



# **Synthesis of high-grade struvite from municipal effluents and application in the remediation of acid mine drainage**

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## **PREFACE**

The basis of this research stemmed from my interest and passion in circular economy, green technologies, and sustainability towards environment and water resource management. Specifically, as the world moves towards ensuring sustainability of water use, building climate resilience and strengthening integrated management, there will be a greater need to develop processes and eco-friendly technologies that will focus on pollution control, drinking water purification, wastewater treatment, minerals recovery from wastes, water process optimizations and waste/wastewater beneficiation and valorisation. It is my passion to develop systems and technologies that will ensure sustainable water resource management and ultimately ensure access to water of good quality for all and a safe environment for everyone.

I am thanking God for his grace and protection over my life and making everything possible. In truth, I cannot have done this work without the motivation, encouragement and support from my supervisors' Dr Vhahangwele Masindi, a Research Scientist at Magalies Water, who initiated and held my hand throughout this study. Prof Elvis Fosso-Kankeu and Prof HWJP Neomagus senior lecturers at the North-west university, School of Chemical and Minerals Engineering for their guidance, facilitation, and supervision throughout this project. Your advice and tenacity made what seemed unachievable, very much possible at the end.

I would likewise love to express thanks to the Council for Scientific and Industrial Research (CSIR) for financially supporting the study by giving me an MSc Bursary. I would also wish to acknowledge all faculties and support staff of the School of Chemical and Minerals Engineering, Water Pollution and Monitoring Initiatives Group and Magalies water, for their unceasing assistance, continual help and giving me access to the departmental facilities for my project work.

My sincerest gratitude equally goes to my support system, my partner John Mohumutshi who supported me with love, and understanding, my mother Vivian Mamakoa for her love and understanding. To my friends and my children (Khomotso, Mmakgabo and Ditheto Mamakoa) who have been a source of motivation throughout the duration of this study.

**DEDICATED TO THE MEMORY OF MY GRANDMOTHER:**

**SEKOTI FRANCINAH MAMAKOA**

**1942-2020**

## ABSTRACT

Access to clean water resource is a fundamental need and right to all citizen in any given country. However, the water needs to comply with different standards, specifications and guidelines thus ensuring that potential ecotoxicological effects are not ensued from the consumption of contaminated water. In recent decades, the contamination of the environment with municipal wastewater (MWW) and acid mine drainage (AMD) has been a matter of primary concern. This has impaired the quality of water and its suitability to nurture natural life and make its inherent values. In this study, we explored the synthesis of struvite from municipal wastewater and appraise its application for the treatment of acid mine drainage. Batch experiments were used to accomplish the goals of this study, specifically the one-factor-at-a-time (AFAAT) initiative as process parameters. Evaluated parameters include contact time (mixing time) and feed dosage whereas temperature and pH were ambient. Characterisations of feed and product solid samples were done using HR-SEM-EDS, FTIR, XRD and XRF. Aqueous samples were characterised using inductively coupled plasma mass spectrometry (ICP-MS), inductively coupled plasma optical emission spectrometry (ICP-OES), Gallery-plus and multi-parameter probes. Synthesis of struvite was done at 1 g: 100 mL of activated magnesite and municipal wastewater, respectively. The mixtures were mixed at 60 minutes at 300 rpm. The product sludge was used for AMD treatment. The obtained results revealed 30 minutes of equilibration and 15 g of dosage in 1000 mL at 300 rpm of mixing speed. Interaction of struvite with AMD led to > 99% removal efficacy for Al, Fe, Mn and other metals except for sulfate, which demonstrated close to 30% removal efficacy. XRD confirmed the synthesis of struvite with 60% purity. This was further confirmed by elevated concentration of phosphate in XRF results. After the interaction of struvite and Raw Acid Mine Drainage (RAMD), the product mineral confirmed the presence of Fe-based minerals and gypsum hence denoting that Fe and sulfates are removed from AMD. The pH was observed to be  $\geq 9.5$  and this was suitable for attenuation of all the chemicals. Thus, this technology could valorise struvite synthesized from municipal wastewater effluents and open new horizons for the effective and sustainable management of wastewater effluents and AMD. This will minimize the footprints of acid mine drainage and municipal wastewater on different spheres of the environment. Although an economic feasibility and life cycle analysis need to be done to conclusively proof the feasibility of this technology.

**Keywords:** Struvite, acid mine drainage, municipal wastewater, treatment, minerals recovery, minerals synthesis.

## **ACADEMIC OUTPUTS RELATED TO THIS STUDY**

### **PRESENTATIONS AND CONFERENCES**

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## **ABBREVIATIONS AND ACRONYMS**

AMD Acid mine drainage

RAMD Raw Acid Mine Drainage

AFAAT A-factor-at-a-time

CSIR Council for Scientific and Industrial Research

SEM Scanning electron microscope

EDS Energy dispersive X-ray spectrometry

XRD X-ray diffraction

XRF X-ray fluorescence spectroscopy

FTIR Fourier transform infrared spectroscopy

ICP-OES Inductively coupled plasma optical emission spectrometry

ICP-MS Inductively coupled plasma mass spectrometry

SA South Africa

SS Supersaturation

MWW Municipal wastewater

MAP Magnesium Ammonia Phosphate

LMIC Low and middle-income countries

DNA Deoxyribonucleic Acid

RO reverse osmosis

FO forward osmosis

UF ultrafiltration

NF nanofiltration

# CHAPTER 1 INTRODUCTION

## 1.1 BACKGROUND INFORMATION

The main sources of water pollution in developing countries are industrial, municipal, and agricultural wastes (United Nations, 2017). According to the United Nations (2017), specifically the World Water Development Report, 80 % of water is wastewater, of which close to 95% are currently released into the environment without treatment and this results in contaminated drinking water which causes over 800,000 deaths globally and worsening global water pollution in most rivers across the developing world (United Nations, 2017). This is common in low and middle-income countries (LMIC). In South Africa particularly, the pollution of freshwater sources by mine water discharge and poorly treated or raw sewage has exacerbated the scarcity of water. This is primarily influenced by rapid population growth, reduced rainfall patterns, and increased water demand (Muller, 2015, Hassan, 2013).

Wastewater mainly contains pollutants such as solids, organic waste, nutrients, and microorganisms. The nutrients mainly found in wastewater are ammonia, nitrates, phosphates, magnesium, and calcium (Negwamba et al., 2019). The overabundance of phosphate in wastewater presents an opportunity to harness the nutrient due to the fact that its discharge to the environment together with ammonia foster eutrophication (Liu et al., 2013; Shaddel et al., 2019). The eutrophication phenomenon is a disadvantage to water bodies and aquatic life, as it reduces water quality because it promotes excess growth of unwanted organisms, and biomass which accumulates in the sediment, contributing to sediment oxygen demand and in the long term depletes oxygen in water. Photosynthetic biomass dissolves carbon dioxide, which causes a decrease in the pH of the waterbodies (Daneshgar et al., 2018).

Phosphorus is also valuable for reuse as a fertiliser because it is a vital element of life, it is a major component of DNA and is involved in the metabolism of living cells, but its reserves are said to be depleting (Stolzenburg et al., 2015). Therefore, it is important to manage the high levels of ammonia and phosphate to conserve the environment and comply with strict environmental regulations and harness the phosphorus for fertilisation and other industrial applications. Recent studies have focused on the recovery of ammonia and phosphate as struvite (Bayuseno, 2018, Mavhungu, 2020). However, there has not been evidence of the application of struvite beyond its use as a fertiliser, hence this presents the new opportunity for research.

The Acid Mine Drainage (AMD) legacy in South Africa has altered the capability of the environment to sustain life (Nordstrom et al., 2015, Masindi, 2016). AMD remains the largest

liability faced by the mining industry due to the extent of its impacts. This waste stream has been observed to threaten the water resources, human health, and the environment (McCarthy, 2012, Besseling, 2013, Naidoo, 2015, Kefeni et al., 2017). The large volumes of AMD produced by the Witwatersrand goldfields in Gauteng Province, South Africa amounts to ~60 ML/d, carrying sulfate ( $\text{SO}_4$ ) concentrations of ~4.5 to 5 g/L and ferrous iron ( $\text{Fe}^{2+}$ ) concentrations of up to ~1.5 g/L (Bologo et al., 2012, Masindi, 2016). The Mpumalanga coal basins can have up to  $\pm 18$  g/L of sulfate and  $\pm 6$  g/L of Fe-species (McCarthy, 2012, Bologo et al., 2012).

