the mobility of Cr [136], [140], [143].

Land topography: It has been reported that GLDs cannot be used on hillsides due to their weak uniaxial compressive strengths. Consequently, several studies investigated ways to enhance this geotechnical property of GLDs. Maurice, Villain and Hargelius (2009) ascertained that GLDs from the clarifying tank (GLDs removed from the process by allowing them to settle at the bottom of the clarifying tank) exhibited lower hydraulic conductivity than pre-coat segregated GLDs. The high hydraulic conductivity in the pre-coat segregated GLDs is caused by the high amount of CaO in the AMD. This means that using pre-coat segregated GLDs as a sealing layer may not be as effective as soils with lower hydraulic conductivity and thus runs a risk of perhaps sliding down/tearing apart and hence unveils the S^{2-} bearing minerals to the oxidising environment. Incorporating fly ash or biological sludge can decrease the hydraulic conductivity of GLDs by a magnitude of 1. When these amendment materials were both incorporated, the hydraulic conductivity decreased by a further magnitude of 1 [140], [145], [146].

Weather conditions: In very cold areas, the freeze-thaw cycles may cause shrinkage and expansion, which may, in turn, lead to the cracking of the sealing layer, thus allowing the ingression of water and O_2 into the tailings. This intrusion will then induce oxidation of the sulfide-bearing minerals within the tailings [140], [146].

Using GLDs as a single dry cover

Other studies have focused on using GLDs as partial or alternative materials for traditional sealing layer materials in AMD treatment to reduce the costs incurred when synthetic materials or soils are used as sealing layers. For example:

Ragnvaldsson *et al.* (2014) investigated the feasibility of using GLDs, on a pilot scale, and in an operational mine, to replace high-density polyethylene sealing layers. In short, two waste rock piles with sloped sides and flat tops were constructed on top of 1-2% sloped polyethylene liners. The liners were there to collect the leachates that might be formed. One pile served as control whereas the second pile was covered with a 30 cm layer of

GLDs, on the top and sides. The top side was then covered again with a high-density polyethylene liner that diverted water away from the pile, thus reducing the amount of water that might infiltrate the piles. Flow meters were installed at each pile to measure the quantities of the leachates. The leachate from each pile was collected biweekly for one year and analysed for metal content. The results indicated that the test pile produced 40% less leachate than the control pile. This indicated that the GLDs that was mounted on the sides of the waste rock pile also contributed towards the reduction of water infiltration. Chemical analysis of the AMD showed that although there was no significant difference in pH levels of the two leachates, the concentration of metal load in the test leachate decreased by ≥50% for 13 of the 20 metal elements. The researchers postulated that such differences in metal concentrations may have been due to: (i) the GLDs might have increased the pH of the incoming water hence initially minimising the sulfide oxidation induction rate which ultimately reduces the dissolution of other metals found in the rock waste, and; the precipitation of Fe could have impacted on the chemistry of other metals. The study concluded that this technology could reduce the AMD treatment costs of an operational mine by ~10 % due to the 40% lower leachate production as well as the low concentrations of most metals in the leachate. These findings could benefit not only the mine but also the environment as the carbon footprint involved during the synthesis of polyethylene used for sealing mine wastes, and mining, burning, and transportation of $CaCO_3$ limestone/lime (CaO) and the sludge produced if vast quantities of AMD were to be treated. Although the results of this study have shown the positive effects of using GLDs in partially substituting the polyethylene which is sometimes used for covering tailings, careful considerations pertaining to the integrity of the cover should be considered. For example, a cover should always be able to block away either one or both of the elements needed for sulfide oxidation. Thus, using GLDs in the open air means that they will dry out and may eventually crack, and this would allow water and oxygen to infiltrate the tailings.

Later on, Mäkitalo *et al.*(2015) investigated two ways of blending GLDs and till. A mobile asphalt plant and a construction loader with a crushing bucket were used, as seen in Figure 5. Different ratios of GLDs: till (till with about 30% and less than 10 % of particles which are less than 0.063 mm) were mixed for varying periods. The GLDs ratios used ranged from 5 -15%. The study confirmed that blending fine till with GLDs depletes its good hydraulic conductivity thus implying that fine tills should not be amended. Vigorous mixing resulted in the mix having high water content (due to the water that is unbound from GLDs), high porosity, and low hydraulic conductivity. Decreased hydraulic conductivity was also noticed after long mixing times. When using a loader, long mixing times affected the consistency of the results because it is possible that the loader could have incorporated the particles from the ground. The addition of coarse material may decrease the conductivity, whereas finer particles may increase it. This is because, naturally, fine soil particles have low hydraulic conductivity and blending them may only lead to depletion of their suitable hydraulic conductivity property.

Figure 5: A construction loader and asphalt plant used in mixing till and GLDs (Mäkitalo et al., 2015).

High water content and low dry density on the asphalt blended 10% GLDs: till (30% sand) was observed whereas the same blend of the loader had precisely the opposite properties. The overall conclusion of this study was that if either technology were to be used, 5% GLDs should be blended with till with high sandy particles. In this way, the blends produced a high compaction degree which is observed when the blend has high dry density and low water content. This indicates that the compaction degree is preferable to hydraulic conductivity (Mäkitalo *et al.*, 2015).

GLDs amendment using other materials

Mäkitalo *et al.*, (2015) and Sirén et al. (2016) have investigated soils that are used in mine waste rock or tailings as sealing layers need to meet specific geotechnical properties such as low hydraulic conductivity, small particle size, and high density of compaction. If the soils found in the periphery of mines are not suitable to be used for constructing sealing layers, the mines will have to procure soil for this purpose. This is a costly endeavour. Therefore, to curtail these costs, cheaper materials may be used to improve the properties of the surrounding soils as layers. Sirén *et al.* (2016) studied the effect of adding different quantities of green liquor dregs into diverse types of soils and evaluated the feasibility of using the resulting mixtures as sealing layers. This was a pilot-scale study that used 400 m^2 cells that constituted construction of a 0.2 m foundation, 5 m sealing, and 1.5 m protection layers. Clay, sandy, and fine-grained tills were used as layers to which were added ~10% GLDs. The mixtures were compacted using a hydraulic plate compactor. The results showed that the addition of up to 10% GLDs to the clay soils increased its naturally low hydraulic conductivity. On the other hand, the same quantities of GLDs lowered the hydraulic conductivities of fine-grained and sandy soils. Thus, GLDs could only be used as local soil amendment material in soils that generally have poor geotechnical properties.

3.3.2. Mitigation of AMD with GLDs

GLDs are generally alkaline waste materials. One of the first studies in which GLDs were used in the neutralisation of the acidic effluents was conducted by Pöykiö and his group (2006). They used GLDs to neutralise Kraft mill acidic wastewater and reported that GLDs were excellent as neutralising agents due to their high pH (~10.7), comparable liming value to that of $CaCO_3$ (39%), and fast-acting capacity [134].

In 2011, Pérez-López *et al.* characterised GLDs and used them to neutralise two different AMD leachates. SEM/EDX and XRD analyses of the GLDs samples were conducted before and after the reaction with AMD. XRD analyses showed that the GLDs contained 80% calcite. These XRD results were confirmed by the presence of rhombohedral structures which were evident on SEM micrographs. Furthermore, this study showed an effective metal removal from the AMD, as presented in Table 5. It could be concluded that GLDs are effective in raising the pH of AMD and reducing some metals even to 100%. However, it should be noted that the dosage used here may not be taken as the universal dosage because GLDs may sometimes constitute mineral phases, as per Table 4, which may have preferential dissolution to calcite and hence limiting its dissolution- this obviously depends on the pH of AMD and the mineral phase quantities. However, Sebogodi *et.al.* (2019) showed that the different carbonic mineral phases composed in the GLDs play a significant role in the AMD neutralisation mechanism. That is, their nature, quantities, degree of solubility facilitate the neutralisation process. Thus, other minerals dissolve readily in the medium while some like $CaCO_3$ require lower pH values to dissolve.

Additionally, the quantities of the respective NPEs in GLDs should be considered as they may leach out into the AMD and increase the costs of post-treatment. Therefore, it is imperative to keep the dosages as low as possible. The pH at which other metals precipitate is vital in choosing the GLDs feed quantities. Thus, some may be immobilised by adding excess neutralising reagent.

***Table 5*: Chemical composition and properties of AMD samples used in a study by [108]**

SAMPLE	SO_4^{2-}	Al	As	Ca	Cd	Cu	Cr	Fe	K	Mg	Mn	Ni	Si	Zn	pH	EC	Eh
$\mathbf{AMD_{CM}}^{*}$	3783	95	0.45	284	0.43	2.2	3.7#	348	2.2	324	17	0.81	40	399	3.61	5.09	510
$\mathbf{AMD_{CM}}^{+}$	24	100	100	-	75	100	100	100	-	-	-	47	-	32	6.60	6.01	
$\mathbf{AMD_{TH}}^{*}$	15558	657	1.6	272	0.88	54	0.18	2172	3.5	1423	109	4.2	32	332	2.62	11.09	605
$\mathbf{AMD_{TH}}^{+}$	38	100	100	-	74	100	100	100	-	-	-	70	-	64	6.01	8.57	

* Mineral concentrations are in (mg/L) except for # which is in µg/L before treatment

+Mineral removal efficiency in % (after treatment)

-Not accounted for in terms of removal efficiency

EC = Electrical conductivity (mS/cm)

Eh = Redox potential(mV)

4.0. Cost-benefit analysis: Limestone vs. GLDs

To ascertain potential benefits that may be achieved by replacing limestone with GLDs, we performed a simple cost-benefit analysis, Table 6. Available GLDs at the reference local mills is about 100,000 tons/year. Based on our experimental data, the optimum GLD dosage is 1 g/l. The volume of AMD treat was at 25(m^3/day), as at the local reference AMD treatment plant. This translates to approximately 7.5 tons/year of GLDs. Therefore, enough amount of GLDs available may be sufficient to run at least 1000 AMD plant with the same capacity as the reference plant. The process cost (labour, utility, and maintenance excluded) is almost 17 % less than that of the limestone-based neutralisation process. The distance from the Kraft pulp to the AMD plant, however, should be limited to 20 km.

GLDs application discussed in this review represents a good starting point for future commercial applications of GLDS. Cost-benefit analysis favours the use of GLD against limestone. However, the distance from the Kraft pulp to the AMD plant should be limited to 20 km. It is also worth noting that characteristics of the dregs, differ significantly and are mill specific. This implies that there is no single solution for all dregs, and it is imperative that dregs produced at each mill be evaluated so that potential applications can be determined. The overall process economics GLDs/lime process vs. limestone/lime process, pilot trials, and detailed process design and economic analyses.

Another option, depending on the quantities of the AMD that is being treated, may be to adopt the recently developed macro-algae (sea-weed) facilitated aerobic wetland to polish the GLDs treated AMD [165], [166]. This inventory is based on the competitive advantage that the macro-algae that were explored do not suffer from having low metabolic activity during the cold season as compared to the traditionally used macrophytes and microbials. Furthermore, the effectiveness of the macro-algae species (*Oedogonium crassum, Klebsormidium acidophilum,* and *Microspora quadrata*) is based on the fact that their metal content need increases with the increasing metal concentrations of their surrounding environment. Generally, the species were used to absorb Al, Fe, Mg, Mn, and ZN from AMD at varying pH levels viz.; 3, 5, and 7. The outcome of the study showed that *O. crassum* was the most effective species, followed by *K.klebsii* and *M. Tumudula.* In addition, pH levels seemed to affect the rate of these metals bioaccumulation. That is, metal accumulation increased with increasing pH levels [167].

In 2018, Oberholter *et al*. took this study further by conducting a pilot study on using the same macro-algae species for removal of S, Mg, Ca, and P in a pilot scale. In this study, the macro-algae species were subjected to the AMD with different pH levels (3, 5, 6.4, and 7). The study showed that *M. tumudula* was the most significant species to absorb S and P. This was most efficient at pH 5 and 7, respectively. High bioaccumulation of metals (Ca and Mg) by *O. crassum* that was reported in the previous study was also confirmed in this study. The effectiveness of these species to absorb S and dissolved metals together with the added advantage that they absorb better at higher pH values make the inventory to be a good post-treatment for GLDs treated AMD.

Table 6: AMD treatment costs: limestone vs. GLDs

Neutralizing agent	Dosage rate (g/L)	AMD flow rate (m^3/day)	Volume of AMD treated (m^3/year)	Limestone consumed (ton/year)	Cost of neutralizing agent (R/year)	Process cost (R/ m^3)	Remarks
Limestone -S	4	25	7 5 00	30	18 000	2.4	Reference plant
GLD -S	4	25	7500	30	14 310	1.9*	
	4	25	7500	30	35 775	4.77**	
Limestone -E	1	25	7 500	7.5	4 500	0.6	
GLD - E	1	25	7500	7.5	3 576	0.5*	
	1	25	7500	7.5	8 944	1.2**	
	1	25	7500	7.5	17 888	2.5***	

- The price of limestone is R 600 per ton (pricing 2016).
- Price of GLD (refer to transport cost only: R 23.85 /km/ton, 2016 pricing)
- The plant operating 300 days per annum.
- The AMD flow rate is 25 m^3/day (as the reference plant).
- Limestone – E denotes that cost estimation is based on experimental data
- Limestone – S & GLDs – S denotes that cost estimation is based on a reference plant, but the AMD characteristics differ from the one used in this study.
- **Note**: *refers to 20 Km distance from the pulp mill to the AMD plant,

  ** refers to 50 Km distance from the pulp mill to the AMD plant,

  *** refers to100 Km distance from the pulp mill to the AMD plant.

5.0. Summary

Conventional methods of using naturally sourced materials for handling AMD are not only causing ecological disturbances, but they are also led to depletion of these resources. Thus, there is a need to use alternative AMD treatment procedures that are sustainable and eco-friendly. This review indicates that GLDs can be used as such an alternative for the treatment of AMD. Its use is a symbiotic process that is beneficial to both the mining and chemical pulp leading to avoidance of disposal a hazardous waste (GLDs) in landfills and emission of hazardous wastes (AMD) into the environment – a beneficial contribution to the circular economy.

However, its use and applicability may be limited by several factors, including:

- Characteristics of GLDs that are mill specific: this means that there could never be a universal way of using GLDs in treating AMD just as there is no universal way of treating AMD. Therefore, every GLDs produced should be characterised before valorisation for AMD treatment.
- Transportation costs between AMD and GLDs sources may be prohibitive.
- Post-treatment costs of AMD may be high if GLDs dosages are not optimised. The costs are related to the leaching of NPEs from GLDs into the AMD during treatment.
- The quality of the GLD concerning its constituent quantities of calcite will affect its AMD treatment efficacy.

Furthermore, research concerning the upscaling of the already available experimental work needs to be conducted, the longevity of using GLDs in sealing layers and in blending them with tailings, post-treatment and its costs need to be studied and evaluated, and possible repurposing of the wastes that may be produced during AMD handling. In pursuit of using ecologically sound methods of treating AMD, polishing off the neutralised AMD with algal biomass that absorbs metals from the water should be explored.

Acknowledgements

The authors of this article would like to thank the Council of Scientific and Industrial Research (CSIR), National Research Foundation (NRF), and University of KwaZulu-Natal (UKZN) for their financial support.

References

[1] N. National Environmental Management: Waste Act, *Government Gazette*, vol. 525, no. 3. South Africa, 2009.

[2] U. Nations, ‘General Assembley 70 session:Transforming our world: the 2030 Agenda for Sustainable Development’, *General Assembley 70 session*, vol. 16301, no. October. pp. 1–35, 2015, doi: 10.1007/s13398-014-0173-7.2.

[3] J. Johakimu, T. Bush, and L. A. Lucia, ‘Green liquor impregnation and kraft pulping of South African Pinus Patula- A practical approach to provide cost savings in a kraft mill’s pulping operation’, *Tappsa J.*, vol. 2, p. 6, 2011.

[4] C. Biermann, *Handbook of Pulping and Papermaking*, Second. Sand Dieogo, California: Elsevier, 1996.

[5] P. Bajpai, *Biotechnology for Pulp and Paper Processing*. Singapore: Springer Singapore, 2018.

[6] V. Ribeiro dos Santos, M. Dezena Cabrelon, E. de Sousa Trichês, and E. Quinteiro, ‘Green liquor dregs and slaker grits residues characterization of a pulp and paper mill for future application on ceramic products’, *J. Clean. Prod.*, vol. 240, 2019, doi: 10.1016/j.jclepro.2019.118220.

[7] M. Mäkitalo, J. Mácsik, C. Maurice, and B. Öhlander, ‘Improving Till by Adding Green Liquor Dregs in Sealing Layers to Control AMD–A Pilot Study’, in *mwen.info*, 2015, p. 7.

[8] H. Tran and E. K. Vakkilainnen, ‘The Kraft Chemical Recovery Process’, *TAPPI Kraft Recover. Course*, pp. 1–8, 2008.

[9] Department of environmental Affairs (DEA), *National Pricing Strategy for Waste*

Management (NPSWM), vol. 904, no. 40200. 2016, p. 48.

[10] M. Mäkitalo, C. Maurice, Y. Jia, and B. Öhlander, 'Characterization of Green Liquor Dregs, Potentially Useful for Prevention of the Formation of Acid Rock Drainage', *Minerals*, vol. 4, no. 2, pp. 330–344, 2014, doi: 10.3390/min4020330.

[11] P. Farage, A. Augusta, and P. Rezende, 'Intermediate covering of municipal solid waste land fi lls with alkaline grits , dregs and lime mud by-products of kraft pulp production', *J. Clean. Prod.*, vol. 239, pp. 1–8, 2019, doi: 10.1016/j.jclepro.2019.117985.

[12] C. M. Torres, C. M. Silva, L. G. Pedroti, W. E. Fernandes, F. C. . Ballotin, and J. C. Zanuncio, 'Cement Portland production with dregs and grits from kraft pulp mills incorporated to clinker', *6th Int. Work. | Adv. Clean. Prod.*, 2017.

[13] H. Nurmesniemi, R. Pöykiö, P. Perämäki, and T. Kuokkanen, 'The use of a sequential leaching procedure for heavy metal fractionation in green liquor dregs from a causticizing process at a pulp mill', *Chemosphere*, vol. 61, no. 10, pp. 1475–1484, 2005, doi: 10.1016/j.chemosphere.2005.04.114.

[14] K. R. Sebogodi, J. K. Johakimu, and B. B. Sithole, 'Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa', *J. Clean. Prod.*, vol. 246, p. 118979, Oct. 2020, doi: 10.1016/j.jclepro.2019.118979.

[15] R. Modolo, A. Benta, V. M. Ferreira, and L. M. Machado, 'Pulp and paper plant wastes valorisation in bituminous mixes', *Waste Manag.*, vol. 30, no. 4, pp. 685–696, 2010, doi: 10.1016/j.wasman.2009.11.005.

[16] D. Ragnvaldsson *et al.*, 'A novel method for reducing acid mine drainage using green liquor dregs', *Environ. Chem. Lett.*, vol. 12, no. 3, pp. 443–447, 2014, doi: 10.1007/s10311-014-0469-z.

[17] K. K. Kefeni, T. A. M. Msagati, and B. B. Mamba, 'Acid mine drainage: Prevention, treatment options, and resource recovery: A review', *J. Clean. Prod.*, vol. 151, pp. 475–493, 2017, doi: 10.1016/j.jclepro.2017.03.082.