Acid mine drainage results when pyrite ( $\text{FeS}_2$ ), a common constituent of many mineral deposits in SA (both coal and gold) encounters oxygenated water and atmospheric air, it undergoes oxidation to produce  $\text{H}_2\text{SO}_4$ . This leads to the release of a drainage that is acidic, and rich in sulfate and metal ions into the environment (Amos et al., 2015, Masindi et al., 2016a). These minerals may be entrenched in the mined rock or crushed rock deposited on waste heaps (tailings). Figure 1 shows the AMD seepage from tailings and pumps at Grootvlei Mine.



**Figure 1-1: AMD seepage from tailings (A) and Pumps at the Grootvlei Mine (B) (WRC, 2011)**

The main constituents found in acid mine drainage are  $\text{H}^+$ ,  $\text{SO}_4^{2-}$  and Fe (II). Masindi et al. (2017) further highlighted that AMD contains Al (III) and Mn (II), As, Cu, Ni, Zn, Co and Cr and alkaline earth metals such as Mg and Ca (Masindi et al., 2015, Kefeni et al., 2017).

The high acidity of AMD causes adverse effects on aquatic ecosystems due to the deteriorating quality of water in the receiving environment, and it reduces the buffering capacity of water. AMD can be recognized by a yellowish or orange deposit in stream channels from the precipitation of

ferric ( $\text{Fe}^{3+}$ ) hydroxide and oxy-hydroxide and oxy-hydrosulfates. These precipitates of ferric ( $\text{Fe}^{3+}$ ) hydroxide and oxy-hydroxide and oxy-hydrosulfates lead to a reduction in dissolved oxygen concentrations in affected water bodies during their formation and have abrasive effects on biota and clog streambeds- once formed. It also prevents the penetration of light to aquatic ecosystem hence suffocating aquatic organisms (Zick, 2011, Oberholster et al., 2014, Simate and Ndlovu, 2014).

Traditionally, AMD has been managed and treated using different alkaline agents (Na, Ca and Mg) which have been successful in neutralisation and metals attenuation (Masindi et al., 2018, Masindi et al., 2019). On the other hand, struvite, contains magnesium ammonium phosphate, as well as traces of periclase and brucite (Mavhungu et al., 2019) which could present comparable neutralisation characteristics when applied to the treatment of AMD. The Fe present in AMD can form a complex with phosphate in struvite hence fostering the precipitation of metals as hydroxides. Other techniques such as filtration, ion exchange, adsorption and phytoremediation have been employed for AMD treatment, however, each technique has its advantages and disadvantages. Adsorption has a challenge of adsorbent saturation and limited capacity at elevated concentration (Kajjumba., 2013). Filtration has a challenge of brine generation and high-energy requirements (Masindi et al., 2019). Phytoremediation uses plants and they have exceptionally fine line of requirements in terms of nutrients and toxicant (Das, 2018, Masindi 2016a) and ion exchange pose secondary pollution and they generate brine to be dispose during the regeneration process (Gaikwad, 2010, Masindi, 2016a).

## **1.2 PROBLEM STATEMENT**

The pollution of freshwater sources by mine water discharge and poorly treated or raw sewage has exacerbated the scarcity of water. This has been caused by rapid population growth, reduced rainfall patterns, and increased water demand (Muller, 2015, Hassan, 2013). The discharge of partially treated acid mine drainage and/or wastewater poses a great burden on the freshwater resources which will not just expand the treatment cost yet additionally present a wide scope of chemical and microbial contaminants to the water. The release of AMD to receiving water causes a myriad of issues leading to the loss of habitats for aquatic organisms, stalled plant growth, corroded infrastructure, and killing of intolerant species. This is due to the acidity and heavy metal loads present in AMD.

Two key classifications of AMD treatment choices exist, the active and passive treatment. Conventionally, active chemical treatment options used alkaline industrial chemicals like calcium hydroxide ( $\text{Ca}(\text{OH})_2$ ) or limestone ( $\text{CaCO}_3$ ) to neutralise and remove metals as metal hydroxide

precipitates and sulfate as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) sludge (Olds et al., 2013; Tolonen et al., 2014). The passive treatment methods have been used as economic alternative to active treatment because it does not necessitate continuous chemical input, this lowers maintenance costs and has lesser environmental impacts because environmentally appropriate substances are generally used during the treatment. There are numerous downsides however, which limit their usage in recent mining activities. For instance, passive treatments involve longer treatment progression time for efficient remediation of AMD and as such they are less effective than active methods (Kefeni., 2017).

The phosphorus from domestic, agricultural, and industrial waste streams also causes other environmental problems. This is due to the inefficient nutrient management present in wastewater. The nutrient if not harnessed efficiently, it is removed in wastewater treatment plants during the biological wastewater treatment using anaerobic digesters and result in deposits of the compound known as struvite ( $\text{NH}_4\text{MgPO}_4 \cdot 6\text{H}_2\text{O}$ ) or magnesium ammonium phosphate (MAP) in the pipe walls and high phosphorus concentrations in the side streams (supernatant) from the sludge dewatering equipment (Liu, et al., 2018).

These side streams result in eutrophication when released into the water bodies (Dumas et al., 2011; Yetilmezsoy et al., 2017). Therefore, the sustainability of South Africa's critical water resources relies heavily on sustainable wastewater management (Ashton et al., 2012). Eutrophication control strategies that focus on P removal have been explored, although, there has not been tangible proof of improvements to the environment using these P-based strategies. Recently, numerous watershed nonpoint source investigations have yielded pretty much nothing or, at times, no enhancement in P deficit decrease, even after effecting the best management practice (Meals et al., 2010). It was until recent where struvite has been explored for management of P and N in natural waters and harvesting P as fertiliser.

This study attempts to beneficiate the two waste streams by synthesizing the struvite from municipal effluent and valorise it as a reactive compound for the remediation of acid mine drainage. This will communicate with the phenomena of the circular economy and zero waste discharge.

### **1.3 RESEARCH MOTIVATION**

The treatment of municipal wastewater and acid mine drainage are important in safeguarding water resource quality worldwide (Strosnider et al., 2013). South Africa has been unsuccessful in addressing the massive environmental and health impacts caused by the wastes from mines burrowed over a century back extending along one of the world's biggest gold stores and left

communities presented to dangerous impacts due to the outflow of acidic water from mines (Africa news, 2017). Most municipalities are also struggling to effectively manage the phosphate and ammonia resulting from wastewater treatment plants. Mining companies and the South African government have undertaken to come up with sustainable, effective, and economically viable technologies to remediate mine effluents (Rukuni and Maree, 2016).

An immense array of remediation procedures and innovations are accessible however, a significant number of the techniques used to remediate AMD are restricted in execution because of poor performance, planning errors, troublesome comprehension of their usefulness, significant expenses, use of unsafe synthetic substances, exhaustion of natural resources and the addition of more wastes (Moodley et al, 2018). This calls for a new approach to treating AMD that would not be destructive to the environment (Kefeni et al, 2017).

This study will assist in managing the impacts of phosphorus and ammonia on receiving water and improve the operational efficiency of wastewater treatment plants by harnessing phosphorus and ammonia as struvite. The struvite synthesized from wastewater treatment effluent has been proven to be an environmentally and economically viable method to reduce and recover phosphorus from wastewater and thereby minimizing environmental degradation (Mavhungu et al., 2019, Yetilmezsoy et al., 2017). Numerous studies have demonstrated struvite as a viable water-dissolvable phosphorus fertilizer in neutral and marginally acidic soils (Plaza et al, 2009; Massey et al., 2007). Rahman et al., (2014) found that struvite increases the soil pH when it is utilized as a fertilizer and as a result, it is appropriate for acidic soils.

Studies done by (Perwitasari et al., 2018; Vol'khin et al., 2015) indicated that struvite can successfully be applied as heavy metals (Pb, Cu, Zn, and Ni) sorbent in the soil. The application of struvite as a fertilizer has been successfully proven; however, its application for acid mine drainage treatment has not been explored. This would then be the first study in design and implementation to investigate the usage of struvite synthesized from wastewater supernatant using magnesite as a precursor for the treatment of AMD.

This research would be environmentally sustainable since the materials will be locally available and abundant. Wastewater effluent for struvite synthesis which is collected at no cost from wastewater treatment plants will always be available. The pre-cursor (magnesite) used is readily available. Masindi et al. (2015a) indicated that magnesite deposits (approximately 60 megatons) are available in South Africa. The study would use the supernatant from the anaerobic digesters at wastewater treatment works in the Tshwane Metropolitan municipality and test the by-product's (struvite) suitability to treat AMD.

## 1.4 RESEARCH OBJECTIVES

### 1.4.1 Main objective

The overall objective of this study is to evaluate the synthesis of struvite from municipal wastewater and explore its application on the treatment of acid mine drainage.