[18] I. Park *et al.*, 'A review of recent strategies for acid mine drainage prevention and

mine tailings recycling', *Chemosphere*, vol. 219, pp. 588–606, 2019, doi: 10.1016/j.chemosphere.2018.11.053.

[19] S. Trope, 'An in depth look back at South Africa's mining history', *Living Lifestyle*, 2016. http://www.living-lifestyle.co.za/an-in-depth-look-back-at-south-africas-mining-history/ (accessed May 14, 2020).

[20] S. Matsumoto, H. Shimada, and T. Sasaoka, 'The Key Factor of Acid Mine Drainage (AMD) in the History of the Contribution of Mining Industry to the Prosperity of the United States and South Africa: A Review', *Nat. Resour.*, vol. 07, no. 07, pp. 445–460, 2016, doi: 10.4236/nr.2016.77039.

[21] Mineral Council, 'Mining in SA - Minerals Council South Africa', *Mineral Council South Africa*, 2020. https://www.mineralscouncil.org.za/sa-mining (accessed May 14, 2020).

[22] Victor Munnik, G. Hochmann, M. Hlabane, and Stephen Law, 'The Social and Environmental Consequences of Coal Mining in South Africa: A Case Study', Cape Town, 2010.

[23] N. Mokonyane, 'Disused mines: what's being done? | SAnews', *South African Government News Agency*, 2015. https://www.sanews.gov.za/south-africa/disused-mines-what's-being-done (accessed May 14, 2020).

[24] D. B. Johnson and K. B. Hallberg, 'Acid mine drainage remediation options: A review', *Sci. Total Environ.*, vol. 338, no. 1-2 SPEC. ISS., pp. 3–14, 2005, doi: 10.1016/j.scitotenv.2004.09.002.

[25] T. S. McCarthy, 'The impact of acid mine drainage in South Africa', *S. Afr. J. Sci.*, vol. 107, no. 5/6, pp. 1–7, 2011, doi: 10.4102/sajs.v107i5/6.712.

[26] P. C. Singer and W. Stumm, 'Acidic Mine Drainage: The Rate-Determining Step', *Science (80-.).*, vol. 167, no. 3921, pp. 1121–1123, Feb. 1970, doi: 10.1126/science.167.3921.1121.

[27] V. Masindi, M. S. Osman, and A. M. Abu-Mahfouz, 'Integrated treatment of acid mine drainage using BOF slag, lime/soda ash and reverse osmosis (RO): Implication for the production of drinking water', *Desalination*, vol. 424, no.

September, pp. 45–52, 2017, doi: 10.1016/j.desal.2017.10.002.

[28] A. G. Udayabhanu and B. Prasad, ‘Studies on environmental impact of acid mine drainage generation and its treatment: an appraisal’, *Indian J. Environ. Prot.*, vol. 30, no. 11, p. 15, 2010.

[29] V. Masindi, V. Akinwekomi, J. P. Maree, and K. L. Muedi, ‘Comparison of mine water neutralisation efficiencies of different alkaline generating agents’, *J. Environ. Chem. Eng.*, vol. 5, no. 4, pp. 3903–3913, 2017, doi: 10.1016/j.jece.2017.07.062.

[30] E. Fosso-Kankeu, A. Manyatshe, and F. Waanders, ‘Mobility potential of metals in acid mine drainage occurring in the Highveld area of Mpumalanga Province in South Africa: Implication of sediments and efflorescent crusts’, *Int. Biodeterior. Biodegrad.*, vol. 119, pp. 661–670, 2017, doi: 10.1016/j.ibiod.2016.09.018.

[31] H. Tutu, T. S. McCarthy, and E. Cukrowska, ‘The chemical characteristics of acid mine drainage with particular reference to sources, distribution and remediation: The Witwatersrand Basin, South Africa as a case study’, *Appl. Geochemistry*, vol. 23, no. 12, pp. 3666–3684, 2008, doi: 10.1016/j.apgeochem.2008.09.002.

[32] G. A. Jones, S. E. Brierly, S. J. J. Geldenhuis, and J. R. Howard, ‘Research on the Contribution of Mine Dumps to the Mineral Pollution Load at the Vaal Barrage’, *Water Res. Comm. Rep.*, no. 136/1, p. 89, 1988.

[33] K. Naicker, E. Cukrowska, and T. S. McCarthy, ‘Acid mine drainage arising from gold mining activity in Johannesburg, South Africa and environs’, *Environ. Pollut.*, vol. 122, no. 1, pp. 29–40, 2003, doi: 10.1016/s0269-7491(02)00281-6.

[34] Gardguide, ‘Chapter 2 - GARDGuide’, *The International Network for Acid Prevention INAP*, 2012. http://www.gardguide.com/index.php/Chapter_2 (accessed Apr. 27, 2020).

[35] J. Pope, N. Newman, D. Craw, D. Trumm, and R. Rait, ‘Factors that influence coal mine drainage chemistry West Coast, South Island, New Zealand’, *New Zeal. J. Geol. Geophys.*, vol. 53, no. 2–3, pp. 115–128, 2010, doi: 10.1080/00288306.2010.498405.

[36] T. I. Ojonimi, F. Asuke, M. A. Onimisi, and Y. Onuh, ‘Acid Mine Drainage (AMD): an environmental concern generated by coal mining Acid’, *J. Degrad. Min. Lands Manag.*, vol. 6, no. 4, pp. 1875–1881, 2019, doi: 10.15243/jdmlm.2019.064.1875.

[37] N. Belzile, Y.-W. Chen, M.-F. Cai, and Y. Li, ‘A review on pyrrhotite oxidation’, *J. Geochemical Explor.*, vol. 84, no. 2, pp. 65–76, Sep. 2004, doi: 10.1016/J.GEXPLO.2004.03.003.

[38] N. F. Gray, ‘Environmental impact and remediation of acid mine drainage: A management problem’, *Environ. Geol.*, 1997, doi: 10.1007/s002540050133.

[39] G. Street, ‘Impact of Temperature on the Rate of Formation of Sulfuric Acid in Mine Tailings’, vol. 32, no. 4, pp. 1155–1157, 2013, doi: 10.1002/ep.

[40] Y. Yunmei, Z. Yongxuan, A. E. Williams-jones, and G. Zhenmin, ‘A kinetic study of the oxidation of arsenopyrite in acidic solutions : implications for the environment’, vol. 19, pp. 435–444, 2004, doi: 10.1016/S0883-2927(03)00133-1.

[41] H. Anawar, ‘Impact of climate change on acid mine drainage generation and contaminant transport in water ecosystems of semi-arid and arid mining areas’, *Phys. Chem. Earth*, vol. 58–60, pp. 13–21, 2013, doi: 10.1016/j.pce.2013.04.002.

[42] C. L. Corkhill and D. J. Vaughan, ‘Applied Geochemistry Arsenopyrite oxidation – A review’, *Appl. Geochemistry*, vol. 24, no. 12, pp. 2342–2361, 2009, doi: 10.1016/j.apgeochem.2009.09.008.

[43] S. A. Waksman, ‘Microörganisms Concerned in the Oxidation of Sulfur in the Soil: IV. A Solid Medium for the Isolation and Cultivation of Thiobacillus thiooxidans.’, *J. Bacteriol.*, 1922.

[44] W. W. LEATHEN, S. A. BRALEY, and L. D. MCINTYRE, ‘The role of bacteria in the formation of acid from certain sulfuritic constituents associated with bituminous coal. II. Ferrous iron oxidizing bacteria.’, *Appl. Microbiol.*, 1953.

[45] J. F. Durand, J. Meeuvis, and M. Fourie, ‘The threat of mine effluent to the UNESCO status of the Cradle of Humankind World Heritage Site’, *J. Transdiscipl. Res. South. Africa*, vol. 6, no. 1, pp. 73–92, 2010, doi: 10.4102/td.v6i1.125.

[46] S. Naidoo, *Acid Mine Drainage in South Africa: Development Actors, Policy Impacts,*

and Broader Implications. 2017.

[47] Havard Law School International Human Rights Clinic, *The Cost of Gold: Environmental, Health, and Human Rights Consequences of Gold Mining in South Africa's West and Central Rand*. 2016.

[48] J. L. Gardea-Torresdey, J. R. Peralta-Videa, G. de la Rosa, and J. G. Parsons, 'Phytoremediation of heavy metals and study of the metal coordination by X-ray absorption spectroscopy', *Coord. Chem. Rev.*, vol. 249, no. 17–18, pp. 1797–1810, Sep. 2005, doi: 10.1016/J.CCR.2005.01.001.

[49] S. K. Sethy and S. Ghosh, 'Effect of heavy metals on germination of seeds.', *J. Nat. Sci. Biol. Med.*, vol. 4, no. 2, pp. 272–5, Jul. 2013, doi: 10.4103/0976-9668.116964.

[50] T. Medinski, 'SOIL CHEMICAL AND PHYSICAL PROPERTIES AND THEIR INFLUENCE ON THE PLANT SPECIES RICHNESS OF ARID SOUTH-WEST AFRICA', no. March, 2007.

[51] P. Singh and A. Nel, 'A comparison between *Daphnia pulex* and *Hydra vulgaris* as possible test organisms for agricultural run-off and acid mine drainage toxicity assessments', *Water SA*, vol. 43, no. 2, p. 323, 2017, doi: 10.4314/wsa.v43i2.15.

[52] J. Dabrowski, P. J. Oberholster, J. M. Dabrowski, J. Le Brasseur, and J. Gieskes, 'Chemical characteristics and limnology of Loskop Dam on the Olifants River (South Africa), in light of recent fish and crocodile mortalities', *Water SA*, vol. 39, no. 5, p. 675, 2013, doi: 10.4314/wsa.v39i5.12.

[53] J. Holman, 'Coal giant recognises water management responsibility', *Creamer Engineering News*, 2008. .

[54] P. J. Oberholster, J. G. Myburgh, P. J. Ashton, and A. M. Botha, 'Responses of phytoplankton upon exposure to a mixture of acid mine drainage and high levels of nutrient pollution in Lake Loskop, South Africa', *Ecotoxicol. Environ. Saf.*, 2010, doi: 10.1016/j.ecoenv.2009.08.011.

[55] F. Solomon, 'Impacts of metals on aquatic ecosystems and human health', 2008.

[56] R. Singh, N. Gautam, A. Mishra, and R. Gupta, 'Heavy metals and living systems: An overview', *Indian J. Pharmacol.*, vol. 43, no. 3, p. 246, 2011, doi: 10.4103/0253-

7613.81505.

[57] M. Monachese, J. P. Burton, and G. Reid, ‘Bioremediation and Tolerance of Humans to Heavy Metals through Microbial Processes: a Potential Role for Probiotics?’, *Appl. Environ. Microbiol.*, vol. 78, no. 18, pp. 6397–6404, 2012, doi: 10.1128/aem.01665-12.

[58] W. E. Sharpe and R. S. Adams, ‘HR502686 AR502687’, 1998.

[59] J. F. Durand, ‘The impact of gold mining on the Witwatersrand on the rivers and karst system of Gauteng and North West Province, South Africa’, *J. African Earth Sci.*, vol. 68, pp. 24–43, 2012, doi: 10.1016/j.jafrearsci.2012.03.013.

[60] V. P. (Bill) Evangelou and Y. L. Zhang, ‘A review: Pyrite oxidation mechanisms and acid mine drainage prevention’, *Crit. Rev. Environ. Sci. Technol.*, vol. 25, no. 2, pp. 141–199, May 1995, doi: 10.1080/10643389509388477.

[61] B. G. Lottermoser, *Mine Wastes: Characterization, Treatment and Environmental Impacts*. Springer Berlin Heidelberg, 2010.

[62] M. Zhang and H. Wang, ‘Utilization of Bactericide Technology for Pollution Control of Acidic Coal Mine Waste’, *Adv. Eng. Res.*, vol. 129, no. Iceesd, pp. 667–670, 2017, doi: 10.2991/iceesd-17.2017.120.

[63] M. F. Cai, Z. Dang, Y. W. Chen, and N. Belzile, ‘The passivation of pyrrhotite by surface coating’, *Chemosphere*, vol. 61, no. 5, pp. 659–667, 2005, doi: 10.1016/j.chemosphere.2005.03.032.

[64] Y. W. Chen, Y. Li, M. F. Cai, N. Belzile, and Z. Dang, ‘Preventing oxidation of iron sulfide minerals by polyethylene polyamines’, *Miner. Eng.*, vol. 19, no. 1, pp. 19–27, 2006, doi: 10.1016/j.mineng.2005.04.007.

[65] P. Ačai, E. Sorrenti, T. Gorner, M. Polakovič, M. Kongolo, and P. de Donato, ‘Pyrite passivation by humic acid investigated by inverse liquid chromatography’, *Colloids Surfaces A Physicochem. Eng. Asp.*, vol. 337, no. 1–3, pp. 39–46, 2009, doi: 10.1016/j.colsurfa.2008.11.052.

[66] R. Pérez-López, J. Cama, J. M. Nieto, and C. Ayora, ‘The iron-coating role on the oxidation kinetics of a pyritic sludge doped with fly ash’, *Geochim. Cosmochim.*

Acta, vol. 71, no. 8, pp. 1921–1934, 2007, doi: 10.1016/j.gca.2007.01.019.

[67] R. Fan *et al.*, ‘The Formation of Silicate-Stabilized Passivating Layers on Pyrite for Reduced Acid Rock Drainage’, *Environ. Sci. Technol.*, vol. 51, no. 19, pp. 11317–11325, 2017, doi: 10.1021/acs.est.7b03232.

[68] Z. Diao *et al.*, ‘Silane-based coatings on the pyrite for remediation of acid mine drainage’, *Water Res.*, vol. 47, no. 13, pp. 4391–4402, 2013, doi: 10.1016/j.watres.2013.05.006.

[69] Y. Ouyang *et al.*, ‘Pyrite oxidation inhibition by organosilane coatings for acid mine drainage control’, *Miner. Eng.*, vol. 72, pp. 57–64, 2015, doi: 10.1016/j.mineng.2014.12.020.

[70] J. Liu, L. Zhou, F. Dong, and K. A. Hudson-Edwards, ‘Enhancing As(V) adsorption and passivation using biologically formed nano-sized FeS coatings on limestone: Implications for acid mine drainage treatment and neutralization’, *Chemosphere*, vol. 168, pp. 529–538, 2017, doi: 10.1016/j.chemosphere.2016.11.037.

[71] I. Park, C. B. Tabelin, K. Seno, S. Jeon, M. Ito, and N. Hiroyoshi, ‘Simultaneous suppression of acid mine drainage formation and arsenic release by Carrier-microencapsulation using aluminum-catecholate complexes’, *Chemosphere*, vol. 205, pp. 414–425, 2018, doi: 10.1016/j.chemosphere.2018.04.088.

[72] I. Park, C. Baltazar, K. Magaribuchi, and K. Seno, ‘Suppression of the release of arsenic from arsenopyrite by carrier-microencapsulation using Ti-catechol complex’, *J. Hazard. Mater.*, vol. 344, pp. 322–332, 2018, doi: 10.1016/j.jhazmat.2017.10.025.

[73] X. Li, N. Hiroyoshi, C. B. Tabelin, K. Naruwa, C. Harada, and M. Ito, ‘Suppressive effects of ferric-catecholate complexes on pyrite oxidation’, *Chemosphere*, vol. 214, pp. 70–78, 2019, doi: 10.1016/j.chemosphere.2018.09.086.

[74] M. Mbonimpa, M. Aubertin, M. Aachib, and B. Bussière, ‘Diffusion and consumption of oxygen in unsaturated cover materials’, *Can. Geotech. J.*, vol. 40, no. 5, pp. 916–932, 2003, doi: 10.1139/t03-040.

[75] B. Bussière, M. Benzaazoua, M. Aubertin, and M. Mbonimpa, ‘A laboratory study of

covers made of low-sulphide tailings to prevent acid mine drainage', *Environ. Geol.*, vol. 45, no. 5, pp. 609–622, 2004, doi: 10.1007/s00254-003-0919-6.

[76] E. Mylona, A. Xenidis, and I. Paspaliaris, 'Inhibition of acid generation from sulphidic wastes by the addition of small amounts of limestone', *Miner. Eng.*, vol. 13, no. 10, pp. 1161–1175, 2000, doi: 10.1016/S0892-6875(00)00099-6.

[77] S. Miller, Y. Rusdinar, R. Smart, J. Andrina, and D. Richards, 'Design and Construction of Limestone Blended Waste Rock Dumps - Lessons Learned From a 10-Year Study At Grasberg', vol. 2006, no. 2, pp. 1287–1301, 2006, doi: 10.21000/jasmr06021287.

[78] C. B. Tabelin *et al.*, 'Arsenic, selenium, boron, lead, cadmium, copper, and zinc in naturally contaminated rocks: A review of their sources, modes of enrichment, mechanisms of release, and mitigation strategies', *Sci. Total Environ.*, vol. 645, pp. 1522–1553, 2018, doi: 10.1016/j.scitotenv.2018.07.103.

[79] J. Skousen *et al.*, 'Review of Passive Systems for Acid Mine Drainage Treatment', *Mine Water Environ.*, vol. 36, no. 1, pp. 133–153, Mar. 2017, doi: 10.1007/s10230-016-0417-1.

[80] J. G. Skousen, P. F. Ziemkiewicz, and L. M. McDonald, 'Acid mine drainage formation, control and treatment: Approaches and strategies', *Extr. Ind. Soc.*, vol. 6, no. 1, pp. 241–249, 2019, doi: 10.1016/j.exis.2018.09.008.

[81] J. Taylor, S. Pape, and N. Murphy, 'A Summary of Passive and Active Treatment Technologies for Acid and Metalliferous Drainage (AMD)', *Proc. 5th Aust. Work. Acid Drain.*, no. 29, pp. 1–49, 2005.

[82] B. Gazea, K. Adam, and A. Kontopoulos, 'A review of passive systems for the treatment of acid mine drainage', *Miner. Eng.*, vol. 9, no. 1, pp. 23–42, Jan. 1996, doi: 10.1016/0892-6875(95)00129-8.

[83] P. L. Younger, S. A. Banwart, and R. S. Hedin, 'Mine Water Hydrology', *Mine Water*. Springer Netherlands, pp. 127–270, 2002, doi: 10.1007/978-94-010-0610-1_3.

[84] C. Zipper and J. Skousen, 'Passive Treatment of Acid Mine Drainage', *Acid Mine Drainage, Rock Drainage, and Acid Sulfate Soils*. John Wiley & Sons, Inc., pp. 339–

353, 2014, doi: 10.1002/9781118749197.ch30.

[85] J. J. Schoeman and A. Steyn, ‘Investigation into alternative water treatment technologies for the treatment of underground mine water discharged by Grootvlei Proprietary Mines Ltd into the Blesbokspruit in South Africa’, *Desalination*, vol. 133, no. 1, pp. 13–30, 2001, doi: 10.1016/s0011-9164(01)00079-0.

[86] C. Wolkersdorfer and R. Bowell, ‘Contemporary Reviews of Mine Water Studies in Europe, Part 1’, *Mine Water Environ.*, vol. 23, no. 4, pp. 162–182, 2004, doi: 10.1007/s10230-004-0060-0.