### 1.4.2 Specific objectives

To achieve the main objective of this study, the following specific objectives were undertaken:

- To determine the physicochemical properties of municipal effluents and acid mine drainage using different analytical techniques
- To synthesize struvite from municipal effluent using thermally activated cryptocrystalline magnesite as the precursor.
- To optimise conditions that are suitable for the treatment of acid mine drainage using struvite as a feedstock.
- To employ different analytical techniques to verify the product sludge and point out the fate of different contaminants and mechanisms thereof.
- To compare the quality of product water with different water quality guidelines and specifications.

## 1.5 HYPOTHESIS

- Struvite synthesized from municipal effluents can be successfully applied for the treatment of acid mine drainage.

## 1.6 THESIS LAYOUT

**Chapter 1:** Contains the clarification of the background information to the study, an explanation of the research problem, motivation of the research, the research objectives, and the hypothesis.

**Chapter 2:** Reviews the research literature relating to understanding of the formation of AMD and its environmental impacts and the treatment technologies available. The wastewater and wastewater characteristics, and their impacts on the environment are also discussed. Struvite formation and its applications have been explained in detail. The legal requirements pertaining to wastewater and industrial effluent discharge was also discussed in the chapter.

**Chapters 3:** The chapter explains the experimental plan that was followed for the study. This chapter will also discuss the type of data that is used in the study. It will also provide information

on how the data is collected and limitations towards using such data in research. The methodological rationale for the research design, ethical consideration, and obtaining authorization letter from the municipality will also be discussed.

**Chapter 4:** The chapter will concentrate on data presentation and analyses of the results. In-depth discussion on the fate of different contaminants will also be presented in this section. Factors that contribute to the attenuation of different contaminants will also be discussed.

**Chapter 5:** Summarizes and concludes the outcomes of the research in relation to the proposed objectives and hypothesis of the study. Recommendations for future research will be made in this chapter and this will be drawn from the gaps, which were identified from the findings of this study.

## CHAPTER 2 LITERATURE REVIEW

This section infer an in-depth and precise literature review relating to the understanding of the general water cycle-demand relationships, formation of acid mine drainage (AMD), physicochemical properties, associated environmental and social impacts, and available treatment technologies. Thenceforth an understanding of struvite chemistry, formation stoichiometry and its potential application would meticulously be elucidated. A summary of the literature review, gaps that need to be perched and future research outlooks will also be unpacked.

### 2.1 SOUTH AFRICA'S WATER CYCLE CRISIS

South Africa's water system is in crisis due to the country being a semi-arid country owing to its climatic features which makes it vulnerable to water stresses, mainly due to prevalent drought conditions. South Africa receives close to half (465mm) of the global annual (860mm) rainfall and the rainfall is not evenly distributed across the country and seasons (Water and sanitation Master plan, 2018). It is expected that water scarcity will persist due to the negative impacts from climate change which result to low rainfall, low yields for groundwater and its recharge, degradation of the wetlands and surface water resources, water losses and increased demand owing to population growth accompanied by notorious anthropogenic activities, such as agriculture, industries, and mining, urbanization and wastage, and the drying up of catchments due to alien plants invasion (Water and sanitation Master plan, 2018). An overview of the water cycle crisis in South Africa is given in Figure 2-1.

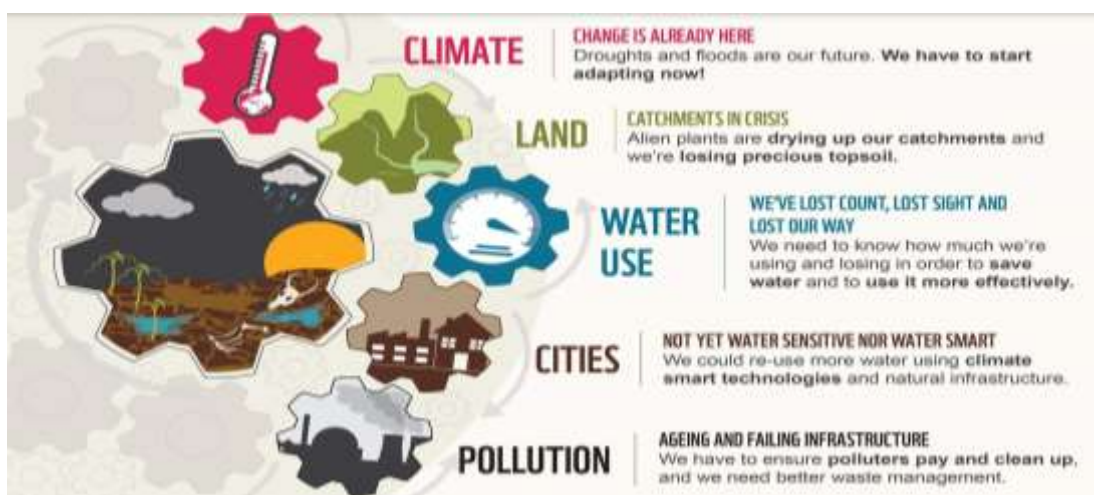


Figure 2-1: Water cycle crisis in South Africa (WWF, 2019)

## **2.2 ACID MINE DRAINAGE**

### **2.2.1 Mining in South Africa**

South Africa relies heavily on mining, it has been the main thrust behind our economy for almost 150 years, (KPMG, 2013). According to the KPMG report (2013) the industry has and keeps on forming our nation's socio-political and development. To date, the mining sector contributes 18% to the GDP and 20% of all investment in the country with an annual income of R330 billion (Chamber of mines, 2016).

It is, therefore, undeniable that the mining sector has played and is still playing a vital role in the fiscal growth of South Africa. Though, with huge environmental impacts, since mining activities are notorious for their environmental footprint (Omotehinse and Ako, 2019, Naidoo, 2015). The issue of AMD is the most hazardous risk as far as its ramifications. Coal and gold mining have grave consequences for the management of water in that it severely influences water quality and presents a considerable danger to water resources in South Africa (Naidoo, 2015). The hydrological and geological features of the mining sites can be changed by mining processes, which will impact the soil moisture, surface runoff, evapo-transpiration processes, and groundwater behaviours (DWAF, 2008).

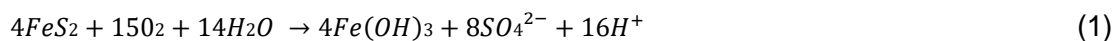
For a country plagued by water security crisis due to its alarming climatic fluctuations which makes it vulnerable to water stresses and other ecological challenges (Hassan, 2013). Primarily, the flowing of elevated levels of acid water into the water systems and hydrological networks and endangers the communities as well as ecosystems of a receiving environment (Ramontja et al., 2011, Masindi, 2016a). This place excessive stress upon the country's economy and water-stressed areas, potentially undermining the agrarian and industrial sectors (Africa news, 2017). In light of the above, thorough management practices to avert or reduce water pollution are essential to water management and for mining operations to be sustainable (DWAF, 2008).

### **2.2.2 Formation of acid mine drainage**

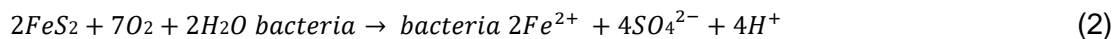
Geologically, gold, coal and copper deposits are associated with sulfide bearing minerals such as pyrite amongst others. During the mining process, the mined rock is crushed, and the gold is extracted, the crushed rock is then dumped on waste piles or tailings, when it rains the rainwater oxidizes the pyrite and forms sulfuric acid ( $H_2SO_4$ ). Similarly, when a mine is abandoned, the pumping ceases and water floods the mine, and the pyrite is oxidised, and sulfuric acid ( $H_2SO_4$ ) produced contaminates the groundwater. Therefore, AMD forms when pyrite encounters

oxygenated water, it then undergoes oxidation to produce sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) and dissolved iron (Bologo, 2012, Masindi, 2016 and Kefeni et al., 2017).

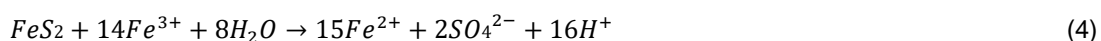
Oxidizing bacteria, prevalently acidophiles, for example, acidithiobacillus go about as impetuses to build the pace of pyrite oxidation. Sulfate and other heavy metals, like, iron, copper, lead, nickel, manganese, cadmium, aluminum and zinc, are discharged into the water once the ore is exposed, thus, rendering the water metalliferous (Masindi., 2016 and Kefeni et al., 2017). The formation of AMD may be depicted by the following chemical equation (1) (Masindi et al., 2015, Kefeni et al., 2017):



There are three fundamental chemical reactions that depict the development of AMD from pyrite the pyrite oxidation, ferrous oxidation and iron hydrolysis as seen in equation (2).