[87] D. . Everett, J. Du Plesis, and H. W. Gussman, ‘THE TREATMENT OF UNDERGROUND MINE WATERS FOR THE REMOVAL OF CALCIUM AND SULPHATES BY A GYP-CIX PROCESS ABSTRACT’, in *International Mine Water Association Symposium 1993*, 1993, no. 1, p. 29.

[88] D. Howard, C. Grobler, R. E. G. Robinson, and P. M. Cole, ‘SUSTAINABLE PURIFICATION OF MINE WATER USING ION EXCHANGE TECHNOLOGY’, no. October, pp. 447–453, 2009.

[89] Ö. Yavuz, Y. Altunkaynak, and F. Güzel, ‘Removal of copper, nickel, cobalt and manganese from aqueous solution by kaolinite’, *Water Res.*, vol. 37, no. 4, pp. 948–952, 2003, doi: 10.1016/s0043-1354(02)00409-8.

[90] F. Rouquerol, J. Rouquerol, K. S. W. Sing, G. Maurin, and P. Llewellyn, ‘Introduction’, *Adsorption by Powders and Porous Solids*. Elsevier, pp. 1–24, 2014, doi: 10.1016/b978-0-08-097035-6.00001-2.

[91] T. Motsi, N. A. Rowson, and M. J. H. Simmons, ‘Adsorption of heavy metals from acid mine drainage by natural zeolite’, *Int. J. Miner. Process.*, vol. 92, no. 1–2, pp. 42–48, Jul. 2009, doi: 10.1016/J.MINPRO.2009.02.005.

[92] C. A. Cravotta III and C. S. Kirby, ‘ACIDITY AND ALKALINITY IN MINE DRAINAGE: PRACTICAL CONSIDERATIONS’, *J. Am. Soc. Min. Reclam.*, vol. 2004, no. 1, pp. 334–365, 2004, doi: 10.21000/jasmr04010334.

[93] T. Ramontja *et al.*, ‘Mine Water Management in the Witwatersrand Gold Fields

With Special Emphasis on Acid Mine Drainage', Jan. 2011.

[94] D. B. Johnson, 'Chemical and microbiological characteristics of mineral spoils and drainage waters at abandoned coal and metal mines', *Water, Air, Soil Pollut. Focus*, vol. 3, no. 1, pp. 47–66, 2003, doi: 10.1023/A:1022107520836.

[95] V. R. K. Vadapalli, J. N. Zvimba, M. Mathye, H. Fischer, and L. Bologo, 'Acid mine drainage neutralization in a pilot sequencing batch reactor using limestone from a paper and pulp industry', *Environ. Technol. (United Kingdom)*, vol. 36, no. 19, pp. 2515–2523, 2015, doi: 10.1080/09593330.2015.1036786.

[96] G. Madzivire, L. F. Petrik, W. M. Gitari, G. Balfour, V. R. K. Vadapalli, and T. V Ojumu, 'Role of Ph on Sulphate Removal From Circumneutral Mine Water Using Coal Fly Ash', in *International Mine Water Conference*, 2009, no. 19-23 October, pp. 462–471.

[97] S. S. Potgieter-Vermaak, J. H. Potgieter, P. Monama, and R. Van Grieken, 'Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage', *Miner. Eng.*, vol. 19, no. 5, pp. 454–462, 2006, doi: 10.1016/j.mineng.2005.07.009.

[98] D. G. McDonald and A. F. Grandt, 'Limestone-Lime Treatment of Acid Mine Drainage- Full Scale', 1981. doi: EPA-600/S7-81-033.

[99] J. P. Maree, M. de Beer, W. F. Strydom, A. D. M. Christie, and F. B. Waanders, 'Neutralizing Coal Mine Effluent with Limestone to Decrease Metals and Sulphate Concentrations', *Mine Water Environ.*, vol. 23, no. 2, pp. 81–86, 2004, doi: 10.1007/s10230-004-0043-1.

[100] A. J. Geldenhuys, J. P. Maree, M. De Beer, and P. Hlabela, 'An integrated limestone / lime process for partial sulphate removal', no. May 2002, pp. 345–354, 2003.

[101] R. C. Wilmoth, 'Combination limestone-lime neutralization of ferrous iron acid mine drainage', US Environmental Protection Agency, Cincinnati, Ohio, 1978.

[102] V. Masindi, W. M. Gitari, H. Tutu, M. De Beer, and N. Nekhwevha, 'Neutralization and Attenuation of Metal Species in Acid Mine Drainage and Mine Leachates Using Magnesite: a Batch Experimental Approach', *An Interdiscip. Response to Mine*

Water Challenges, 2014.

[103] J. P. Maree, M. Mujuru, V. Bologo, N. Daniels, and D. Mpholoane, ‘Neutralisation treatment of AMD at affordable cost’, *Water SA*, vol. 39, no. 2, 2013, doi: 10.4314/wsa.v39i2.7.

[104] V. R. K. Vadapalli, J. N. Zvimba, M. Mathye, H. Fischer, and L. Bologo, ‘Acid mine drainage neutralization in a pilot sequencing batch reactor using limestone from a paper and pulp industry’, *Environ. Technol.*, vol. 36, no. 19, pp. 2515–2523, 2015, doi: 10.1080/09593330.2015.1036786.

[105] M. W. Gitari, L. F. Petrik, O. Etchebers, D. L. Key, E. Iwuoha, and C. Okujeni, ‘Treatment of Acid Mine Drainage with Fly Ash: Removal of Major Contaminants and Trace Elements’, *J. Environ. Sci. Heal. Part A*, vol. 41, no. 8, pp. 1729–1747, 2006, doi: 10.1080/10934520600754425.

[106] Kumar V.R. Vadapalli *et al.*, ‘Neutralization of acid mine drainage using fly ash, and strength development of the resulting solid residues’, *S. Afr. J. Sci.*, vol. 104, no. 7–8, pp. 317–322, 2008.

[107] L. F. Petrik, R. A. White, M. J. Klink, S. Vernon, C. L. Burgers, and M. V Fey, ‘Utilization of South African Fly Ash to Treat Acid Coal Mine Drainage , and Production of High Quality Zeolites from the Residual Solids’, vol. 2, 2003.

[108] R. Pérez-López, D. Quispe, J. Castillo, and J. M. Nieto, ‘Acid neutralization by dissolution of alkaline paper mill wastes and implications for treatment of sulfide-mine drainage’, *Am. Mineral.*, vol. 96, no. 5–6, pp. 781–791, 2011, doi: 10.2138/am.2011.3685.

[109] T. Motsi, N. A. Rowson, and M. J. H. Simmons, ‘Adsorption of heavy metals from acid mine drainage by natural zeolite’, *Int. J. Miner. Process.*, vol. 92, no. 1–2, pp. 42–48, 2009, doi: 10.1016/j.minpro.2009.02.005.

[110] X. Querol *et al.*, ‘Synthesis of zeolites from coal fly ash: an overview’, *Int. J. Coal Geol.*, vol. 50, no. 1–4, pp. 413–423, 2002, doi: 10.1016/s0166-5162(02)00124-6.

[111] M. De Beer, J. P. Maree, J. Wilsenach, S. Motaung, L. Bologo, and V. Radebe, ‘Acid Mine Water Reclamation using the ABC Process’, 2010.

[112] V. Bologo, J. P. Maree, and F. Carlsson, 'Application of magnesium hydroxide and barium hydroxide for the removal of metals and sulphate from mine water', *Water SA*, vol. 38, no. 1, 2012, doi: 10.4314/wsa.v38i1.4.

[113] J. P. Smit, 'THE TREATMENT OF POLLUTED MINE', in *International Mine Water Association 1999*, 1999, pp. 467–471.

[114] A. Neba, 'THE RHODES BioSURE PROCESS AND THE USE OF SUSTAINABILITY INDICATORS IN THE DEVELOPMENT OF BIOLOGICAL MINE WATER TREATMENT', 2006.

[115] Aveng, 'Aveng Water Blueprint for Treatment of AMD', 2009. http://www.avengwater.co.za/news-room/press-releases/emalahleni-blueprint-treatment-amd. (accessed May 15, 2017).

[116] C. J. M. Macdonald, 'Water usage in the South African pulp and paper industry', 2004.

[117] PAMSA, 'Industry Progress Report: Paper in Perspective', Johannesburg, 2016.

[118] PAMSA, 'South African Pulp and Paper Industry: Annual summary 2019 statistics', Johannesburg, 2019.

[119] Safiri, 'Eastern Cape Freight Databank-Forestry', *Eastern Cape Freight Databank-Forestry*, 2011. https://www.safiri.co.za/ec/forestry.html (accessed May 01, 2018).

[120] F. M. Martins, J. M. Martins, L. C. Ferracin, and C. J. da Cunha, 'Mineral phases of green liquor dregs, slaker grits, lime mud and wood ash of a Kraft pulp and paper mill', *J. Hazard. Mater.*, vol. 147, no. 1–2, pp. 610–617, 2007, doi: 10.1016/j.jhazmat.2007.01.057.

[121] M. J. Quina and C. T. Pinheiro, 'Inorganic waste generated in kraft pulp mills: The transition from landfill to industrial applications', *Appl. Sci.*, vol. 10, no. 7, 2020, doi: 10.3390/app10072317.

[122] M. Naqvi, J. Yan, and E. Dahlquist, 'Black liquor gasification integrated in pulp and paper mills: A critical review', *Bioresour. Technol.*, vol. 101, no. 21, pp. 8001–8015, 2010, doi: 10.1016/j.biortech.2010.05.013.

[123] M. Cardoso, É. D. de Oliveira, and M. L. Passos, 'Chemical composition and physical properties of black liquors and their effects on liquor recovery operation in Brazilian pulp mills', *Fuel*, vol. 88, no. 4, pp. 756–763, 2009, doi: 10.1016/j.fuel.2008.10.016.

[124] Y. Sewsynker-sukai, A. Naomi, and E. B. G. Kana, 'Recent developments in the application of Kraft pulping alkaline chemicals for lignocellulosic pretreatment: potential beneficiation of green liquor dregs waste', *Bioresour. Technol.*, no. March, p. 123225, 2020, doi: 10.1016/j.biortech.2020.123225.

[125] K. Manskinen, H. Nurmesniemi, and R. Pöykiö, 'Total and extractable non-process elements in green liquor dregs from the chemical recovery circuit of a semi-chemical pulp mill', *Chem. Eng. J.*, vol. 166, no. 3, pp. 954–961, 2011, doi: 10.1016/j.cej.2010.11.082.

[126] D. Sanchez and H. Tran, 'Treatment of lime slaker grit and green liquor dregs - Current practice', in *2005 TAPPI Engineering, Pulping, Environmental Conference - Conference Proceedings*, 2005, p. 9.

[127] P. (Pratima) Bajpai, *Environmentally friendly production of pulp and paper*. Wiley, 2013.

[128] A. Shrinath and B. Chris, 'A review of issues related to green liquor quality, and approaches towards improved clarification', in *Pulp and Paper International Congress*, pp. 1–10.

[129] M. Golmaei, T. Kinnarinen, E. Jernström, and A. Häkkinen, 'Study on the filtration characteristics of green liquor dregs', *Chem. Eng. J.*, vol. 317, pp. 471–480, 2017, doi: 10.1016/j.cej.2017.02.104.

[130] I. Moodley, C. M. Sheridan, U. Kappelmeyer, and A. Akcil, 'Environmentally sustainable acid mine drainage remediation: Research developments with a focus on waste/by-products', *Miner. Eng.*, vol. 126, no. August 2017, pp. 207–220, 2018, doi: 10.1016/j.mineng.2017.08.008.

[131] Komline-Sanderson, 'Rotary Drum Vacuum Filter | Komline-Sanderson'. http://www.komline.com/products/rotary-drum-vacuum-filter/ (accessed Jul. 18, 2019).

[132] M. C. Monte, E. Fuente, A. Blanco, and C. Negro, 'Waste management from pulp and paper production in the European Union', *Waste Manag.*, vol. 29, no. 1, pp. 293–308, Jan. 2009, doi: 10.1016/J.WASMAN.2008.02.002.

[133] K. Taylor and B. Mcguffie, 'Investigation of non-process element chemistry at Elk Falls mill - Green liquor clarifier and lime cycle', *Pulp Pap. Canada*, vol. 108, no. 2, pp. 27–32, 2007.

[134] R. Pöykö, H. Nurmesniemi, T. Kuokkanen, and P. Perämäki, 'Green liquor dregs as an alternative neutralizing agent at a pulp mill', *Environ. Chem. Lett.*, vol. 4, no. 1, pp. 37–40, 2006, doi: 10.1007/s10311-005-0031-0.

[135] L. Sartz, 'Alkaline by-products as amendments for remediation of historic mine sites', 2010.

[136] M. Mäkitalo, J. Mácsik, C. Maurice, and B. Öhlander, 'Improving Properties of Sealing Layers Made of Till by Adding Green Liquor Dregs to Reduce Oxidation of Sulfidic Mine Waste', *Geotech. Geol. Eng.*, vol. 33, no. 4, pp. 1047–1054, 2015, doi: 10.1007/s10706-015-9886-4.

[137] I. Martínez-Lage *et al.*, 'Concretes and mortars with waste paper industry: Biomass ash and dregs', *J. Environ. Manage.*, vol. 181, pp. 863–873, Oct. 2016, doi: 10.1016/j.jenvman.2016.06.052.

[138] R. M. Novais, J. Carvalheiras, L. Senff, and J. A. A. Labrincha, 'Upcycling unexplored dregs and biomass fly ash from the paper and pulp industry in the production of eco-friendly geopolymer mortars: A preliminary assessment', *Constr. Build. Mater.*, vol. 184, pp. 464–472, Sep. 2018, doi: 10.1016/j.conbuildmat.2018.07.017.

[139] T. Kinnarinen, M. Golmaei, E. Jernström, and A. Häkkinen, 'Separation, treatment and utilization of inorganic residues of chemical pulp mills', *J. Clean. Prod.*, vol. 133, pp. 953–964, 2016, doi: 10.1016/j.jclepro.2016.06.024.

[140] Y. Jia, C. Maurice, and B. Öhlander, 'Effect of the alkaline industrial residues fly ash, green liquor dregs, and lime mud on mine tailings oxidation when used as covering material', *Environ. Earth Sci.*, vol. 72, no. 2, pp. 319–334, Jul. 2014, doi: 10.1007/s12665-013-2953-3.

[141] A. H. Österås, I. Sunnerdahl, and M. Greger, 'The impact of wood ash and green liquor dregs application on Ca, Cu, Zn and Cd contents in bark and wood of Norway spruce', *Water. Air. Soil Pollut.*, vol. 166, no. 1–4, pp. 17–29, 2005, doi: 10.1007/s11270-005-7747-0.

[142] R. Modolo, A. Benta, V. M. Ferreira, and L. M. Machado, 'Pulp and paper plant wastes valorisation in bituminous mixes', *Waste Manag.*, vol. 30, no. 4, pp. 685–696, 2010, doi: 10.1016/j.wasman.2009.11.005.

[143] Y. Jia, C. Maurice, and B. Öhlander, 'Mobility of as, Cu, Cr, and Zn from tailings covered with sealing materials using alkaline industrial residues: a comparison between two leaching methods', *Environ. Sci. Pollut. Res.*, 2016, doi: 10.1007/s11356-015-5300-2.

[144] L. Alakangas, E. Andersson, and S. Mueller, 'Neutralization/prevention of acid rock drainage using mixtures of alkaline by-products and sulfidic mine wastes', *Environ. Sci. Pollut. Res.*, 2013, doi: 10.1007/s11356-013-1838-z.

[145] C. Maurice, L. Villain, and K. Hargelius, 'Green liquor dregs for the remediation of abandoned mine tailings – opportunities and limitations', *8th Int. Conf. Acid Rock Drain.*, pp. 1–6, 2009.

[146] Y. Jia, D. Stenman, M. Mäkitalo, C. Maurice, and B. Öhlander, 'Use of Amended Tailings as Mine Waste Cover', *Waste and Biomass Valorization*, vol. 4, no. 4, pp. 709–718, 2013, doi: 10.1007/s12649-013-9232-0.

[147] Y. Jia, C. Maurice, and B. Öhlander, 'Metal Mobilization in Tailings Covered with Alkaline Residue Products: Results from a Leaching Test Using Fly Ash, Green Liquor Dregs, and Lime MudMobilisierung von Metallen in Abraumhalden die mit alkalischen Rückständen abgedeckt wurden: Ergebnisse von ', *Mine Water Environ.*, vol. 34, no. 3, pp. 270–287, 2015, doi: 10.1007/s10230-014-0317-1.

[148] S. Sirén, C. Maurice, L. A.-12th I. M. Water, and U. 2016, 'Green liquor dregs in mine waste remediation, from laboratory investigations to field application', 2016.

[149] R. Pérez-López, J. Castillo, D. Quispe, and J. M. Nieto, 'Neutralization of acid mine drainage using the final product from CO2 emissions capture with alkaline paper

mill waste', *J. Hazard. Mater.*, vol. 177, no. 1–3, pp. 762–772, 2010, doi: 10.1016/j.jhazmat.2009.12.097.

[150] N. T. (Nigel T. . Faithfull, *Methods in agricultural chemical analysis : a practical handbook*. Cabi Pub, 2002.

[151] F. Cabral, H. M. Ribeiro, L. Hilário, L. Machado, and E. Vasconcelos, 'Use of pulp mill inorganic wastes as alternative liming materials', *Bioresour. Technol.*, vol. 99, no. 17, pp. 8294–8298, 2008, doi: 10.1016/j.biortech.2008.03.001.

[152] R. Pöykiö, H. Nurmesniemi, T. Kuokkanen, and P. Perämäki, 'Green liquor dregs as an alternative neutralizing agent at a pulp mill', *Environ. Chem. Lett.*, vol. 4, no. 1, pp. 37–40, 2006, doi: 10.1007/s10311-005-0031-0.

[153] R. Pöykiö, H. Nurmesniemi, T. Kuokkanen, and P. Perämäki, 'The use of a sequential leaching procedure for assessing the heavy metal leachability in lime waste from the lime kiln at a caustizicing process of a pulp mill', *Chemosphere*, vol. 65, no. 11, pp. 2122–2129, 2006, doi: 10.1016/j.chemosphere.2006.06.018.

[154] T. Zakir, 'Evaluation and Control of Pirssonite Scale Formation in Green Liquor Systems of the Kraft Process', University of Toronto, 2011.

[155] T. Zakir, H. Tran, and V. G. Papangelakis, 'Formed in the Kraft Mill Green Liquor', vol. 12, no. 1, pp. 53–59, 2013.

[156] U. Y. Stambulska, M. M. Bayliak, and V. I. Lushchak, 'Chromium(VI) toxicity in legume plants: Modulation effects of rhizobial symbiosis', *Biomed Res. Int.*, vol. 2018, no. Table 1, 2018, doi: 10.1155/2018/8031213.

[157] R. Jobby, P. Jha, A. K. Yadav, and N. Desai, 'Biosorption and biotransformation of hexavalent chromium [Cr(VI)]: A comprehensive review', *Chemosphere*, vol. 207, pp. 255–266, 2018, doi: 10.1016/j.chemosphere.2018.05.050.

[158] F. MARTINS, J. MARTINS, L. FERRACIN, and C. DACUNHA, 'Mineral phases of green liquor dregs, slaker grits, lime mud and wood ash of a Kraft pulp and paper mill', *J. Hazard. Mater.*, vol. 147, no. 1–2, pp. 610–617, 2007, doi: 10.1016/j.jhazmat.2007.01.057.

[159] M. Chaplin, 'Ice III (ice-three)', *Water structure and science*, 2011.

http://www1.lsbu.ac.uk/water/ice_iii.html (accessed Jan. 13, 2017).

[160] F. Bouchelaghem, ‘A numerical and analytical study on calcite dissolution and gypsum precipitation’, *Appl. Math. Model.*, vol. 34, no. 2, pp. 467–480, 2010, doi: 10.1016/j.apm.2009.06.004.

[161] A. N. Zaitsev, J. Keller, J. Spratt, E. N. Perova, and A. Kearsley, ‘Nyerereite-pirssonite-calcite-shortite relationships in altered natrocarbonatites, Oldoinyo Lengai, Tanzania’, *Can. Mineral.*, vol. 46, no. 4, pp. 843–860, 2008, doi: 10.3749/canmin.46.4.843.

[162] D. Feng, C. Aldrich, and H. Tan, ‘Treatment of acid mine water by use of heavy metal precipitation and ion exchange’, *Miner. Eng.*, vol. 13, no. 6, pp. 623–642, Jun. 2000, doi: 10.1016/S0892-6875(00)00045-5.

[163] CSIR, ‘Characterising the risk of human exposure and health impacts from acid mine drainage in South Africa’, no. March, pp. 1–183, 2013.

[164] J. P. Maree, G. J. Van Tonder, A. M. Van Niekerk, and C. Naidoo, ‘The collection , treatment and utilization of water accumulated in the coal mines located in the Upper Olifants River catchment’, no. March 2000. COALTECH 2020, 2000.

[165] P. J. Oberholster, P. H. Cheng, A. M. Botha, and B. Genthe, ‘The potential of selected macroalgal species for treatment of AMD at different pH rangesin temperate regions’, *Water Res.*, vol. 60, no. 21, pp. 82–92, 2014, doi: 10.1016/j.watres.2014.04.031.

[166] P. J. Oberholster, P. H. Cheng, A. M. Botha, P. Hobbs, and L. Hill, ‘Assessment of selected macroalgae for use in a biological hybrid system for treating sulphur in acid mine drainage (AMD)’, *J. Appl. Phycol.*, vol. 30, no. 2, pp. 1361–1370, 2018, doi: 10.1007/s10811-017-1314-0.

[167] P. J. Oberholster, P.-H. Cheng, A.-M. Botha, and B. Genthe, ‘The potential of selected macroalgal species for treatment of AMD at different pH ranges in temperate regions’, *Water Res.*, vol. 60, pp. 82–92, 2014, doi: 10.1016/j.watres.2014.04.031.

[168] G. Walser, ‘Economic impact of world mining’, *Uranium Prod. Cycle Environ.*, vol. 2, p. 86, 2000.

[169] V. Masindi, M. S. Osman, and R. Shingwenyana, 'Valorization of acid mine drainage (AMD): A simplified approach to reclaim drinking water and synthesize valuable minerals-Pilot study', *J. Environ. Chem. Eng.*, vol. 7, no. 3, p. 103082, 2019, doi: 10.1016/j.jece.2019.103082.

[170] G. S. Simate and S. Ndlovu, 'Acid mine drainage: Challenges and opportunities', *J. Environ. Chem. Eng.*, vol. 2, no. 3, pp. 1785–1803, 2014, doi: 10.1016/j.jece.2014.07.021.

[171] J. Skousen, A. Rose, G. Geidel, J. Foreman, R. Evans, and W. A. Hellier, 'Handbook of technologies for avoidance and remediation of acid mine drainage national mine land reclamation center', *West Virginia Univ. Morgat. WV*, vol. 132, 1998.

[172] S. E. Pratt, 'All that glitters...Acid Mine Drainage: The Toxic Legacy of Gold Mining in South Africa', *Earth*, vol. 56, no. 10, p. 30, 2011.

[173] R. Johnston, 'Arsenic and the 2030 Agenda for Sustainable Development', pp. 12–14, 2016, doi: 10.1201/b20466-7.

[174] A. C. Żołnowski, W. Sądej, M. S. Suski, A. Wyrwas, and D. Skrocki, 'Impact of Paper Mill Waste on Physicochemical Properties of Soil, Crop Yield, and Chemical Composition of Plants', *Clean - Soil, Air, Water*, vol. 1900080, pp. 1–8, 2019, doi: 10.1002/clen.201900080.

[175] M. S. Thopil, R. C. Bansal, L. Zhang, and G. Sharma, 'A review of grid connected distributed generation using renewable energy sources in South Africa', *Energy Strateg. Rev.*, vol. 21, no. August 2017, pp. 88–97, 2018, doi: 10.1016/j.esr.2018.05.001.

[176] V. Masindi, E. Chatzisymeon, I. Kortidis, and S. Foteinis, 'Assessing the sustainability of acid mine drainage (AMD) treatment in South Africa', *Sci. Total Environ.*, vol. 635, pp. 793–802, 2018, doi: 10.1016/j.scitotenv.2018.04.108.

[177] V. Masindi, M. S. Osman, R. N. Mbhele, and R. Rikhotso, 'Fate of pollutants post treatment of acid mine drainage with basic oxygen furnace slag: Validation of experimental results with a geochemical model', *J. Clean. Prod.*, vol. 172, pp. 2899–2909, Jan. 2018, doi: 10.1016/J.JCLEPRO.2017.11.124.

[178] S. Motaung *et al.*, ‘Recovery of Drinking Water and By-products from Gold Mine Effluents’, *Int. J. Water Resour. Dev.*, vol. 24, no. 3, pp. 433–450, Sep. 2008, doi: 10.1080/07900620802150475.

[179] G. M. Ochieng, E. S. Seanego, and O. I. Nkwonta, ‘Impacts of mining on water resources in South Africa: A review’, *Scientific Research and Essays*. 2010.

[180] D. B. Johnson and K. B. Hallberg, ‘Acid mine drainage remediation options: a review’, *Sci. Total Environ.*, vol. 338, no. 1–2, pp. 3–14, 2005, doi: 10.1016/j.scitotenv.2004.09.002.

[181] R. Perez-Lopez, D. Quispe, J. Castillo, and J. M. Nieto, ‘Acid neutralization by dissolution of alkaline paper mill wastes and implications for treatment of sulfide-mine drainage’, *Am. Mineral.*, vol. 96, no. 5–6, pp. 781–791, 2011, doi: 10.2138/am.2011.3685.

[182] Y. Jia, C. Maurice, and B. Öhlander, ‘Metal Mobilization in Tailings Covered with Alkaline Residue Products: Results from a Leaching Test Using Fly Ash, Green Liquor Dregs, and Lime Mud’, *Mine Water Environ.*, vol. 34, no. 3, pp. 270–287, Sep. 2015, doi: 10.1007/s10230-014-0317-1.

[183] K. Manskinen, *Utilisation aspects of ashes and green liquor dregs from an integrated semichemical pulp and board mill*, no. June 2013. 2013.

Paper #3

Submitted to the Journal of Cleaner production

Co-disposal of acid mine drainage and green liquor dregs: Optimization of pH and electrical conductivity of acid mine drainage as a result of neutralization with green liquor dregs

Keolebogile R. Sebogodi*,**, Jonas K. Johakimu* and B. Bruce Sithole*,**.

**Biorefinery Industry Development Facility, Chemicals Cluster, Council for Scientific and Industrial Research (CSIR), South Africa.*

***Discipline of Chemical Engineering, University of KwaZulu-Natal, Durban, South Africa*

Corresponding author: sebogodirevelation@gmail.com; sitholeb1@ukzn.ac.za

Abstract

Alkaline industrial wastes can be beneficiated in symbiotic applications for the treatment of acidic industrial wastes such as acid mine drainage (AMD). Thus they are being explored and used as alternatives to limestone ($CaCO_3$) and its derivatives such as lime $Ca(OH)_2$ One such waste is green liquor dregs (GLDs) from chemical Kraft pulp mills. The potential of GLDs to neutralize AMD has been demonstrated; however, there is a dearth of information on optimization of parameters that are relevant in the neutralization of AMD – the parameters are crucial in ascertaining the techno-economic of the beneficiation process. Thus, this study aimed to optimize the parameters involved in neutralization of AMD using GLDs samples from Kraft mills in South Africa and the results were contrasted against those obtained with traditional neutralization technologies that use $Ca(OH)_2$ or $CaCO_3$. The study entailed statistically designed experiments that employed a Box-Behnken Design and Response Surface Methodology to optimize the variables involved in the neutralization process. The results showed that reagent dosage was the most significant independent variable, whereas stirring speed was the least significant parameter. The observations and results herein provide the opportunity for an industrial symbiotic approach in mitigating AMD problems in mining industry while at the same time mitigating waste management challenges in Kraft pulp mills.

Keywords: Green liquor dregs, acid mine drainage, industrial waste, neutralization, Kraft pulp mills, co-disposal.

1. Introduction

Energy is one of the primary vital drivers of the economy. In South Africa, coal is the primary source of this economy driver. Most of the grid energy and liquid fuels in the country are derived from coal (Fosso-Kankeu, Manyatshe and Waanders, 2017; Thopil *et al.*, 2018). Although coal plays an important role in building the economy of the country, the underlying consequences of its mining activities play a more momentous role in depreciating the quality of what is not only the second primary key business driver but also a fundamental need to human being and his environment, water (Fosso-Kankeu, Manyatshe and Waanders, 2017; Naidoo, 2017; Masindi, Chatzisymeon, *et al.*, 2018; Oberholster *et al.*, 2018). This is due to the sulphuric acid that results from the interaction between water, oxygen, and sulphide bearing minerals, such as pyrite (Fosso-Kankeu, Manyatshe and Waanders, 2017; Oberholster *et al.*, 2018; Sebogodi, Johakimu and Sithole, 2020), see Eqn. 1. Continual production of this acid in low quantities results in it being neutralised by the surrounding soils according to Eqn. 2 (Fosso-Kankeu, Manyatshe and Waanders, 2017; Masindi, Osman, *et al.*, 2018; Sebogodi, Johakimu and Sithole, 2020).

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

$$CaCO_3 + H_2SO_4 \rightarrow Ca^{2+} + SO_4^{2-} + CO_2 + H_2O \qquad (2)$$

However, the surrounding soils may not be able to neutralise it when it is generated in excessive quantities, which is catalysed by earth-moving activities such as mining and hence the reaction would rather proceed to produce more acid according to Eqn. 3-5. In the presence of acidophiles, such as the *Thiobacillus* species, this process becomes more prevalent as they expose the sulphide mineral to the oxidising environment (McCarthy, 2011; Fosso-Kankeu, Manyatshe and Waanders, 2017; Masindi, Osman, *et al.*, 2018; Sebogodi, Johakimu and Sithole, 2020).

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

$$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+ \quad (4)$$

$$FeS_2 + 15/2O_2 + 7/2\ H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \quad (5)$$

Nevertheless, the inability of the surrounding soils to neutralise the acid may result in the dissolution of the surrounding rocks and release of their contents (metals) into the acid. The now metal-rich acid is washed into the environment affecting soil, plants, and animals. The well-being of the population is also at risk as buildings, caves, and bridges may collapse due to dissolution of walls and foundations (Motaung *et al.*, 2008; Ochieng, Seanego and Nkwonta, 2010).

This problem can be mitigated by technologies that entail neutralisation and or whole treatment of this metal-rich acid mine drainage. The mechanisms involved in the technologies include pH control, chelation, redox, ion exchange, and adsorption. Amongst these pH control, especially using limestone ($CaCO_3$) and/or its derivatives such as $Ca(OH)_2$ and CaO are extensively used. This is due to the cost-effectiveness and abundance of $CaCO_3$ (Johnson and Hallberg, 2005; Kefeni, Msagati and Mamba, 2017; Moodley *et al.*, 2018). However, it worth noting that limestone ($CaCO_3$) is relatively less active than $Ca(OH)_2$ and CaO, and is, therefore, is used to treat AMD characterised by lower acidity level.

Coal, the second main mineral in South Africa, is mined in about eighteen coalfields. These coalfields are found in the Free State, Gauteng, KwaZulu-Natal, Limpopo, and Mpumalanga provinces. However, the largest seams are found in Mpumalanga and KwaZulu-Natal (Victor Munnik *et al.*, 2010; CSIR, 2013). The quantities and the time it takes to generate the AMD in mine voids and dams of coalfields are dependent on the size of the mines and the concentration of sulphide minerals in the coal. For example, coal in the Highveld coalfield in Mpumalanga contains about 8,5% pyrite (Fosso-Kankeu, Manyatshe and Waanders, 2017), and this could mean it could take centuries before its pyrite is exhausted due to oxidation. Additionally, this coalfield generates about 459.9 Ml (1.26 Ml/day) of AMD annually (Maree *et al.*, 2000). From this, it can be deduced that neutralisation of the AMD would require excessive amounts of $CaCO_3$ that would exhaust all carbonate reserves in the country. Hence, the AMD quandary is a continual problem in the country (and all states with coal mining) that is currently using unsustainable technologies for AMD treatment.

Consequently, researchers have been searching for greener solutions for the treatment of AMD. One of their ground-breaking discoveries at this stage was to explore and use alkaline wastes hidden in industrial landfills as an alternative for $CaCO_3$. Such an initiative would also help in valorising the inorganic industrial wastes and reduce costs associated with transporting them and maintaining the landfill dispose of permits (Gitari *et al.*, 2006; Perez-Lopez *et al.*, 2011; Vadapalli *et al.*, 2015; Sebogodi, Johakimu and Sithole, 2020)

The pulp and paper industry generates large amounts of waste materials that could be beneficial in a symbiotic economy with the mining industry. One of these is a highly alkaline waste that is generated as a waste product in the Kraft pulp mills. The waste, called green liquor dregs (GLDs) is a highly alkaline inorganic waste that is formed during the processing of recovering alkali and sulphur consumed in chemical conversion of wood into pulp(Gitari *et al.*, 2006; Vadapalli *et al.*, 2015) and is disposed of by landfilling.

In South Africa, ~ 100 000 tons of GLDs are produced and landfilled annually, and this is not eco-friendly and cost-effective (Sebogodi, Johakimu and Sithole, 2020). This is because the continual production of these wastes increases their management costs and further purchasing of new landfills once the current landfills are congested (Perez-Lopez *et al.*, 2011; Sebogodi, Johakimu and Sithole, 2020). In a pursuit to do away with the skyrocketing costs involved in maintaining GLDs landfills and in anticipation of pending tax penalties, several studies encompassing characterisation and valorisation of GLDs have been reported (Perez-Lopez *et al.*, 2011; Manskinen, 2013; Jia, Maurice and Öhlander, 2015; Mäkitalo *et al.*, 2015; Sebogodi, Johakimu and Sithole, 2020). Perez-Lopez *et al.*, 2011 reported that GLDs could neutralise the pH of AMD samples from 3.0 and 5.6 to 6.8 and 8.0, respectively. There was a concurrent 100% reduction of metal ion concentrations such as Fe, Cr, and Zn. Recently, Sebogodi *et al.,* 2020 have also shown similar results and reported that mineralogy of GLDs plays a major part in facilitating the neutralisation process. These studies, however, have not entailed the optimisation of the neutralisation process. Moreover, both of them focused on treating the AMD that originated from gold mines. This study aims to optimise the independent variables involved in the neutralisation of coal mine AMD by application of GLDs. Box-Behnken Design and Response Surface Methodology (RSM) were used in the optimisation study.

Samples of AMD from coalmines were characterised, and the pH, chemical composition, and acidity level were studied. Samples of GLDs from the two local Kraft pulp mills were characterised, and their mineralogical and chemical composition, particle size, and liming factor level were studied. Key neutralisation process variables, namely, dosage, stirrer rotation speed, and reaction time, were evaluated and optimised. Finally, we determined whether the heavy metals in the GLDs were leaching into the treated AMD.

1. Materials and Methods

1.1. Materials

1.1.1. AMD

The AMD sample was collected from a Kromdraai catchment point in Mpumalanga Province, South Africa. This sample originated from coalfields in the area.

1.1.2. Neutralising Reagents

Green liquor dregs (GLDs) were collected at GLDs filter point at two South African Kraft mills and labelled GLD A and B. These samples were in paste form.

Limestone ($CaCO_3$) and lime ($Ca(OH)_2$) samples were supplied by Idwala Industrial Holdings (Durban, South Africa) and were used as reference materials.

1.1.3. Characterisation Techniques

1.1.3.1. Neutralising Reagents Characterisation

1.1.3.1.1. Particle size distribution

1000 g of $CaCO_3$, $Ca(OH)_2$, GLD A, and GLD B samples were dried in a vacuum oven at 105°C until a constant mass was obtained. The GLDs samples, which were now rock-solid, were crushed into powder using a rod mill. The powdered samples (including reference samples) were sieved through a 75µm mesh before further analysis for particle size distribution using a particle size analyser (Shimadzu SALD-310).

1.1.3.1.2. Surface morphology and elemental analysis

1.1.3.1.2.1. SEM/EDX

The surface morphology of the neutralising reagents was studied using ZEISS Field Emission Gun- Scanning Electron Microscope (SEM). Elemental analysis of the observed areas was determined by Oxford Energy Dispersive X-ray (EDX) probe, which was fixed to the SEM instrument.

1.1.3.1.2.2. ICP

Extensive chemical analysis of these neutralising reagents was further determined by using inductively coupled plasma techniques. Chemical Thermo I Cap inductively coupled plasma atomic emission spectroscopy/Agilent 7900 inductively coupled plasma-mass spectroscopy was used for ICP-AES/ICP-MS for this purpose.

1.1.3.1.2.3. XRF

A PANalytical Axios Wavelength Dispersive spectrometer fitted with a Rh tube was used to quantify the elemental composition of neutralising reagents and sludge.

1.1.3.1.3. Mineralogical Characterisation

1.1.3.1.3.1. XRD

The identity in terms of mineral phases of the neutralising reagents was determined by using X-ray diffraction analysis (XRD). A Panalytical Empyrean diffractometer using a Cobalt radiation generated at 40 mA and 40 kV, at the scanning range which ranged from 3-9^{o} was used. An X'Pert Highscore Plus software was used to quantify the mineral phases within the samples using the Rietveld method.

1.1.4. AMD Characterization

The pH and electrical conductivity (Ec) were measured using a Hanna HI 98195 multi-parameter instrument. Sulphate (SO_4^{2-}) concentration was measured using turbidity methods. The pH, electrical conductivity (Ec), and ICP-AES/ICP-MS results were used to estimate the acidity level of the AMD. This was done by using both manual calculations, as per Eqn. 6(Cravotta III and Kirby, 2004).

$$\text{Acidity (mg/L } CaCO_3) = 50(10^{(3-pH)} + 3(C_{Fe}/55.8) + 2(C_{Mn}/54.9) + 3(C_{Al}/27.0)) \quad (6)$$

Where C: is the concentration of a specific metal in mg/L.