Pyrite (FeS<sub>2</sub>) is a common constituent of numerous mineral deposits (both coal and gold), it is the predominant type of sulfur mineral found in the lithology and stratigraphy of these mineral deposits. When pyrite oxidation occur, sulfur is oxidized to sulfate and ferric iron is released (Equations 3-5). The acidity that developed promotes the discharge of more minerals (Al, Mn and trace metals) which are linked to the extracted minerals (Amos et al., 2015). The formation of AMD can be represented by the following equations (3-5):



AMD is categorised by elevated acidity, poisonous metals, and sulfate concentrations. Depending on the activities of a specific mine, the high sulfate concentrations and metals in the water may fluctuate. Commonly, the water has increased levels of salts, poisonous metals, and a low pH (Kefeni et al., 2017). The dissolved iron can precipitate to form red, orange, or yellow deposits primarily due to Fe oxidation. Heavy metals such as copper, lead, and mercury from acid run-off are then dissolved into groundwater and surface water and has serious implications for water management in South Africa as it badly impacts the quality of water and becomes a substantial hazard to water resources (Naidoo, 2015).

### **2.2.3 Ecological impacts of acid mine drainage**

AMD presents sulfuric acid and substantial metals into the environment, and this severely damages the normal fauna and flora on exposure. Heavy metals in the surrounding geology reacts with sulfuric acid at a low pH and becomes soluble, hence increasing the dissolved ions. The presence of harmful heavy metals in the mine wastewater surpasses the drinking water guidelines, making it unacceptable for some uses. The high measure of hardness, disposition, or sedimentation of metal particles alongside bacterial pollution further renders the water unsuitable for drinking. Besides, contact with this sort of water either straightforwardly or in a roundabout way may prompt numerous illnesses both in plants and animals and in people (McCathy, 2012, Naidoo, 2015, Das, 2018).

AMD does not only contaminate local surroundings but can also affect distant areas if the water is discharged into the water sources (i.e. rivers, lakes, or groundwater) (Das, 2018). The acidic water generally permeates deep into the soil and through penetrable rocks to the groundwater. The contaminated water gets spread out further over a wide region through groundwater development. The contaminated groundwater is eventually devoured by people either from wells or bore wells hence posing various health challenges. The acidic mine water additionally destroys mine plants and prompts contamination of the mine surface (Das, 2018, Masindi, 2016b).

The high acidity of AMD water may affect development rates and the proliferation of fishes. It causes loss of sodium particles from the blood of fishes, influences the functioning of gills, at last, prompting death. Furthermore, the ferric hydroxide present in the seepage water may form a precipitate, totally layering the lower part of the streams, consequently making it ill-suited for the development of benthic organisms (Simate and Ndlovu, 2014).

### **2.2.4 Effects of AMD on aquatic resources**

Post formation of AMD, various metals are then discharged into the surrounding areas, which becomes accessible to natural life forms such as biological organisms (Forstner and Wittmann, 2012). AMD causes adverse effect to aquatic animals as the waste material becomes a disaster in the oceans due to bodies of effluents received. In countless cases, fish and other edible organisms are concentrated by harmful substances which enter the food chain. In water, for instance, when the fishes are exposed specifically to metals and low pH on their gills, impeded breath may come about because of constant and intense harmfulness. Fish are likewise accessible in an indirect way to metals through ingestion of debased residue and sustenance material (Singla et al., 2017). A usual weathering resulting from oxidation of sulfide is the arrangement of iron hydroxide ( $\text{Fe}(\text{OH})_3$ ), a red/orange colour present in large number of streams

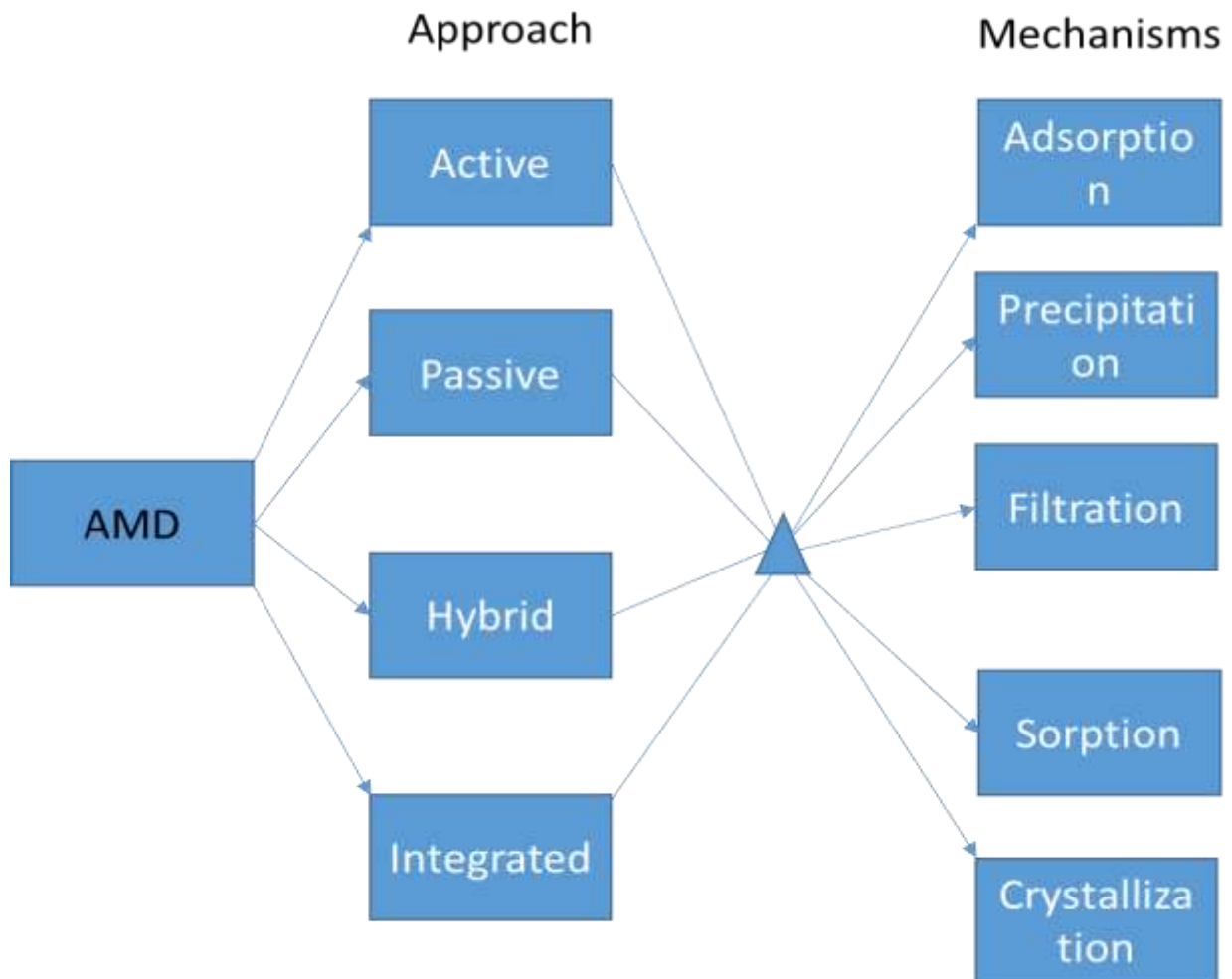
influenced by AMD. Iron hydroxides as well as oxy-hydroxides cover the surface of stream dregs and stream beds devastating natural surroundings, lessening accessibility of clean rock utilized for bringing forth, and decreasing fish sustenance material, for example, benthic large scale spineless creatures (Kaur, 2018). Corrosive mine seepage, portrayed by acidic metalliferous conditions in water, is in charge of physical, synthetic, and natural corruption of stream environment (Forstner and Wittmann, 2012).

### **2.2.5 Effects of AMD on health**

Sulfuric Acid has well-informed impacts through direct exposure, which should be counteracted through the mine's relief measures. Sulfuric Acid is, to a great degree destructive and it can bring about extreme irritation of skin and extreme lung damage, and hazardous accrual of liquid (pneumonic edema) (Kaur, 2018). Thenceforth, sulfuric acid in AMD can disturb and continuously damage to the eyes hence leading to possible visual deficiency (Cheremisinoff and Rosenfeld, 2010). In the event where the water is swallowed, it can devour mouth, throat, and stomach (Cheremisinoff and Rosenfeld, 2010, Kaur, 2018). Extended exposure in low levels can lead to Dermatitis (red, bothersome, dry skin) and Break-up of the teeth (Kaur, 2018).

### **2.2.6 Acid mine drainage treatment options**

The sole purpose of AMD treatment is to increase pH and remove metal concentrations. Several AMD methods have been used to reclaim and treat acid mine drainage. Two main categories of AMD treatment options exist, namely active and passive treatment. The technologies are depicted in the Figure 2-2. The use of chemical treatment is considered expensive due to frequent maintenance requirements and the purchase of chemicals. Chemical treatment is currently the most used remediation technology (Kefeni et al., 2017; Masindi, 2016c). Passive treatments such as constructed wetlands and limestone channels have been used as alternative. These are preferred owing to their economic benefits. However, they have their limitations as they require time for the reactions to occur and metals concentrations to be reduced.



**Figure 2-2: Categories of AMD treatment (Masindi, 2016c, Kefeni et al., 2017)**

### 2.2.5.1 Active treatment

This type of treatment comprise the use of alkaline substances to precipitate metals, methods such as adsorption (Motsi et al., 2011), ion exchange (Gaikwad et al., 2010), filtration in a form of membranes (Alkhubhri et al., 2012; Ricci et al., 2015), distillation and crystallization (Naidu et al., 2019, Park et al., 2019). Conventionally active chemical treatment that has been widely used for the neutralization of AMD has been through the use of industrial alkaline chemicals like limestone ( $\text{CaCO}_3$ ) or calcium hydroxide ( $\text{Ca(OH)}_2$ ) and remove metals as precipitates of metal hydroxides and sulfate as gypsum ( $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ ) sludge (Olds et al., 2013; Tolonen et al., 2014). The application of magnesium-based salts as pre-treatment for AMD has also been used (Bologo, 2009, Masindi, 2016a, Tansel et al., 2018). Amongst the active treatment techniques, precipitation has been perceived as the most promising method owing to its ability to remove contaminants at any concentration through an elevated pH.

#### 2.2.5.1.1 Chemical treatment systems

Chemical treatment systems add incredibly alkaline chemicals, for example,  $\text{CaCO}_3$ ,  $\text{NaOH}$ ,  $\text{Ca(OH)}_2$ ,  $\text{CaO}$ ,  $\text{Na}_2\text{CO}_3$ , and  $\text{NH}_3$  (Simate and Ndlovu, 2014, Masindi, 2016a). The system increases the pH of the drainage until metals are precipitated and can settle out in a holding pond. Sufficient alkalinity is required to raise the pH of the water and supply hydroxide to make insoluble metal hydroxides that settle out. The essential pH for metals to precipitate goes from 6 - 9 beside ferric iron which precipitates at  $\text{pH} > 3.5$ . Metal hydroxides precipitation vary contingent on pH.

#### 2.2.5.1.2 Adsorption

Adsorption refers to a process whereby a gas or liquid solute collects on the outside of a solid or a liquid, creating a molecular or atomic film. The material adsorbed is called the adsorbate or solute and the adsorbing phase is the adsorbent (El-Naas and Alhajja, 2016). Adsorption technology has seen significant interest of late as one of the most practical and efficient approaches for the treatment of numerous types of wastewaters (Kajjumba, 2013). It is in fact considered by many to be superior compared to other physical and chemical technologies.

#### 2.2.5.1.3 Ion-exchange

The trading of particles between at least two electrolyte solutions is known as ion-exchange. It can likewise allude to the trade of particles on a strong substrate to the soil solution. Using particle exchange surfaces, such as high cation-exchange capacity earth and pitches, metals are expelled from liquid solutions through particle exchange. In any case, it has disadvantages relying on certain boundaries, for instance, contact time, the concentration of the solution, pH of the supernatant's solution, and temperature. It is similarly costly and difficult to use for a bigger scale and its adequacy is limited to a convergence of metals. For wastewater treatment and constriction of metals from aqueous solution, normal and synthetic dirt, zeolites and engineered saps have been used (Gaikwad, 2010, Masindi, 2016a, Kefeni et al., 2017).

#### 2.2.5.1.4 Filtration

Filtration technologies such as reverse osmosis (RO), forward osmosis (FO) and ultrafiltration (UF) have received significant attention in mine water desalination, however, their application is limited owing to high maintenance costs (Masindi et al., 2019). The use of nanofiltration (NF) and reverse osmosis (RO) processes for AMD remediation pulled more researchers of late. This is because of to their ability to retain salt and metals. Their applications were evaluated by Aguiar et al., (2016) in comparison, they highlighted that NF had higher saturate transition and adequate solutes retaining efficacy than RO. Additionally, the examination accomplished the most water recuperation pace of 60% with the NF270 film from gold AMD for a one-step treatment at improved conditions, after which the pervade transition decrease was honed, exhibiting higher membrane fouling (Aguiar et al., 2016). The NF270 membrane belongs to the group of high permeability NF membranes <https://www.foreverpureplace.com/FILMTEC-NF270-4040-Nano-Filtration-Membrane-p/nf270-4040.htm>.

#### 2.2.5.2 Passive treatment

The passive treatment has been in use since the early 1990s (Yadav and Jamal, 2015). This category of treatment incorporates biological treatment with constructed wetlands, chemical treatment with limestone drains, and sulfate-reducing bioreactors (Tolonen et al., 2014; Zipper and Skousen, 2014). According to Neculita et al (2007), a permeable responsive boundary is also one of the most used passive treatment choices, which utilizes either chemical or biological processes. Majority of the passive treatment options are used at abandoned mines (Lukacs and Ortolano, 2015; Song and Choi, 2015), due to their low operational cost and maintenance.

##### 2.2.5.2.1 Phytoremediation

Phytoremediation is the use of green plants and their associated microbiota, man-made and engineered ecosystems, constructed wetlands and soil adjustments, to mimic naturally occurring wetland ecosystems. It is one of the emergent technologies for treatment of acid mine wastewater which can be applied to both water and soil affected by corrosive mine seepage. Soil affected by corrosive mine seepage may dissolve to the encompassing water bodies causing contamination. Thus, remediation of both soil and water close to the mining sites is imperative (Das, 2018, Masindi 2016a).

There are two main phytoremediation methods, phytoextraction and phytostabilisation. The phytoextraction process includes extraction of heavy metals by the plants and their stockpiling in various parts, for example, roots, stems, and leaves. Whereas phytostabilisation attempts to give

a vegetative cover that ties corrosive sulfate polluted soils that are profoundly inclined to erosion. Plants tolerant to certain metals are generally used in the process of phytoremediation of mining sites (Das, 2018).

#### 2.2.5.2.2 Open Limestone Channels

Open limestone channels are constructed to pre-treat AMD effluent, by raising the pH of effluent, through reacting calcite with carbonic acid. The process has experienced some problems whereby the  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$  extant in AMD are presented to the environment, and create metal hydroxides, in this way covering surface of the limestone channel known as shielding. The covering diminishes limestone pore space, lessening the solvency of limestone and balance of corrosive (Alcolea et al., 2012). Therefore, tremendous amounts of limestone are fundamental to create the alkalinity to guarantee long haul achievement of open limestone channels.

#### 2.2.5.2.3 Limestone Ponds

In limestone ponds, limestone is set at the lower part of the pond and water moves up through the limestone. In case lime is covered by Fe and Al hydroxide, the lime in the lake will be blended using a mixing material to remove the limestone and the precipitates. If the limestone is exhausted by breaking down, the new limestone will be acquainted with the chamber so balance and precipitation of metals can happen (Masindi et al., 2016).

#### 2.2.5.2.4 Alkalinity Producing Systems

The alkalinity producing systems (APS) are developed with a layer of treated compost on top of a bed of limestone. AMD falls on top of this layer and is drained into the perforated pipes, set in the lower segment of the limestone layer. The water by then travels through the normal layer and limestone. The limestone at that point gets separated by the anaerobic water with the formation of hydroxide particles. At the point when the water is brought into the perforated pipes and is delivered into the adjacent settling lakes, reoxygenation of the water and precipitation of the metals occurs (Deocampo and Jones, 2014).

## **2.3 WASTEWATER TREATMENT FACILITIES POLLUTION**

### **2.3.1 Pollution due to aging and failing infrastructure.**

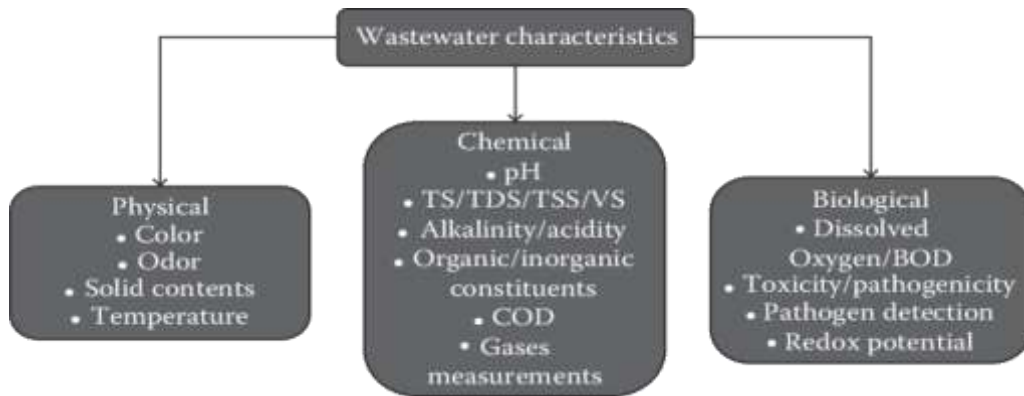
Pollution from agriculture, mining, and failing wastewater treatment infrastructure remains one of the biggest threats to our water security. This is supported by the United Nations world water development report (2017) which indicates that industrial, municipal, and agricultural wastes are

regarded as the main sources of water pollution in developing countries. In South Africa, the wastewater effluent is the main cause of common water contamination load (Singh and Kaushal, 2013). According to the water and sanitation masterplan (2018), approximately 56% of the over 1150 municipal wastewater treatment works (WWTWs) and approximately 44% of the 962 water treatment works (WTWs) in the country are in a poor or critical condition and need urgent restoration and skilled operators. Some 11% of this infrastructure is completely dysfunctional. Between 1999 and 2011 the extent of main rivers in South Africa classified as having a poor environmental condition increased by 500%, with some streams pushed beyond the point of recovery (National water and sanitation masterplan, 2018).