1.2. Methods

1.2.1. Optimisation of Neutralisation of AMD Using Box-Behnken Design (BBD)

In this study, 1000 mL of AMD sample was neutralised using the four neutralising reagents viz.; $Ca(OH)_2$, $CaCO_3$, GLD A and GLD B. Variation of parameters contact time, dosage, and mixing speed were performed according to data shown in Table 1 to facilitate the neutralisation process. The interaction that results between this variation and the response variables (pH and Ec) was designed and studied using the Box-Behnken Design (BBD). That is, fifteen (15) experimental runs, Table 2, were designed and analysed for each neutralising reagent using Statistica 13.4 Software (TIBCO Software Inc., California, USA).

Table 26: Coded values of the AMD neutralisation used in BBD

CODED VALUES	INDEPENDENT VARIABLE	-1	0	1
X_1	Dosage (g/L)	0.5	0.75	1.0
X_2	Time (mins)	60	210	360
X_3	Speed (rpm)	100	175	250

The neutralisation process was performed by filling a beaker, placed under a preset overhead stirrer, with AMD. The samples were conditioned by stirring for 30 mins to help remove any CO_2 that may be trapped in the sample. This was then followed by adding the relevant quantities of neutralising reagents and the stirring continued for a specified period. At the end of the neutralisation process, the samples were first filtered through 45µm Whatman filter paper and then through Whatman Cellulose nitrate filter: this is essential for ICP analysis. pH and Ec of the samples were measured before and after the neutralisation process. The samples were then stored in airtight containers in a cold room until further analysis. The resulting sludge were dried in a vacuum oven at 105^{o}C to constant mass. The samples were kept in airtight containers until analysis.

Table 27: BBD experimental runs and the observed results.

RUNS	Dosage (g/L)	Time (Mins)	Speed (rpm)	$Ca(OH)_2$		$CaCO_3$		GLD A		GLD B	
				pH	**EC (mS/cm)**	**pH**	**EC (mS/cm)**	**pH**	**EC (mS/cm)**	**pH**	**EC (mS/cm)**
6	1,000000	210,0000	100,0000	11,23	2,691	8,73	2,673	8,47	2,993	8,15	2,791
5	0,500000	210,0000	100,0000	8,89	2,645	7,96	2,635	7,60	2,679	7,20	2,656
15	0,750000	210,0000	175,0000	10,71	2,631	9,89	2,683	8,75	2,895	7,88	2,711
10	0,750000	360,0000	100,0000	10,9	2,633	9,92	2,692	8,7	2,899	7,91	2,704
8	1,000000	210,0000	250,0000	9,75	2,602	8,44	2,618	8,27	2,998	8,19	2,73
11	0,750000	60,0000	250,0000	10,89	2,631	9,9	2,68	8,97	2,889	7,96	2,7
13	0,750000	210,0000	175,0000	10,72	2,634	9,88	2,684	8,78	2,892	7,85	2,714
7	0,500000	210,0000	250,0000	8,78	2,631	7,92	2,625	7,56	2,678	7,11	2,657
3	0,500000	360,0000	175,0000	8,80	2,635	7,89	2,63	7,57	2,68	7,00	2,665
14	0,750000	210,0000	175,0000	10,74	2,634	9,88	2,684	8,76	2,894	7,87	2,712
12	0,750000	360,0000	250,0000	10,60	2,635	9,75	2,689	8,6	2,891	7,98	2,725
2	1,000000	60,0000	175,0000	10,70	2,601	8,81	2,67	8,6	2,978	8,09	2,715
9	0,750000	60,0000	100,0000	10,80	2,639	9,91	2,779	8,68	2,876	7,86	2,709
1	0,500000	60,0000	175,0000	8,00	2,628	7,92	2,628	7,49	2,668	7,15	2,655
4	1,000000	360,0000	175,0000	9,81	2,598	8,72	2,679	8,25	3,024	8,26	2,799

1.3. Results and Discussions

1.3.1. Characterisation of Neutralizing Reagents

1.3.1.1. Particle size distribution

The median particle sizes (d_{50}) were 13.553, 13.880, 19.597 and 17.528 for $Ca(OH)_2$, $CaCO_3$, GLD A and GLD B, respectively. The smaller fines presented by these samples suggested that the reaction surface area of the samples decreased from $Ca(OH)_2$ > $CaCO_3$ > GLD B > GLD A. The higher reaction surface is advantageous in facilitating an efficient reaction. Thus, the efficient reaction is expected to decrease with decreasing reaction surface. However, this should not be considered more important than the mineral phases of the samples.

1.3.1.2. Morphological and Elemental Analysis

The rhombohedral structures, which are a clear indication of calcite ($CaCO_3$), were evident on the SEM micrographs of $CaCO_3$ and GLDs samples, Figure 1, of the samples. However, these structures were in small quantities on the micrographs of GLD A. The most of the GLD A SEM micrograph was saturated with orthorhombic structures which could be of another form of carbonate mineral, pirssonite ($Na_2Ca(CO_3)_2.2H_2O$).

EDX, ICP-AES/ICP-MS, and XRF data were used to ascertain the presence and quantities of minerals in the samples. The data showed that the neutralising reagents were constituted of other elements that could have been present in the phases that could not be singled out, e.g., $CaCO_3$ and ($Na_2Ca(CO_3)_2.2H_2O$) on the SEM micrographs. The EDX graphs in Figure 1, XRF and ICP AES/ICP-MS results in Table 3 and 4, respectively, display the presence of different elements and their quantities thereof.

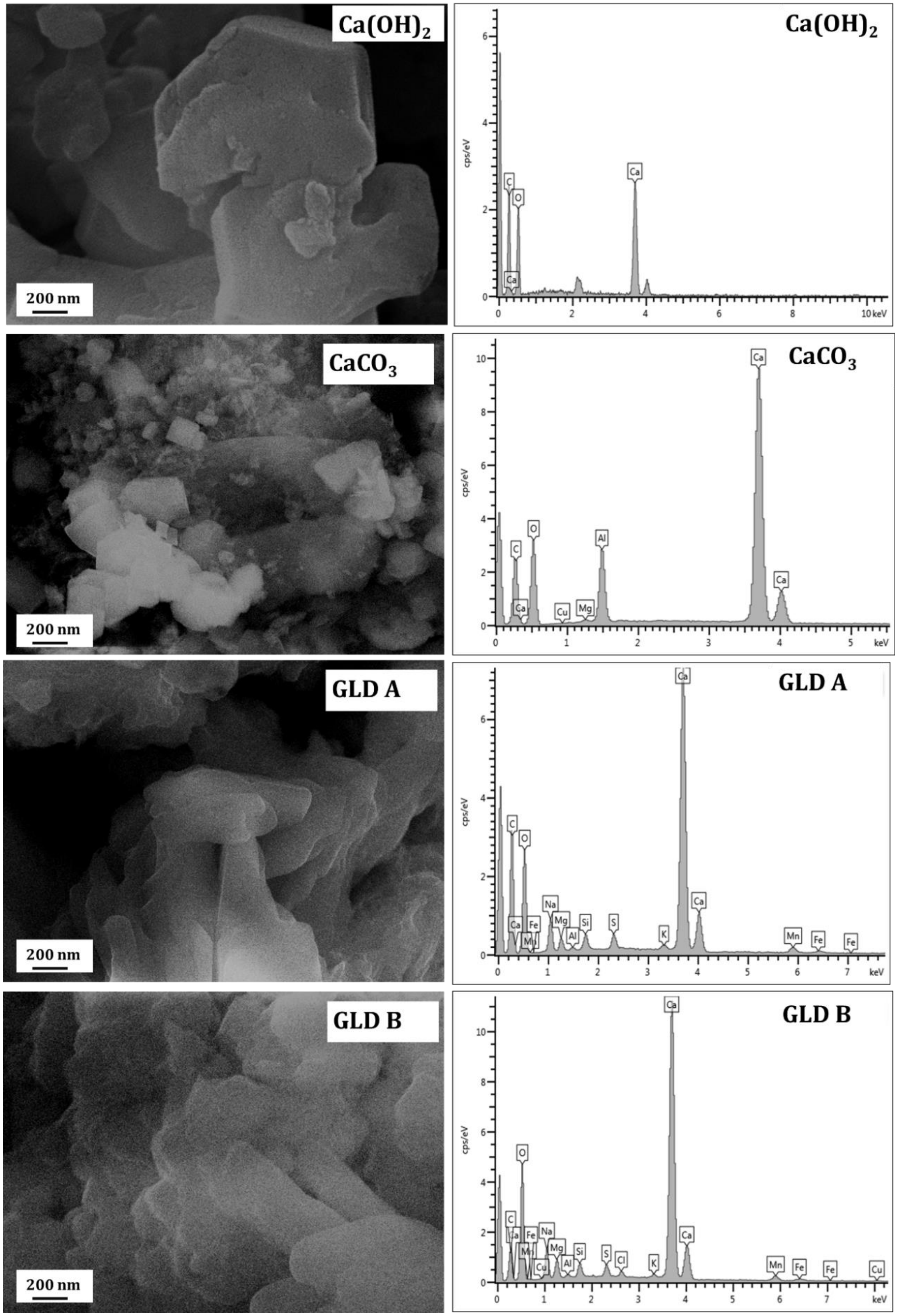

Figure 35: SEM/EDX of raw neutralising reagents.

The presence of additional elements in $CaCO_3$ samples may be attributed to the origin of this sample, i.e. this is a naturally occurring material, which its constituents are influenced by the geological composition of the surrounding soils. Although $Ca(OH)_2$ may have been thought to be free of impurities, the data showed contrary results. This is because both the calcination and slaking process have a negative impact on the quality of the final product. For examples, the calcination process, which leads to over burning or under, burning, produces lime that has inferior quality. The results from these data did not only confirm the identity of GLDs samples but also showed that GLDs composition varies from one mill to another as reported (Sebogodi, Johakimu and Sithole, 2020).

Table 28: XRF results of neutralising reagents and their sludge.

Oxide Wt %	**$Ca(OH)_2$**	**$CaCO_3$**	**GLD A**	**GLD B**	**$Ca(OH)_2$ 1 g/L**	**$CaCO_3$ 1g/L**	**GLD A 1g/L**	**GLD B 1g/L**
Al_2O_3	0,24	19.99	0.98	0.57	2,31	21,68	3,96	3,17
CaO	56.72	42.42	14.61	31.24	38,60	29,47	25,77	40,69
Cr_2O_3	Bld	-	0.72	0.04	Bld	Bld	1,22	0,06
FeO_3	Bld	0.13	0.66	0.57	Bld	Bld	Bld	0,07
K_2O	0,01	0.02	0.61	0.63	0,02	0,03	0,04	0,07
MgO	1,28	0.56	6.13	3.02	9,28	2,25	9,60	3,22
MnO	0,68	0.50	0.99	1.34	3,55	2,60	6,30	1,65
Na_2O	0,01	0.02	14.38	7.28	0,02	0,08	0,36	0,50
P_2O_5	0,01	0.04	0.29	0.26	0,01	0,04	0,50	0,26
SiO_2	1,20	0.81	1.18	2.97	1,54	1,78	2,55	3,94
TiO_2	0,02	0.03	0.04	0.04	0,01	0,03	0,05	0,03
Loi %	38,81	35.07	33.10	39.37	37,99	37,46	41,19	42,38
Sum of concentration	99,16	99.09	73.70	87.37	93,35	95,40	91,56	96,03

Table 29: ICP-AES/ICP-MS results of neutralizing reagents and their sludge mg/L.

Element	Accuracy (%)	$Ca(OH)_2$	$CaCO_3$	GLD A	GLD B	$Ca(OH)_2$ 1g/L	$CaCO_3$ 1g/L	GLD A 1g/L	GLD B 1g/L
B	95,4	338	9,74	67,64	55,01	301,70	259,67	408,0	478,65
V	98,9	2,00	4,45	3,23	2,34	2,00	4,00	6,00	3,00
Cr	99,2	5,00	10,73	5565	255,03	9,00	9,00	4780	235
Co	98,9	12,00	0,88	11,32	13,63	1141	1527	2435	446
Ni	97,7	168	4,68	82,59	37,73	1589	2081	3346	776
Cu	93,7	4,00	30,25	156,94	161,75	37,00	33,00	315	246
Zn	99,9	159828	11,11	308,80	259,27	287313	89103	148244	197222
As	95,4	1,00	0,81	0,54	2,25	6,00	6,00	7,00	8,00
Se	96,9	0,59	0,57	2,99	1,35	1,05	1,10	1,35	0,85
Mo	98,8	0,28	0,38	1,17	0,72	0,81	0,49	0,61	0,35
Cd	97,3	14,00	0,02	0,39	0,18	11,50	9,40	17,40	19,4
Ba	98,1	8,03	10,65	668,62	438,86	16,00	18,02	929	521,3
Hg	97,4	BLD	0,03	0,02	0,04	*33,01	*104,1	*54,00	*93,00
Pb	96,7	0,49	2,72	12,38	11,73	2,40	5,13	22,08	17,30
Al	96,0	1116,4	92380.32	3759,43	2266,22	10925,4	105829,6	19156,1	14245,2
Ca	97,0	434065	268600.8	101030	198049	288756	232915	193024	306582
Fe	97,5	1811,5	870,48	4648,97	3528,13	3287,1	2194,2	9258,5	5850,8
K	96,9	BLD	259,71	5431,67	5419,11	BLD	BLD	BLD	BLD
Mg	95,5	7085	3354,04	36928,39	16381,3	55174	13076	53463	18219
Mn	97,3	5959,0	13,37	7762,37	9547,72	30318,4	21502,2	50536,6	14136,5
Na	99,8	2743	306,58	153011,4	71143,6	1876	1728	5673	7216
P	98,7	154	153,16	1251,82	760,96	150,00	271	2266	1306
Si	96,5	1994	2517,37	6321,21	6247,69	2502	2283	1159	1295
Sr	96,1	64,0	943,74	639,08	520,48	53,10	774,9	534,1	576,8

*μg/L

1.3.1.3. Mineralogical Analysis

The crystalline phases of the neutralising reagent were analysed by XRD, as shown in Figure 2. The prominent peak between 34 $2\theta^{0}$ in the spectra depicts the presence of calcite. The presence of portlandite ($Ca(OH)_2$) is depicted by peaks at 16, 29,34,47, and 55 $2\theta^{0}$. Peaks suggest CaO which may have remained un-slaked in this sample at 32, 37, and 53 $2\theta^{0}$. The Rietveld refinement tool that is built in the Highscore Plus software was further used to identify and quantify other mineral phases in these reagents, as indicated in Table 4. The presence of these mineral phases in $CaCO_3$ and GLDs samples have been discussed previously (Sebogodi, Johakimu and Sithole, 2020).

Table 30: XRD results of neutralising reagents.

Mineral Phase	**$CaCO_3$**	**$Ca(OH)_2$**	**GLD A**	**GLD B**
Pirssonite ($Na_2Ca(CO_3)_2.2H_2O$)	-		80.8	-
Gypsum($CaSO_4.2H_2O$)	24.5		-	-
Hexahydroborite ($CaB_2O_4.6H_2O$)	13.2		-	-
Rancieite ($(Ca,Mn^{2+})_{0.2}(Mn^{4+,}Mn^{3+})O_2.0.6H_2O$)	2.3		-	-
Zeolite *($M_{2/n}.Al_2O_3SiO_2.yH_2O$)	1.6		-	-
Portlandite ($Ca(OH)_2$)		7.7		
Calcite ($CaCO_3$)	58.3	92.3	13.3	75.4
Trona ($Na_2CO_3.NaHCO_3.2H_2O$)	-		-	16.6
ICE III ($H_2O_{(s)}$)	-		-	13
Brucite($Mg(OH)_2$)	-		3.1	-
Ferochromium (FeCr)	-		1.0	-
Paratellurite (TeO_2)	-		0.3	-
Hydrocalumite ($Ca_2Al(OH)_{6.5}Cl_{0.5}.3H_2O$)	-		1.4	-

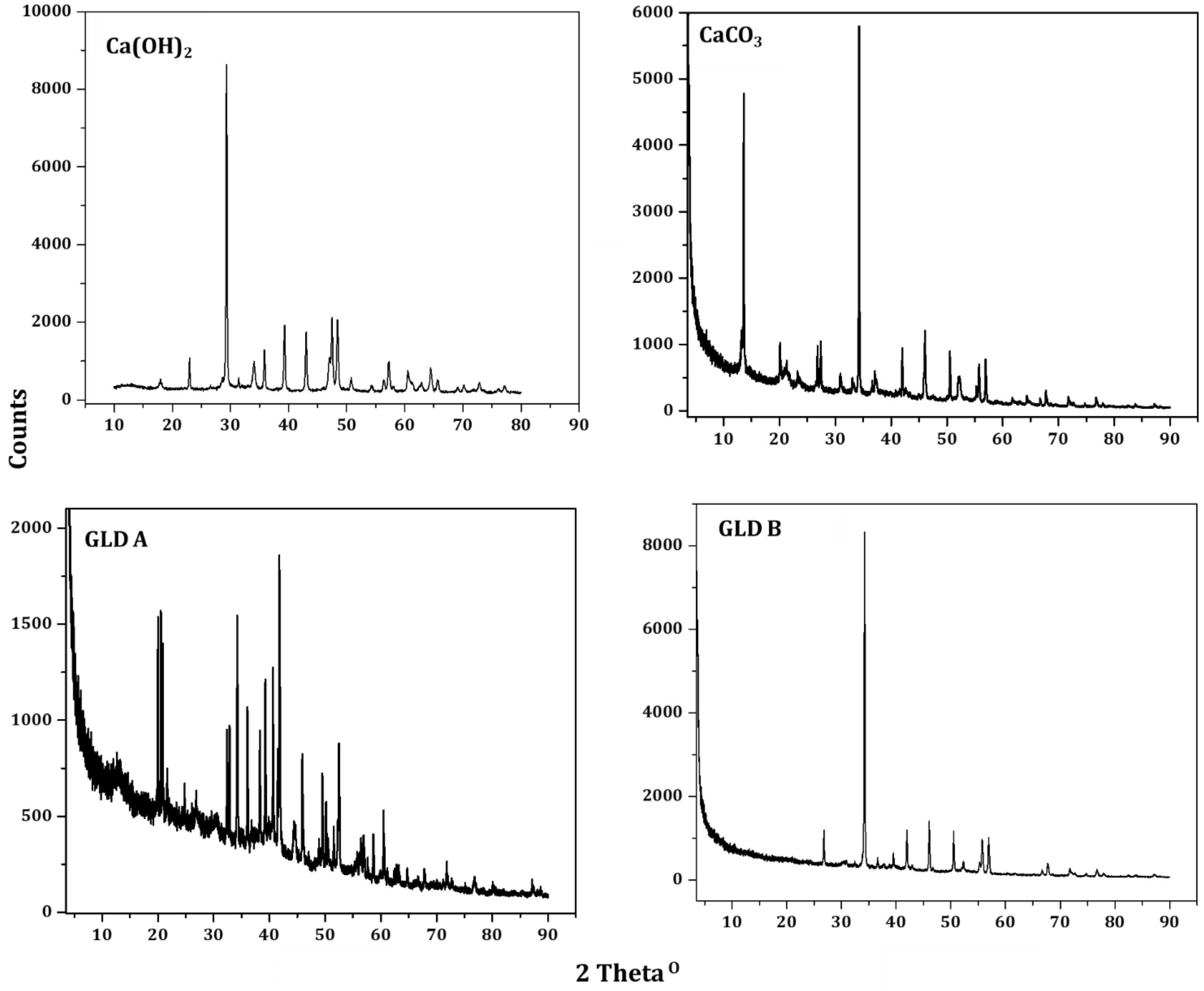

Figure 36: XRD of raw neutralising reagents.