Wastewater can lead to immeasurable problems which may include but not limited to pollution of receiving waters, generation of odorous gases, the proliferation of microbial pathogens, depletion of oxygen in receiving water, and introduction of toxic substances into receiving waters (Metcalf and Eddy, 2014). It is, therefore, important to develop mitigation measures that will safeguard the water resources.

### **2.3.2 Wastewater Characteristics and Composition**

According to Metcalf and Eddy (2014) wastewater is defined as water that is withdrawn, used for some purpose, and then returned polluted in one way or the other due to agricultural return water, industrial effluents, municipal return water, power plants discharge water, mining discharge water, and stormwater. Wastewater encompasses large amounts of organic matter, inorganic matter, and microbial fractions, specifically, nitrogen and phosphorus including a considerable amount of Mg and heavy metals. Over numerous decades, wastewater has been considered as one of the major contaminants released into the environment (Rahman et al., 2014). Wastewater is characterized in terms of physical, chemical, and biological composition as broken down in Figure 2-3.



**Figure 2-3: Wastewater characteristics (Rawat et al., 2013)**

### 2.3.2.1 Physical characteristics

The key physical properties of wastewater comprise total solids, suspended particles, turbidity, colour, temperature, and conductivity. Physical properties could be of natural and anthropogenic origins, but they perform a fundamental part in determining the quality of the water (Metcalf and Eddy, 2014).

### 2.3.2.2 Chemical characteristics

The chemical characteristics of wastewater can be organic or inorganic, of which, inorganic constituents of concern in wastewater include nutrients, non-metallic constituents (e.g. chlorides, pH, alkalinity, nitrogen, phosphorus, and sulfur), metals, and gases (e.g. nitrogen, oxygen, and carbon dioxide from the air and hydrogen sulfide, ammonia, and methane from decomposed organic matter). Nitrogen and phosphorus (together with carbon) are essential for biological growth and when discharged to aquatic environments can lead to the growth of unwanted aquatic organisms. Eutrophication, associated with excess nitrogen and phosphorus, is a classic water quality problem associated with lakes, reservoirs, and estuaries. Metals such as cadmium, chromium, copper, iron, lead, mercury, and zinc are found, naturally, in most waters but some of these metals are priority pollutants, although the status may change over time (Metcalf and Eddy, 2014). This is mainly linked to their ecotoxicological rankings and epidemiological reports.

### 2.3.2.3 Biological characteristics

Organic compounds are usually a combination of C, H, O, & N (Metcalf and Eddy, 2014). In wastewaters, organic matter mainly consists of proteins, carbohydrates, oils, and fats. Laboratory methods used to measure gross concentrations of organic matter (> 1mg/L) in wastewater include

(1) biochemical oxygen demand (BOD) (2) chemical oxygen demand (COD), and (3) total organic carbon (TOC). One of the most important measures of water pollution is the biochemical oxygen demand (BOD) (Metcalf and Eddy, 2014). Nitrogenous Oxygen Demand (NOD) which is the measure of oxygen expected to change over natural and alkali nitrogen into nitrates by nitrifying microbes. Microbial life in wastewater incorporates microorganisms, protozoa, organisms, infections, green growth, rotifers, and nematodes. Oil and grease which start from food waste and oil-based commodities are additionally natural constituents of wastewater. The measure of oil and grease in crude wastewater differs from 10 to 109 mg/L (School of PE, 2018).

### **2.3.3 Eutrophication and its environmental impacts**

The phosphorus and nitrogen from domestic, agricultural, and industrial wastewater lead to serious environmental degradation. These nutrients prevail in wastewater treatment plants and result in deposits in pipe walls and eutrophication if released to the water bodies (Yetilmezsoy et al., 2017). Chrislock et al., (2013) define eutrophication as the excessive plant and algal development brought about by the expanded accessibility of at least one restricting growth factors, for example, daylight, carbon dioxide, and supplement manures required for photosynthesis. Eutrophication is the main source of contamination of numerous freshwater and coastal marine biological systems on the earth. It is indicated that the process occurs naturally over several years in lakes, but anthropogenic activities have exacerbated the rate and extent through both point-source discharges and non-point loadings of nutrients, like Nitrogen (N) and Phosphorus (P), into aquatic ecosystems, with devastating consequences for drinking water sources, fisheries, and recreational water bodies (Chrislock et al., 2013).

According to Jarvie et al., (2013) eutrophication is expected to worsen due to the water body's change in physical conditions (i.e. flow, water temperature, and light), as a result of environmental change or climate instability, furthermore the change in land-use, and alterations to the hydrological cycle, driven by water demand increases, is also anticipated to aggravate eutrophication (Jarvie et al., 2013). Nutrients such as phosphorus and nitrogen can impact the water quality adversely through the loss of dissolved oxygen and algae blooms when discharged into surface waters. These harmful impacts of the nutrients' discharge into the surface waters have led to the implementation of strict regulations concerning the discharge limits from the Wastewater Treatment Plants (WWTPs) (Prabesh, 2018).

### **2.3.4 P and N management techniques**

P is viewed as the essential compelling element for disturbing algal development in freshwaters. In the most recent years, the removal of P contributions from wastewater (point) and farming

(nonpoint) sources has been the fundamental watershed management tool to control freshwater eutrophication (Jarvie et al., 2013). Be that as it may, eutrophication-control strategies that are dependent on P have undergone intensifying investigation since there has not been tangible proof of improvements to the environment using these P-based strategies. In the recent decades, numerous watershed nonpoint source undertakings have yielded pretty much nothing or, at times, no net enhancement in P deficit decrease, even after effecting best management practice (Meals et al., 2010). At times, decreased P focusing to a great extent on point-source P controls, have brought about enhancements in stream ecology. This has led to researchers finding new solutions for P management to safeguard the receiving environment. Recent studies show that methods have been found to manage P and N through the synthesis of struvite from the anaerobic digester supernatant.

### **2.3.5 Struvite synthesis from wastewater effluents**

The precipitation of struvite from waste streams has gained the attention of the scientific community due to its potential for phosphorus recovery (Yan and Shih, 2016). Phosphorus is the most valuable nutrient that can be recovered from struvite for reuse because it is a vital element of life, it is a major component of DNA and is involved in the metabolism of living cells, but its resources are depleting (Stolzenburg et al., 2015, Bing Li, 2018). Phosphorus discharge to the environment together with ammonia eventually leads to eutrophication (Liu et al., 2013; Shaddel et al., 2019), and leads to pipe clogging at wastewater treatment plants. Thus, precipitation of struvite especially from wastewater supernatant is done to also manage the impacts of P and N in receiving natural waters (Yetilmezsoy et al, 2018). The process has proven to be an environmentally and economically viable method to reduce and recover phosphorus from wastewater and reduce the eutrophication in receiving waters (Yetilmezsoy et al, 2018, Mavhungu et al, 2019).

#### **2.3.5.1 Magnesium sources used in the synthesis of struvite**

The addition of precursors in the form of magnesium sources has been recently investigated. Magnesium is often the limiting ion and thus it needs to be increased in wastewater to form struvite (Bergmans et al., 2013; Rahman et al., 2014). Magnesium is added to wastewater as a compound, the options seem infinite but there are better magnesium compounds to use for struvite precipitation than others. Magnesium sources can be compared based on cost, the yield of struvite, the struvite structure formed, and struvite purity (looking at competing ions that would interact in the wastewater). Magnesium sources added in the wastewater depends mostly on the wastewater source, some wastewaters, for example, leachate from landfill sites may require

substantial quantities of magnesium and phosphorus to be added to recover struvite (Huang et al., 2014).

Most of the wastewater treatment plants use insoluble iron and aluminium salts to remove phosphate from sludge and then dispose of the sludge at landfill sites, the water-soluble magnesium sources like  $MgCl_2$  are also used to recover phosphate and form struvite (Kirinovic, 2017). Other sources of magnesium used for struvite formation include insoluble  $MgCO_3$ ,  $Mg(OH)_2$ , and  $MgO$  (Kirinovic, 2017). Struvite can be synthesized using different p-rich waste streams such as calf manure, human urine, anaerobic digester supernatant, and swine waste and the process focuses on three parameters pH, dosage and mixing, and their impact on phosphorous removal (Bing Li et al., 2018, Mavhungu et al., 2019). It is thus important to explore most environmentally friendly, cost-effective, and sustainable magnesium sources to make struvite an attractive form of phosphorus recovery (Mamakoa et al., 2019).

### **2.3.5.2 Struvite precipitation methods and models**

Different methods have been employed to synthesize the struvite. The aqueous precipitation and hydrothermal formation are the common methods used. The aqueous precipitation method focuses on struvite formation through mixing the waste streams with a precursor, monitoring the pH and environmental temperature, which are the parameters of importance for the precipitation and decomposition of struvite (Sutiyono et al., 2016). The hydrothermal synthesis includes heating the reactor at different temperatures for 24hrs, then air cooling and water quenching to room temperature which results in struvite formation (Bayuseno and Schmahl, 2018).

Chemical equilibrium models can be developed to predict and optimize the struvite precipitation process. Gadekar and Pullammanappallil (2010) achieved this by developing a mathematical model which exhibited satisfactory results when compared to experimental data. Harada et al. (2006) developed a chemical equilibrium model that predicted how struvite will precipitate and the model results agreed with experimental results. Liu et al (2013) indicate that the use of the Visual Minteq software to predict struvite precipitation is common in previous studies but the developed models only focus on struvite precipitation and no other important aspects such as struvite purity and salts that co-precipitate with struvite.

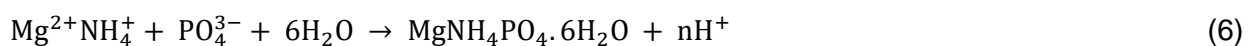
Liu et al (2013) modified Visual Minteq to predict struvite precipitation from urine, the effects that pH and the magnesium to phosphorus mole ratio (Mg/P) have on struvite precipitation were considered in the model and the results were compared to experimental results. The modelling results (where  $MgCl_2$  and seawater are used as magnesium sources) showed that at a Mg/P mole ratio of 1.1:1, all the phosphate was recovered while the recovery of ammonia was only 7%

through struvite precipitation. Shaddel et al (2019) also used Visual Minteq for thermodynamic equilibrium calculations.

Changing physico-chemical parameters to obtain optimal struvite crystallization conditions can be time consuming. The parameters can be inter-dependent and therefore Response surface methodology (RSM) can be used as an optimization tool. The RSM used the Central Composite Design software to optimise struvite precipitation, the software predicted 97.49% of the phosphates will be recovered from the respective wastewater (Kumari et al., 2020). Studies by Rahman et al (2014) Xu et al (2018) and Shaddel et al (2019) also focused on using kinetic models to estimate struvite growth kinetics and it was observed that struvite precipitation fitted well to the first-order kinetic model compared to the second and third-order models and this result was independent on the rate constant and pH.

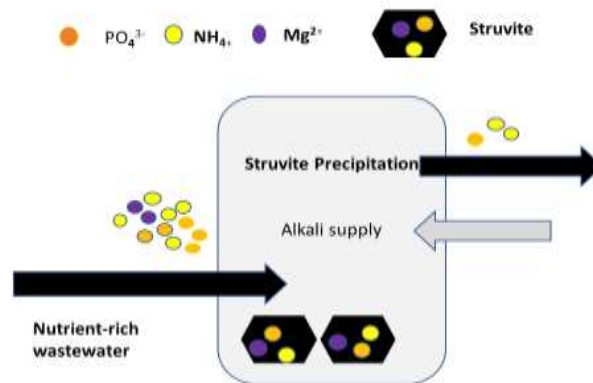
### **2.3.5.3 Chemical properties of struvite**

Struvite is also known as magnesium ammonium phosphate hexahydrate ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ). It is a crystalline phosphate mineral with a molecular weight of 245.43 g/mol and a solubility product ( $K_{sp}$ ) of  $10^{-13.26}$ . The crystal appearance varies, struvite can be in powder form or exist as big single crystals, while the colours vary from white to yellow and brown (Bergmans et al., 2013; Rahman et al., 2014). Struvite is illustrated by the following equation (6):



Rahman et al (2014) highlight that struvite crystals are formed with equal molar concentrations of magnesium, ammonium, and phosphate joint with six water molecules ( $\text{MgNH}_4\text{PO}_4 \cdot 6\text{H}_2\text{O}$ ). It is sparingly dissolvable under neutral and alkaline conditions however, promptly solvent in acid. It is a delicate mineral with low gravity of 1.7. Struvite can be found in orthorhombic or pyramidal crystals or platy mica-like structures of Magnesium Ammonia and Phosphate (MAP) (Rahman et al, 2014).

#### 2.3.5.4 Struvite Formation Process



**Figure 2-4: Struvite formation process (Wen-Wei et al., 2014)**

#### 2.3.5.5 Factors that influence struvite synthesis

The precipitation of struvite is controlled by physico-chemical factors that affect both nucleation and crystal growth. These physico-chemical factors are pH, the degree of magnesium, ammonium, and phosphate supersaturation (concentrations), the existence of competing ions, temperature, and mixing energy (Hallas et al., 2020). The struvite product and the crystal growth rate depend on the production conditions. The basic structure of struvite crystals at a minimum pH of formation is a coffin-like structure while at higher pH values, the crystals are well developed and look like tiny trees or three-dimensional leaves (Prywer et al., 2012).

Nucleation is the first phase to struvite crystallization. Homogeneous primary nucleation takes place in solution and requires high supersaturation for it to spontaneously develop. Homogeneous primary nucleation is followed by heterogeneous primary nucleation and then by surface secondary nucleation (Rahman et al., 2014; Shaddel et al., 2019). Nucleation is affected by pH, supersaturation, competing ions in solution, mixing energy and temperature.

##### 2.3.5.5.1 Time

Crystal size of struvite is influenced by the retention time of the particles inside the reactor. Crystal growth rate increases with the availability of the individual components that form struvite (Shaddel et al., 2019; Kumari et al., 2020). The time between supersaturation and the earliest development of the crystal nuclei is called the induction time  $t_{ind}$  of struvite, i.e. "the time lapse between the

mixing of the solutions containing struvite component-ions and the first measurable detection of struvite nuclei. It is a vital parameter during struvite nucleation (Zeng et al., 2018; Rahman et al., 2014).

#### 2.3.5.5.2 Temperature

Temperature affects the morphology and habit of struvite. Precipitating struvite at 25°C results in rectangular and prismatic shape, while at 37°C square and thick crystals are dominant. At 37°C, struvite also transforms faster into new byrite ( $\text{MgHPO}_4 \cdot 3\text{H}_2\text{O}$ ) than at 25°C (Muryanto, 2017). The change in shape, morphology and phases may influence the tendency of the struvite crystals to agglomerate and subsequently to form scale deposit. It is envisaged that struvite with rectangular and prismatic shape is more difficult to agglomerate than those with square and thick morphology (Muryanto, 2017).

According to Moussa et al. (2011), temperature affected induction time,  $t_{\text{ind}}$ , of struvite, i.e. it affected the time interval between the mixing of the solution containing struvite component-ions and the first measurable detection of struvite nuclei. Crystal nuclei are formed through accumulation of ions, thus, it is obvious that higher temperatures shorten the  $t_{\text{ind}}$ , since at higher temperatures ions may collide among themselves more readily and subsequently encourage the agglomeration.

#### 2.3.5.5.3 Molar ratios

Theoretically, the Mg/P ratio of 1:1 is the optimal ratio for struvite precipitation, at lower ratios, nutrient recovery is reduced. Practically, the 1:1 Mg/P molar ratio does not always yield successful results. Some studies have indicated that having a slightly higher Mg/P molar ratio (1.2:1 or 1.3:1) is beneficial for phosphorus recovery, when the magnesium is in excess, all the phosphorus will react to form struvite crystals, and it will not be present in the effluent water. The optimal Mg/P ratio was found to be 1:1:1 at a pH range of 8-10.5 (Rahman et al., 2014; Zeng et al., 2018; Kumari et al., 2020).