1.3.2. Neutralisation Process

Figures 3-4 and 4-5 show the interactive effects of the three independent variables on pH and Ec, respectively. The graphs show that all the independent variables have played a role in cofounding the response. However, the dosage seems to have played the most significant role in this. That is, an increase in both Ec and pH were realised upon an increase in dosage of the neutralising reagent. However, all neutralising reagents managed to increase the pH of the AMD significantly. GLD B yielded the lowest response due to poor dissolution of its carbonic phase. GLD A and $Ca(OH)_2$ increases Ec considerably with an increase in dosage, whereas the highest dosage of $CaCO_3$ resulted in low Ec: this means that this dosage significantly decreased metal ions in the sample. The increment in Ec was due to the leaching of ions from the reagents used. As expected, $Ca(OH)_2$ dissolved better in water than $CaCO_3$, and this means it released higher calcium ions in the AMD than $CaCO_3$ thus resulting in higher Ec values.

The dark red zones of these three-dimensional graphs indicate that the independent variables had a high impact on the response; thus, the effect of the responses intensifies with the spiralling of colourisation from the dark green to dark red zones. All graphs indicate that dosage is the most significant variable that effected most change in both pH and Ec. However, contact time also played a second significant role since it effected change in both the responses.

1.3.3. Optimisation of Neutralisation by a Box-Behnken Design

The fifteen (15) experimental runs, Table 2, that were conducted in this study allowed for determination of the effects of individual and interaction/combination empirical relationship of independent variables on the response (pH and Ec). These empirical relationships (regression equations) could be used to predict the response under any given range. Thus, the regressed mathematical equations (Eqns. 7-14) for all the reagents are as follows:

$$\mathbf{pH}_{\mathbf{(Ca(OH)2)}} = -1{,}86569074074 + 33{,}88*X_1 - 20{,}2466666667X_1^2 + 0{,}00220111111111*X_2 - 5{,}7962962963e\text{-}006*X_2^2 - 0{,}0157296296296*X_3 + 3{,}63703703704e\text{-}005*X_3^2 \tag{7}$$

$$\mathbf{pH}_{\mathbf{(CaCO3)}} = -5{,}42809074074 + 39{,}375*X_1 - 25{,}2466666667*X_1^2 - 0{,}000768888888889*X_2 + 1{,}31481481481e\text{-}006*X_2^2 + 0{,}00182037037037*X_3 - 7{,}62962962963e\text{-}006*X_3^2 \tag{8}$$

$$\mathbf{pH}_{\mathbf{(GLDA)}} = 0{,}55517037037 + 20{,}265*X_1 - 12{,}3866666667*X_1^2 - 0{,}000298888888889*X_2 - 5{,}18518518519e\text{-}007*X_2^2 + 0{,}000798148148148*X_3 - 2{,}51851851852e\text{-}006*X_3^2 \tag{19}$$

$$\mathbf{pH}_{\mathbf{(GLDB)}} = 4{,}24021851852 + 8{,}195*X_1 - 4{,}05333333333*X_1^2 - 0{,}000142777777778*X_2 + 5{,}18518518519e\text{-}007*X_2^2 - 0{,}00285925925926*X_3 + 8{,}74074074074e\text{-}006*X_3^2 \tag{10}$$

$$\mathbf{Ec}_{\mathbf{(Ca(OH)2)}} = 2{,}69034944444 + 0{,}0935*X_1 - 0{,}078*X_1^2 + 0{,}000237333333333*X_2 - 5{,}61111111111e\text{-}007*X_2^2 - 0{,}00106055555556*X_3 + 2{,}51111111111e\text{-}006*X_3^2 \tag{11}$$

$$\mathbf{Ec}_{\mathbf{(CaCO3)}} = 2{,}30270074074 + 1{,}311*X_1 - 0{,}833333333333*X_1^2 - 0{,}000432277777778*X_2 + 8{,}96296296296e\text{-}007*X_2^2 - 0{,}000662037037037*X_3 + 1{,}0962962963e\text{-}006*X_3^2 \tag{12}$$

$$\mathbf{Ec}_{\mathbf{(GLDA)}} = 1{,}88881796296 + 1{,}939*X_1 - 0{,}863333333333*X_1^2 + 0{,}000110388888889*X_2 - 9{,}81481481482e\text{-}008*X_2^2 + 0{,}000183518518519*X_3 - 4{,}81481481482e\text{-}007*X_3^2 \tag{13}$$

$$\mathbf{Ec}_{\mathbf{(GLDB)}} = 2{,}5233937037 + 0{,}259*X_1 - 0{,}0386666666667*X_1^2 + 0{,}000121444444444*X_2 - 6{,}2962962963e\text{-}008*X_2^2 + 8{,}14814814815e\text{-}006*X_3 - 2{,}51851851852e\text{-}007*X_3^2 \tag{14}$$

Where X_1, X_2, and X_3 represent dosage (g/L), time (minutes), and speed (rpms) respectively.

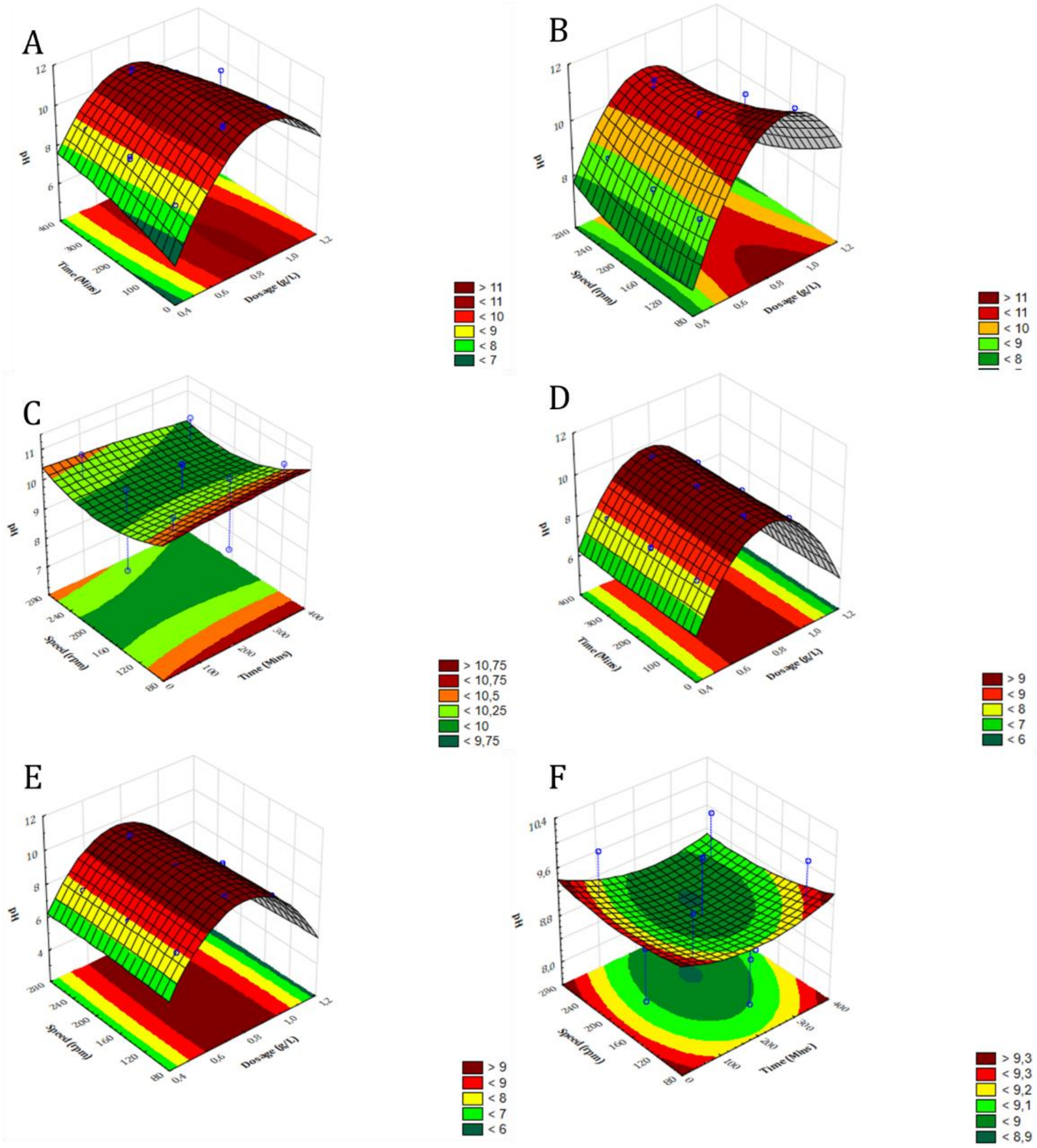

Figure 37: Three dimensional plots of the three variables on pH upon neutralization of AMD with $Ca(OH)_2$ (A-C) and $CaCO_3$ (D-F). The interaction between (A & D) dosage and time, (B&E) speed and dosage, and (C&F) speed and time.

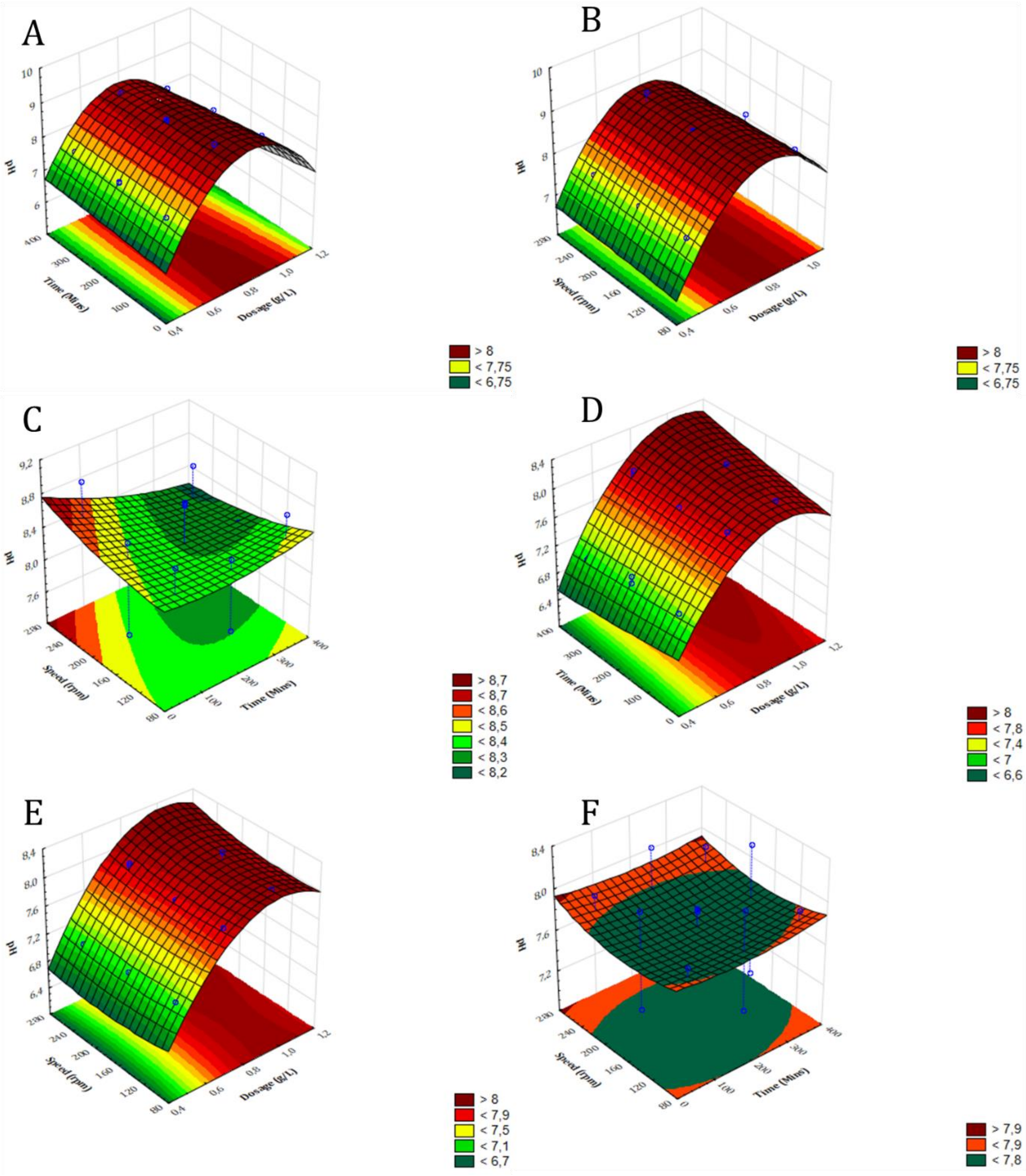

Figure 38: Three-dimensional plots of the three variables on pH upon neutralization of AMD with GLD A (A-C) and GLD B (D-F). The interaction between (A & D) dosage and time, (B&E) speed and dosage, and (C&F) speed and time.

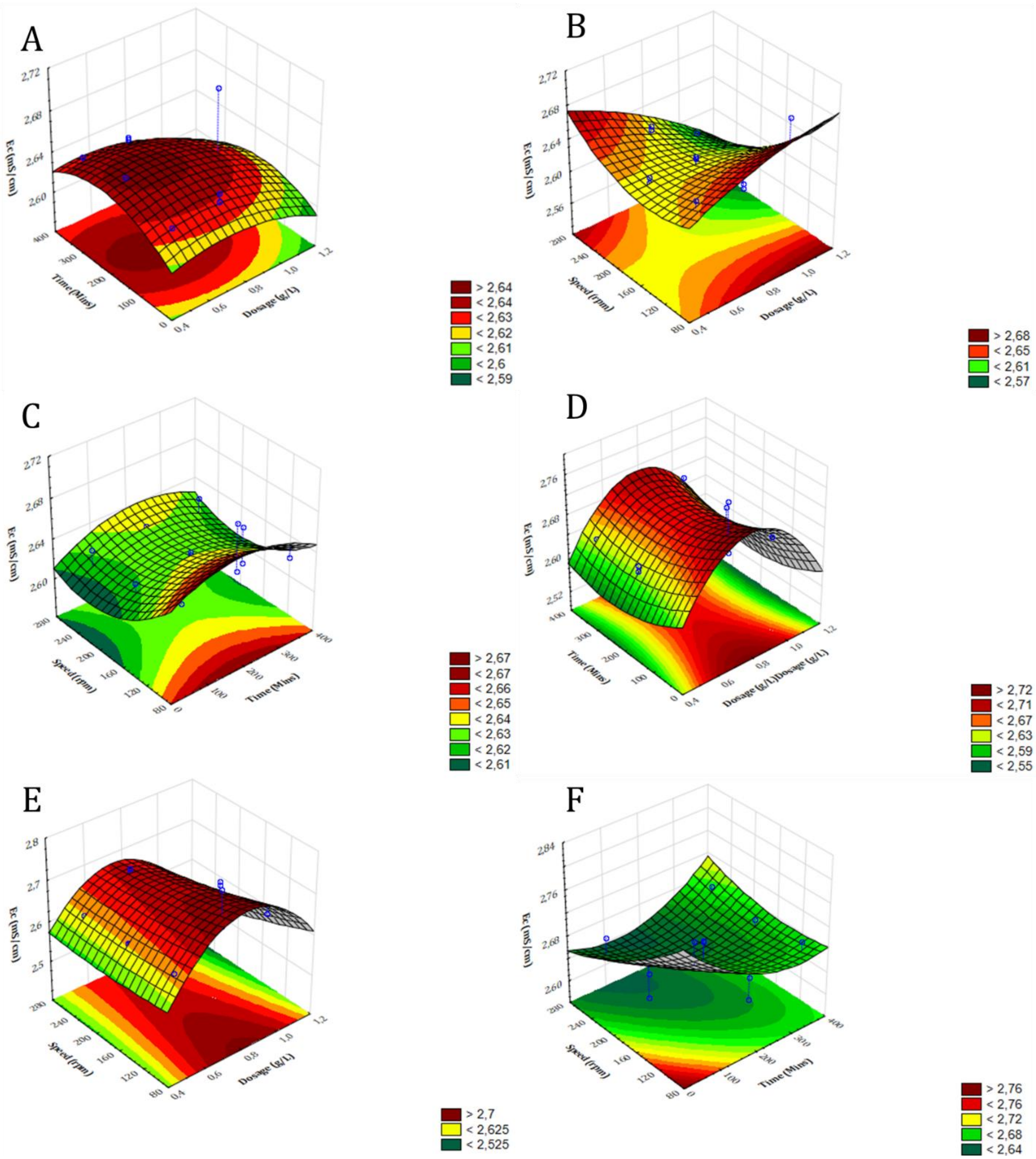

Figure 39: Three-dimensional plots of the three variables on Ec upon neutralization of AMD with $Ca(OH)_2$ (A-C) and $CaCO_3$ (D-F). The interaction between (A & D) dosage and time, (B&E) speed and dosage, and (C&F) speed and time.

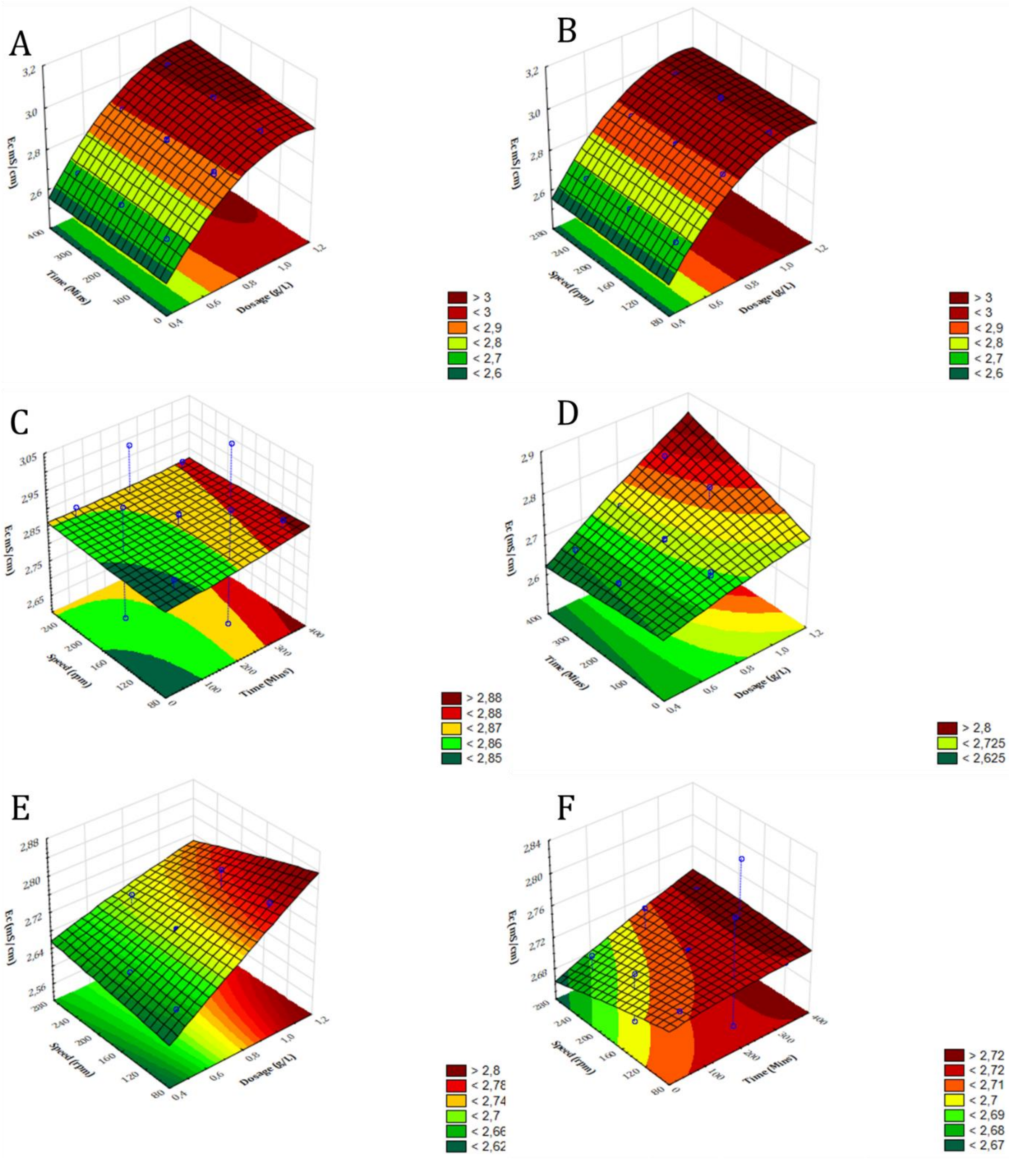

Figure 40: Three-dimensional plots of the three variables on Ec upon neutralization of AMD with GLD A (A-C) and GLD B (D-F). The interaction between (A & D) dosage and time, (B&E) speed and dosage, and (C&F) speed and time.

The Analysis of Variance (ANOVA) results in Table 6 and 7 below, respectively show the optimisation of pH and Ec that resulted after the AMD neutralisation process. The F-values of both dependent values, which are above 1 are regarded as being significant. Specifically, the F values of dosage were very high for all the reagents. This indicated that dosage is the most significant variable.

The statistical fitness of the models (pH and Ec) was confirmed by determination of coefficient values (R^2). The higher values of R^2 that are close to 1 indicate that the variability of the response could be significantly predicted by the models. That is, the R^2 values in the pH model for $Ca(OH)_2$, $CaCO_3$, GLD A, and GLD B were 0.99997, 0.99999, 0.99988, and 0.99982 respectively as shown in Table 6. These values indicate that the models can account for more than 99.5% of the response. The high values of the adjusted determination of coefficient (Adj.R^2) also confirmed the robustness of the model. Additionally, the insignificant differences between the R^2 and adjusted R^2, below 0.2, was observed for all samples. This demonstrated that there is a good relational fit between the experimental work and the mathematical models for all the pre-treatment processes.

The p-value was used to determine the significance of the overall model that was used in this study. In essence, the significance of the model and/or the independent variables used is said to have strong evidence when the p-value is ≤ 0.05. The ANOVA table indicates that dosage remained the most significant variable of all the reagents that were used. Its p-values were below 0,0003 and 0, 0009 for pH and Ec, respectively. On the other hand, the overall p-values of the model used were <0,000001, which implies that the models are very significant. The graphs in Figure 7 further emphasised the correlation that was depicted by R^2, Adj. R^2, and the p-values of the models. That is, the data points of both the observed and predicted data are not scattered, and this shows the fitness of the model.

Table 31: ANOVA for the linear model for pH optimisation.

Reagent	Factor	SS	Df	MS	F	p	Significance
$Ca(OH)_2$	Model					<0,000001	Significant
	(1)Dosage (g/L) L+Q	11,66906	2	5,834531	25005,13	0,000040	
	(2)Time (Mins) L+Q	0,06965	2	0,034823	149,24	0,006656	
	(3)Speed (rpm) L+Q	0,72914	2	0,364572	1562,45	0,000640	
	1*2	0,73528	3	0,245092	1050,39	0,000951	
	1*3	0,70727	2	0,353637	1515,59	0,000659	
	2*3	0,03803	1	0,038025	162,96	0,006080	
	Error	0,00047	2	0,000233			
	Total sum square	14,31804	14				
	R^2=0,99997						
	Adjusted R^2= 0,99977						
$CaCO_3$	Model					<0,000001	Significant
	(1)Dosage (g/L) L+Q	10,31183	2	5,155915	154677,5	0,000006	
	(2)Time (Mins) L+Q	0,01045	2	0,005226	156,8	0,006338	
	(3)Speed (rpm) L+Q	0,04208	2	0,021040	631,2	0,001582	
	1*2	0,02406	3	0,008021	240,6	0,004141	
	1*3	0,01844	2	0,009219	276,6	0,003603	
	2*3	0,00640	1	0,006400	192,0	0,005168	
	Error	10,31183	2	5,155915	154677,5	0,000006	
	Total sum square						
	R^2=0,99999						
	Adjusted R^2=0,99996						

Reagent	Factor	SS	Df	MS	F	p	Significance
GLD A	Model					<0,000001	Significant
	(1)Dosage (g/L) L+Q	3,544206	2	1,772103	7594,726	0,000132	
	(2)Time (Mins) L+Q	0,040108	2	0,020054	85,945	0,011502	
	(3)Speed (rpm) L+Q	0,004946	2	0,002473	10,599	0,086217	
	1*2	0,052538	3	0,017513	75,054	0,013177	
	1*3	0,029513	2	0,014756	63,241	0,015566	
	2*3	0,038025	1	0,038025	162,964	0,006080	
	Error	0,000467	2	0,000233			
	Total sum square	3,816533	14				
	R^2= 0,99988						
	Adjusted R^2= 0,99914						
GLD B	Model					<0,000001	Significant
	(1)Dosage (g/L) L+Q	2,304209	2	1,152105	4937,591	0,000202	
	(2)Time (Mins) L+Q	0,001108	2	0,000554	2,373	0,296441	
	(3)Speed (rpm) L+Q	0,009171	2	0,004585	19,651	0,048423	
	1*2	0,029525	3	0,009842	42,179	0,023249	
	1*3	0,010275	2	0,005138	22,018	0,043445	
	2*3	0,000225	1	0,000225	0,964	0,429648	
	Error	0,000467	2	0,000233			
	Total sum square	2,536960	14				
	R^2=0,99982						
	Adjusted R^2=0,99871						

Table 32: ANOVA for the linear model for Ec optimisation.

Reagent	Factor	SS	Df	MS	F	p	Significance
$Ca(OH)_2$	Model					<0,000001	Significant
	(1)Dosage (g/L) L+Q	0,000704	2	0,000352	117,3000	0,008453	
	(2)Time (Mins) L+Q	0,000590	2	0,000295	98,3865	0,010062	
	(3)Speed (rpm) L+Q	0,002984	2	0,001492	497,3122	0,002007	
	1*2	0,000850	3	0,000283	94,4028	0,010500	
	1*3	0,002582	2	0,001291	430,3958	0,002318	
	2*3	0,000025	1	0,000025	8,3333	0,101973	
	Error	0,000003	0,000000	0,000003			
	Total sum square	0,006752	14				
	R^2=0,99911						
	Adjusted R^2= 0,99378						
$CaCO_3$	Model					<0,000001	Significant
	(1)Dosage (g/L) L+Q	0,012284	2	0,006142	18426,71	0,000054	
	(2)Time (Mins) L+Q	0,001658	2	0,000829	2487,66	0,000402	
	(3)Speed (rpm) L+Q	0,002832	2	0,001416	4247,42	0,000235	
	1*2	0,001452	3	0,000484	1452,38	0,000688	
	1*3	0,000677	2	0,000339	1016,06	0,000983	
	2*3	0,002304	1	0,002304	6912,00	0,000145	
	Error	0,000001	2	0,000000			
	Total sum square	0,022795	14				
	R^2=0,99997						
	Adjusted R^2=0,9998						

Table 7 Continued: ANOVA for the linear model for Ec optimization.

Reagent	Factor	SS	Df	MS	F	p	Significance
GLD A	Model					<0,000001	Significant
	(1)Dosage (g/L) L+Q	0,199318	2	0,099659	42711,08	0,000023	
	(2)Time (Mins) L+Q	0,001012	2	0,000506	216,87	0,004590	
	(3)Speed (rpm) L+Q	0,000036	2	0,000018	7,61	0,116086	
	1*2	0,000475	3	0,000158	67,87	0,014554	
	1*3	0,000009	2	0,000005	1,96	0,338369	
	2*3	0,000110	1	0,000110	47,25	0,020515	
	Error	0,000005	2	0,000002			
	Total sum square	0,219609	14				
	R^2=0,99998						
	Adjusted R^2=0,99985						
GLD B	Model					0,000000	Significant
	(1)Dosage (g/L) L+Q	2,304209	2	1,152105	4937,591	0,000202	
	(2)Time (Mins) L+Q	0,001108	2	0,000554	2,373	0,296441	
	(3)Speed (rpm) L+Q	0,009171	2	0,004585	19,651	0,048423	
	1*2	0,029525	3	0,009842	42,179	0,023249	
	1*3	0,010275	2	0,005138	22,018	0,043445	
	2*3	0,000225	1	0,000225	0,964	0,429648	
	Error	0,000467	2	0,000233			
	Total sum square	2,536960	14				
	R^2=0,99982						
	Adjusted R^2=0,99871						

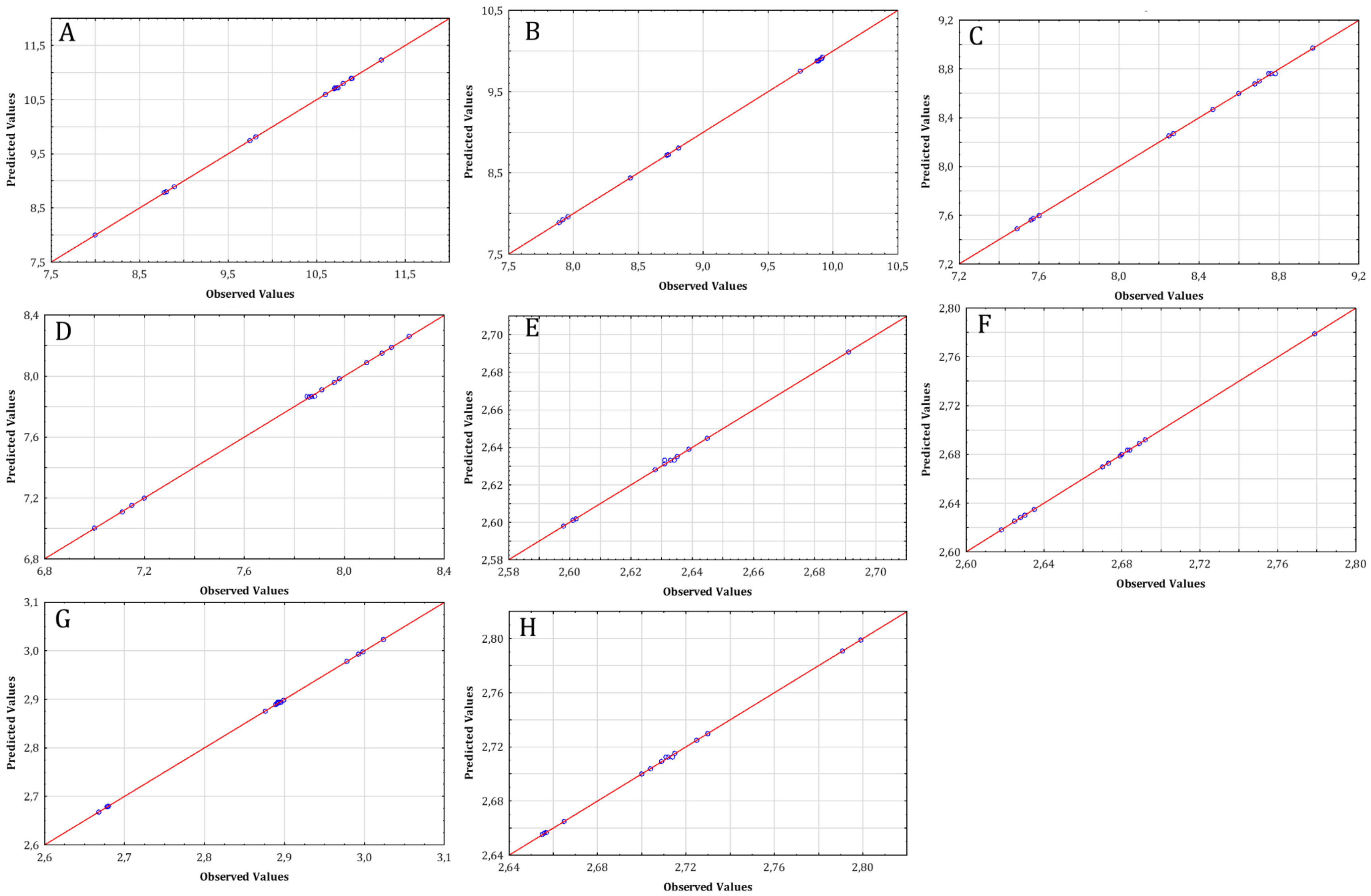

Figure 41: Predicted vs observed values of pH (A-D) and Ec (E-H) for $Ca(OH)_2$, $CaCO_3$, GLD A and G:D B models respectively.

The critical values, Table 8, that were obtained from the software were favourable for raising pH values above the neutralisation point because they were in favour of using high dosages. However, if these were to be taken as optimum conditions, Ec, especially of the GLDs samples, would have increased exponentially as more ions would leach out into the solution. Moreover, the software predicted the values that are out of our data point sets as optimum values. Therefore, the maximum observed (1g/L) dosages of the neutralising reagents were instead chosen as the optimum dosage. Thus, higher observed dosages (1g/L) of the neutralising reagents were instead chosen as the optimum dosage since it was able to raise the pH of AMD to values just above the neutral values will maintain low Ec.

Furthermore, time, which was observed to be the second significant variable, was factored in and we considered taking 210 minutes to allow the dissolution of the carbonate material and stabilisation of ion activity within the sample. It should be noted that the critical values of the reference materials favoured both responses, that is, the higher their dosage, the higher the pH and the more the metal precipitation, which will, in turn, reduce the Ec. However, the same dosage and contact time were used for further analysis for comparison sake.

Table 33: Critical values as predicted by the DOE software.

Reagent	Factor	Critical Values (pH)	Predicted values (pH)	Critical Values (Ec (mS/cm)	Predicted values (Ec (mS/cm))
$Ca(OH)_2$	Dosage (g/L)	0,5994	10.81594	0,5994	2.631486
	Time (Mins)	211,4851		211,4851	
	Speed (rpm)	211,1726		211,1726	
$CaCO_3$	Dosage (g/L)	0,7866	9.92051	0,7866	2.666247
	Time (Mins)	241,1467		241,1467	
	Speed (rpm)	301,9426		301,9426	
GLD A	Dosage (g/L)	1,1230	8.950032	1,1230	3.026067
	Time (Mins)	562,3585		562,3585	
	Speed (rpm)	190,5769		190,5769	
GLD B	Dosage (g/L)	3,3491	8.138708	3,3491	3.015734
	Time (Mins)	964,4118		964,4118	
	Speed (rpm)	16,1765		16,1765	

1.3.4. Characterisation of the neutralised AMD

The interaction of carbonic materials with AMD would generally dissolve/disintegrate the carbonic structure. However, this disintegration occurs at different rates. This difference in dissolution rates could be due to the type of the mineral phase that makes up the carbonate material and the pH range of the AMD. That is, some minerals will dissolve readily at any pH, whereas some would dissolve at a preferential pH, as explained in our previous paper (Sebogodi, Johakimu and Sithole, 2020).

Equations 15 and 16 below are generally used to explain the mechanism of carbonic effect on the AMD. In the equations, the sulphate precipitate in the form of calcium sulphate ($CaSO_4$). However, this may not be appreciably realised at pH values below 12 and thus remaining metastable in the solution. In addition to the pH of 12, the AMD should be fed with the $CaSO_4$ seed, which will facilitate its efficient crystallisation process.

$$CaCO_3 + H_2SO_4 \rightarrow CaSO_4 + CO_2 + H_2O \tag{15}$$

$$Ca(OH)_2 + H_2SO_4 \rightarrow CaSO_4 + 2H_2O \tag{16}$$

The pH, Ec, acidity, and SO_4^{2-} of the AMD changed dramatically as listed in Table 9. The increment in pH was due to the dissolution of carbonate materials. This increment lowered the SO_4^{2-} in the reference materials. Although these findings may be contrary to the conditions of SO_4^{2-} reduction, similar results have been reported elsewhere (Potgieter-Vermaak *et al.*, 2006; Kumar V.R. Vadapalli *et al.*, 2008). Unlike the findings of our previous study, the SO_4^{2-} concentrations found in the case of AMD neutralisation with $CaCO_3$ may have been influenced by the possible simultaneous dissolution of the carbonic phases found in this sample. The AMD used in this study case had a pH value which is best for dissolving most of the calcite in the sample. That is, this simultaneous dissolution may have encouraged a slight reduction of SO_4^{2-} in the solution through precipitation. The SO_4^{2-} concentration, however, increased in the GLDs treated samples because GLDs originates from a sulphate process. The Ec of all the neutralised samples increased with increasing dosage of the reagents.

Table 34: Chemical characteristics of AMD.

Factor	AMD	$Ca(OH)_2$ 1g/L	$CaCO_3$ 1g/L	GLD A 1g/L	GLD B 1g/L
pH	3.8	9,75	8,44	8,27	8,19
Ec (mS/cm)	2.603	2,602	2,618	2,998	2,730
SO_4^{2-} (mg/L)	1706	1662	1689	1930	1910
Acidity (mg/L $CaCO_3$)	2 843.50	6,50	58,10	96,40	81,00
Fe removal efficiency (%)		99,77	99,96	99,81	99,68
Al removal efficiency (%)		99,89	99,71	99,71	91,92
Mn removal efficiency (%)		99,81	40,00	3,85	28,46

Also, this change has also altered the composition of the neutralised AMD, as shown in Table 10. That is, the increased pH that resulted from reagents addition created an environment for different species within the AMD to precipitate and/or to co-precipitate. This precipitation has led to a decrease in all elements that contribute towards AMD formation. Thus, more than 91% decrease in Fe and Al was realised in all neutralised AMD samples. Only the $Ca(OH)_2$ neutralised AMD was found to have a high Mn reduction. This is because Mn precipitates proficiently as pH levels approach 10. Although this significant change was observed in the chemistry of the AMD, some metal ions such as Na, Co, Mg, and Ni leached from the neutralising reagents into the AMD. However, these ions could be easily removed through a post-treatment process step, e.g., using $CaO/Ca(OH)_2$, as used in the limestone-$CaO/Ca(OH)_2$ AMD treatment process.

Table 35: ICP-AES/ICP-MS of AMD and the neutralized filtrates μg/L.

Element	**Accuracy (%)**	**AMD**	**$Ca(OH)_2$ 1g/L**	**$CaCO_3$ 1g/L**	**GLD A 1g/L**	**GLD B 1g/L**
Sb	*98.3*	0,03	0,03	0,02	0,04	0,03
B	*95.4*	48,0	30,1	38,0	46,1	59,3
Sn	97,1	0,03	0,02	0,01	0,02	0,02
V	*98.9*	0,11	0,07	0,02	0,07	0,02
Cr	*99.2*	10,18	0,74	0,71	8,77	2,14
Co	*98.9*	1558,9	1,9	47,3	141,2	124,70
Ni	*97.7*	1738,9	3,5	28,8	82,8	128,20
Cu	*93.7*	96,2	20,6	18,3	23,1	12,1
***Zn**	*99.9*	*22,0*	0,64	0,02	0,03	0,5
As	*95.4*	4,62	0,11	0,10	0,11	0,20
Se	*96.9*	0,20	0,17	0,12	0,30	0,32
Mo	*98.8*	0,06	0,33	0,23	0,70	0,13
Cd	*97.3*	2,27	0,56	0,45	0,66	0,45
Ba	*98.1*	21,2	29,8	28,0	27,7	32,1
Hg	*97.4*	0,25	0,25	0,25	0,25	0,25
Pb	*96.7*	2,24	0,11	0,05	0,08	0,05
***Al**	*96.0*	10,4	0.011	0,03	0,03	0,84
***Ca**	*97.0*	401,3	655,3	492,6	393,9	427,2
***Fe**	*97.5*	1496,4	3,5	0,6	2,9	4,8
***K**	*96.9*	BLD	5,133	1,405	6,247	4,55
***Mg**	*95.5*	143,3	27,19	148,4	152,5	152,4
***Mn**	*97.3*	52,00	0,10	31,2	50,0	37,2
***Na**	*99.8*	10,78	6,263	6,902	150,6	45,38
***P**	*98.7*	BLD	BLD	BLD	0,2154	BLD
***Si**	*96.5*	2,753	0,6258	0,7329	1,144	1,916
***Sr**	*96.1*	0,57	0,61	0,75	0,84	0,64

*mg/L

1.3.5. Characterisation of the Sludge

The sludge that resulted from the AMD neutralisation process was analysed using SEM/EDX, XRF, ICP-AES/ICP-MS, and XRD. Figure 8 shows the morphological evidence that the reaction between the AMD and the calcitic structures had taken place. The granulated assemblies that are evident in the SEM pictures illustrate this. The spherical granules generally indicate that metals from the AMD had been displaced by precipitation, co-precipitation or adsorption onto GLDs (Masindi *et al.*, 2017). The EDX graphs alongside the SEM micrographs and the mapped SEM inserts show the distribution of various elements that were present in the sludge from the neutralised reactants

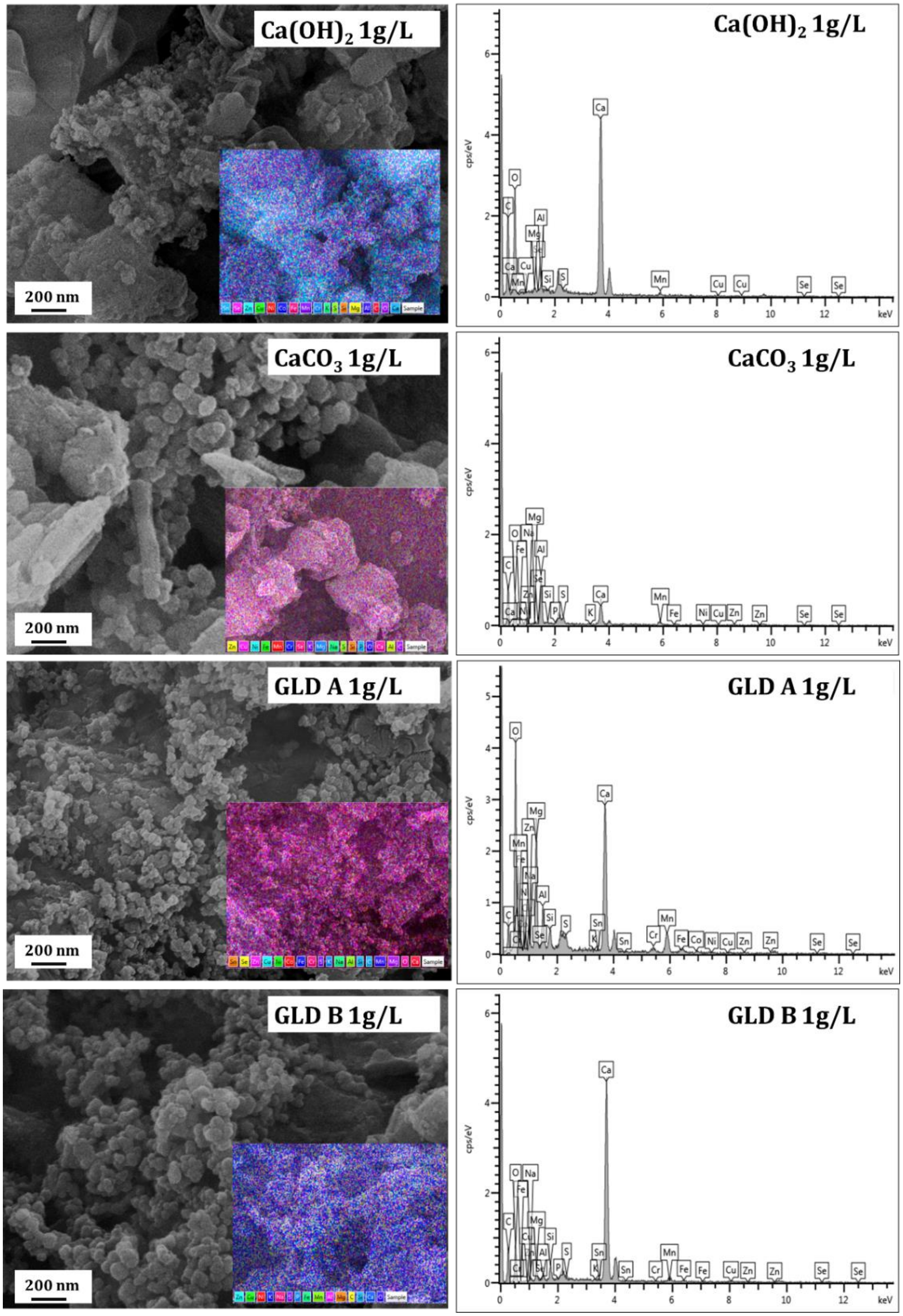

Figure 42: SEM/EDX of precipitates from neutralisation of AMD.

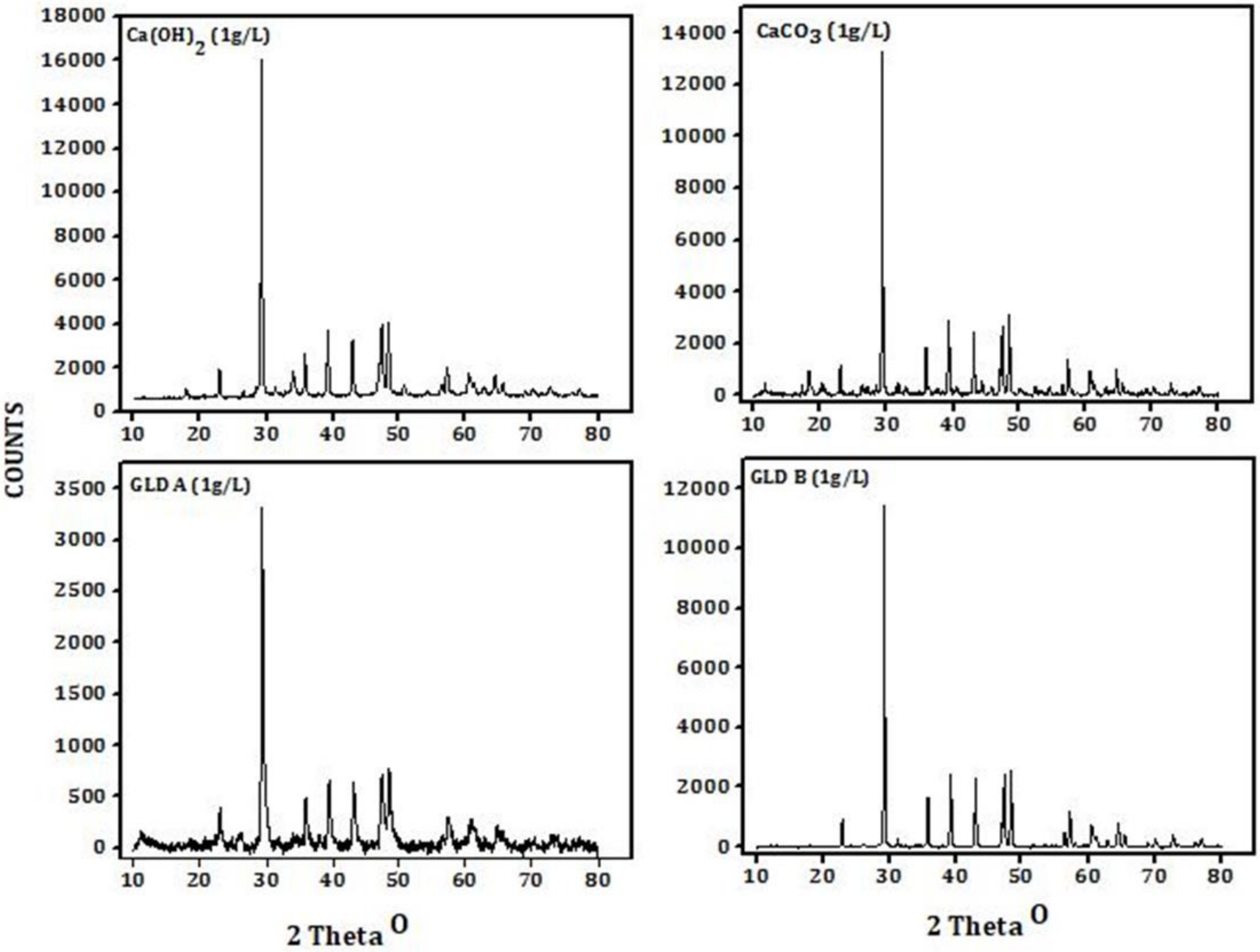

Figure 43: XRD pattern of the reacted neutralising reagents.

The XRF and ICP-AES/ICP-MS results in Tables 2 and 3, respectively further showed that there had been a change in the concentration of elements that were initially composed in the raw neutralising reagents. That is, an increase in either an oxide or elemental concentration further affirms the possible precipitation of that element from the AMD.

XRD graphs in Figure 9 were further used to quantify the mineralogical phases of the sludge. This mineralogical phase quantification and analysis showed that $CaCO_3$ was still the main constituent found in all sludge. Other crystalline phases that were detected in the samples were;

$Ca(OH)_2$: calcite, quartz, periclase, zinc aluminium carbonate hydroxide-hydrate, sodium zinc oxide, natrita, and hematite.

$CaCO_3$: calcite, katoite, hydrogarnet, gibbite, zinc aluminium carbonate hydroxide-hydrate, and bayerite.

GLD A: calcite, graphite, natrite, and magnesium calcite.

GLD B: calcite, magnesium calcite, and graphite

A disadvantage of using this technology is that it is only able to detect the crystalline phases; that is, SO_4^{2-} is said to precipitate in the form of $CaSO_4$ according to Equations 15 and 16. However, the XRD patterns do not indicate the presence of $CaSO_4$. SO_4^{2-} anion may have precipitated as an amorphous phase (instead of a crystalline phase) that could not be detected by XRD.

2. Conclusions

The use of RSM has conclusively revealed how the different independent variables can affect pH and Ec upon neutralisation of AMD with GLDs. Dosage of the neutralising reagent was the most significant variable in this regard. The decreasing order of the significance of the variables was; GLDs dosage > contact time > mixing speed. Although the critical values that were obtained from the DOE software were not evaluated for their effect on the response because they would exponentially raise the Ec, as shown on Table 8, of the treated AMD from leaching of nutrients from the GLDs, the developed model can be used to predict the desired pH and Ec when neutralising AMD with GLDs. Future work on this study will include evaluation of neutralisation of AMD with GLDs on a pilot scale, determination of the techno-economics of the process, and post-treatment of the GLDs neutralised AMD.

3. Acknowledgements

The authors of this article would like to thank the Council of Scientific and Industrial Research (CSIR), National Research Foundation (NRF), and University of KwaZulu-Natal (UKZN) for their financial support. The authors would also like to thank Mondi Richards Bay and Sappi Ngondwana for supplying them with green liquor dregs.

4. References

Cravotta III, C. A. and Kirby, C. S. (2004) 'ACIDITY AND ALKALINITY IN MINE DRAINAGE: PRACTICAL CONSIDERATIONS', *Journal American Society of Mining and Reclamation*. American Society of Mining and Reclamation (ASMR), 2004(1), pp. 334–365. doi: 10.21000/jasmr04010334.

CSIR (2013) 'Characterising the risk of human exposure and health impacts from acid mine drainage in South Africa', (March), pp. 1–183.

Fosso-Kankeu, E., Manyatshe, A. and Waanders, F. (2017) 'Mobility potential of metals in acid mine drainage occurring in the Highveld area of Mpumalanga Province in South Africa: Implication of sediments and efflorescent crusts', *International Biodeterioration and Biodegradation*. Elsevier Ltd, 119, pp. 661–670. doi: 10.1016/j.ibiod.2016.09.018.

Gitari, M. W. *et al.* (2006) 'Treatment of Acid Mine Drainage with Fly Ash: Removal of Major Contaminants and Trace Elements', *Journal of Environmental Science and Health, Part A*. Informa UK Limited, 41(8), pp. 1729–1747. doi: 10.1080/10934520600754425.

Jia, Y., Maurice, C. and Öhlander, B. (2015) 'Metal Mobilization in Tailings Covered with Alkaline Residue Products: Results from a Leaching Test Using Fly Ash, Green Liquor Dregs, and Lime Mud', *Mine Water and the Environment*, 34(3), pp. 270–287. doi: 10.1007/s10230-014-0317-1.

Johnson, D. B. and Hallberg, K. B. (2005) 'Acid mine drainage remediation options: a review', *Science of The Total Environment*. Elsevier BV, 338(1–2), pp. 3–14. doi:

10.1016/j.scitotenv.2004.09.002.

Kefeni, K. K., Msagati, T. A. M. and Mamba, B. B. (2017) 'Acid mine drainage: Prevention, treatment options, and resource recovery: A review', *Journal of Cleaner Production*, 151, pp. 475–493. doi: 10.1016/j.jclepro.2017.03.082.

Kumar V.R. Vadapalli *et al.* (2008) 'Neutralization of acid mine drainage using fly ash, and strength development of the resulting solid residues', *South African Journal of Science*, 104(7–8), pp. 317–322.

Mäkitalo, M. *et al.* (2015) 'Improving Till by Adding Green Liquor Dregs in Sealing Layers to Control AMD–A Pilot Study', in *mwen.info*. 10th International Conference on Acid Mine Drainage and IMWA Annual Conference, p. 7.

Manskinen, K. (2013) *Utilisation aspects of ashes and green liquor dregs from an integrated semichemical pulp and board mill*.

Maree, J. P. *et al.* (2000) 'The collection , treatment and utilization of water accumulated in the coal mines located in the Upper Olifants River catchment'. COALTECH 2020.

Masindi, V. *et al.* (2017) 'Comparison of mine water neutralisation efficiencies of different alkaline generating agents', *Journal of Environmental Chemical Engineering*, 5(4), pp. 3903–3913. doi: 10.1016/j.jece.2017.07.062.

Masindi, V., Chatzisymeon, E., *et al.* (2018) 'Assessing the sustainability of acid mine drainage (AMD) treatment in South Africa', *Science of the Total Environment*. Elsevier B.V., 635, pp. 793–802. doi: 10.1016/j.scitotenv.2018.04.108.

Masindi, V., Osman, M. S., *et al.* (2018) 'Fate of pollutants post treatment of acid mine drainage with basic oxygen furnace slag: Validation of experimental results with a geochemical model', *Journal of Cleaner Production*. Elsevier, 172, pp. 2899–2909. doi: 10.1016/J.JCLEPRO.2017.11.124.

McCarthy, T. S. (2011) 'The impact of acid mine drainage in South Africa', *South African Journal of Science*. Academy of Science of South Africa, 107(5/6), pp. 1–7. doi: 10.4102/sajs.v107i5/6.712.

Moodley, I. *et al.* (2018) 'Environmentally sustainable acid mine drainage remediation: Research developments with a focus on waste/by-products', *Minerals Engineering*.

Elsevier, 126(August 2017), pp. 207–220. doi: 10.1016/j.mineng.2017.08.008.

Motaung, S. *et al.* (2008) ‘Recovery of Drinking Water and By-products from Gold Mine Effluents’, *International Journal of Water Resources Development*. Taylor & Francis Group , 24(3), pp. 433–450. doi: 10.1080/07900620802150475.

Naidoo, S. (2017) *Acid Mine Drainage in South Africa: Development Actors, Policy Impacts, and Broader Implications*. doi: 10.1007/978-3-319-44435-2.

Oberholster, P. J. *et al.* (2018) ‘Assessment of selected macroalgae for use in a biological hybrid system for treating sulphur in acid mine drainage (AMD)’, *Journal of Applied Phycology*. Journal of Applied Phycology, 30(2), pp. 1361–1370. doi: 10.1007/s10811-017-1314-0.

Ochieng, G. M., Seanego, E. S. and Nkwonta, O. I. (2010) ‘Impacts of mining on water resources in South Africa: A review’, *Scientific Research and Essays*.

Perez-Lopez, R. *et al.* (2011) ‘Acid neutralization by dissolution of alkaline paper mill wastes and implications for treatment of sulfide-mine drainage’, *American Mineralogist*. Mineralogical Society of America, 96(5–6), pp. 781–791. doi: 10.2138/am.2011.3685.

Potgieter-Vermaak, S. S. *et al.* (2006) ‘Comparison of limestone, dolomite and fly ash as pre-treatment agents for acid mine drainage’, *Minerals Engineering*, 19(5), pp. 454–462. doi: 10.1016/j.mineng.2005.07.009.

Sebogodi, K. R., Johakimu, J. K. and Sithole, B. B. (2020) ‘Beneficiation of pulp mill waste green liquor dregs: Applications in treatment of acid mine drainage as new disposal solution in South Africa’, *Journal of Cleaner Production*. Elsevier, 246, p. 118979. doi: 10.1016/j.jclepro.2019.118979.

Thopil, M. S. *et al.* (2018) ‘A review of grid connected distributed generation using renewable energy sources in South Africa’, *Energy Strategy Reviews*. Elsevier, 21(August 2017), pp. 88–97. doi: 10.1016/j.esr.2018.05.001.

Vadapalli, V. R. K. *et al.* (2015) ‘Acid mine drainage neutralization in a pilot sequencing batch reactor using limestone from a paper and pulp industry’, *Environmental Technology*. Informa UK Limited, 36(19), pp. 2515–2523. doi: 10.1080/09593330.2015.1036786.

Victor Munnik *et al.* (2010) *The Social and Environmental Consequences of Coal Mining in South Africa: A Case Study*. Cape Town.