Moreover, the concentration of component-ions has direct correlations with the saturation index (SI) of the solution, hence directly influences the nucleation and growth. Higher initial concentrations of P, keeping all other component concentrations and operating conditions constant, resulted in larger diameter of struvite crystals (Fang et al., 2016). Fang et al. (2016) observed an increase of > 300% in diameter of the struvite crystals (20.5  $\mu\text{m}$  to 69.3  $\mu\text{m}$ ) when the initial concentration of P was increased from 155  $\text{mg} \cdot \text{L}^{-1}$  to 930  $\text{mg} \cdot \text{L}^{-1}$ .

#### 2.3.5.5.4 pH

pH level is deemed as the utmost vital variable influencing the precipitation of struvite and the pH level of 9.5 to 10.5 is viewed as the ideal. During the precipitation of struvite, proton (H<sup>+</sup>) is released, hence, bringing down the pH level of the precipitating solution. Consequently, struvite precipitation experiments are ordinarily completed at a specific pH range higher than neutral (Muryanto, 2017). The morphologies of the struvite crystals at pH 7.5 varied from wedge-like to longitudinal elongated crystals which depends on the Mg/P ratio (supersaturation). At this pH and increased supersaturation, the crystals were like the crystals formed at pH 8.5. The crystals in this zone look like twin crystals (duplicates) with an X-shape morphology. Increased supersaturation and pH produced crystals with leaf-like or dendrite morphologies (Shaddel et al., 2019).

According to Saidou et al. (2009) it is indicated that another phosphate mineral, namely Mg<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub>·22H<sub>2</sub>O starts precipitating at the initial solution pH of 10. The formation results from the dominant species of phosphate ions in the form of PO<sub>4</sub><sup>3-</sup> in the solution. It has been observed that various pH levels result in different species of phosphate ions (PO<sub>4</sub><sup>3-</sup>, HPO<sub>4</sub><sup>2-</sup>, H<sub>2</sub>PO<sub>4</sub>) (Crutchik & Garrido, 2016; Bergmans, 2011; Saidou et al., 2009) and subsequently producing other phosphate compounds along with struvite.

The effect of pH on struvite precipitation can also be observed in the variation of the kinetic rates of precipitation. Crutchik & Garrido (2016) explored the kinetics properties and thermodynamic of struvite precipitation and found that for three pH levels 8.2, 8.5 and 8.8 the kinetic rates of precipitation increased as 1.21\*10<sup>-4</sup>, 1.25\*10<sup>-4</sup>, and 1.63\*10<sup>-4</sup> mol m<sup>-2</sup> min<sup>-1</sup>, respectively. Accordingly, the struvite precipitation kinetics (and subsequently its dissolution) are affected by slight variations of pH. As pH increases, the ionic activity product (IAP) also increases which results in the rise of supersaturation; and as such, causes the rise in kinetics rates (Crutchik & Garrido, 2016).

#### 2.3.5.5.5 Mixing

Fang et al. (2016), stated that mixing affects mass transfer. If the mixing is slow enough, it may encourage the transfer of ions or crystal units from the solution onto the crystal surface. Meanwhile, if the mixing is too high, the solutes may have difficulty to attach to the crystal surface. Therefore, mixing may negatively correlate with the crystal growth. It can be concluded that the particle size decreases with the increase in agitation. Furthermore, increased agitation rates yield higher number of crystals but smaller in size due to the breakage of the crystals caused by the collision among the crystals or between the crystals and the agitator. Mixing energy is associated

with crystal size and thus the number of crystals that form while the presence of competing ions in the wastewater affects the development of struvite crystals due to co-precipitation. When struvite nucleates and grows, it is because the system is supersaturated and needs to return to equilibrium (Rahman et al., 2014; Xu et al., 2018; Aguago et al., 2019; Shaddel et al., 2019).

#### 2.3.5.5.6 Co-existing ions

The existence of co-existing ions, even in ppm amounts, has a significant effect on the precipitation of struvite. The effect can be evident, on the alteration of morphology (Saidou et al., 2015; Muryanto & Bayuseno, 2014), crystal phases (Saidou et al., 2015), as well as precipitation rates (Kabdaşli et al., 2017). Two divalent metal ions  $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$ , at 5.0 ppm each, individually affected the precipitation rate and morphology of struvite significantly (Muryanto & Bayuseno, 2014). Saidou et al. (2015) studied the effect of  $\text{Cd}^{2+}$ ,  $\text{Al}^{3+}$ , and  $\text{SO}_4^{2-}$  on struvite precipitation using the degassing method. They showed that higher  $\text{Cd}^{2+}$  concentrations ( $\geq 10$  ppm) enhanced the formation of an amorphous phase alongside struvite. The addition of  $\text{Cd}^{2+} \geq 10$  ppm, saw the crystallinity of struvite reduce to amorphous phase. Thus,  $\text{Cd}^{2+}$  in ppm amounts could be an effective inhibitor for struvite precipitation. The addition of  $\text{Cd}^{2+}$  at 100 ppm is considered maximum due to the occurrence of metal ions like  $\text{Cd}^{2+}$  in wastewater which is considered an impurity and rarely higher than a few ppm. Secondly, to effectively prevent struvite precipitation  $\text{Cd}^{2+}$  is added into the precipitating solution. Hence, adding  $\text{Cd}^{2+}$  in higher amounts is inefficient.

#### 2.3.5.6 Uses of struvite

The end use of struvite depends on particle sizes and quality (Bing Li, 2018). The bigger particles are suitable for application as fertilizer because they are easy to transport, and they lead to a slower fertilizer release rate (Bing Li, 2018). Thus, struvite has so far been applied as a slow-release fertilizer in agriculture due to its ability to release nutrients slowly and increase the availability of good phosphorous. It is the most sustainable alternative to conventional high solubility fertilizers (Bing Li et al, 2018).

Struvite can be used directly on soil since it contains macronutrients (nitrogen and phosphorus) and a secondary macronutrient (magnesium) suitable for increasing soil pH during farming (Shaddel et al., 2019). A few investigations have demonstrated struvite as a compelling water-solvent phosphorus compost in slightly acidic and neutral soils (Plaza et al, 2009; Massey et al 2007). Rahman et al (2014) found that struvite increases the soil pH when it is utilized as a compost and as such, it is appropriate for acidic soils. Studies done by (Perwitasari et al, 2018; Vol'khin et al, 2015) indicated that struvite can successfully be applied as heavy metals (Pb, Cu, Zn, and Ni) sorbent in the soil.

### 2.3.5.7 Feasibility of treating AMD with struvite

Recent studies have focused in the recovery of ammonia and phosphate as struvite (Bayuseno and Schmahl, 2018, Mavhungu et al., 2020). However, its application has never been explored further than as a fertiliser, thus highlight a huge opportunity for research exploration. Studies done by (Perwitasari et al, 2018; Vol'khin et al, 2015) demonstrated that struvite can effectively be applied as significant metals (Pb, Cu, Zn, and Ni) sorbent in the soil. Since struvite crystals are sparingly dissolvable under neutral and basic conditions yet promptly solvent in acid. There has been an immense application of periclase, brucite and magnesite for AMD treatment (Masindi et al., 2018, Masindi et al., 2019). Struvite, which is basically constituted of magnesium, periclase, brucite, ammonium and phosphate (Tansel et al., 2018), could also pose similar neutralisation characteristics, hence the intention to potentially apply it for AMD treatment.

## 2.4 WATER QUALITY POLICIES IN SOUTH AFRICA

Section 24 of the constitution of South Africa specifies that everyone has the right to live in an environment that is not harmful to their health. The National Environmental Management Act (NEMA) 107 of 1998 is a framework to enforce this right, The National Water Act (36 of 1998) points to ensuring the national water resources for manageable use, and special consideration is given to the accessibility of water in adequate amount and good quality for human and environmental need. Based on these pieces of legislation the wastewater discharge standards DWA 2010 guidelines were published.

**Table 2-1: Wastewater discharge limits into a water resource (DWA, 2010)**

Variables and substances	Existing General Standards	Future all discharges
Chemical oxygen demand	75 mg/l	65 mg/l
Colour, odour or taste	No substance capable of producing the variables listed	No substance capable of producing the variables listed
Ionised and unionised ammonia (free and saline ammonia) (as N)	3,0 mg/l	1,0 mg/l
Nitrate (as N)	15	15 mg/l
pH	Between 5,5 and 9,5	Between 5,5 and 7,5
Phenol index	0,1 mg/l	0,01 mg/l
Residual chlorine (as Cl)	0.25 mg/l	0,014 mg/l
Suspended solids	25 mg/l	18 mg/l
Total aluminium (as Al)	-	0,03 mg/l
Total cyanide (as CN <sup>-</sup> )	0,02 mg/l	0,006 mg/l
Total arsenic (as As)	0,02 mg/l	0,01 mg/l

Total boron (as B)	1,0 mg/l	0,5 mg/l
Total cadmium (as Cd)	0,005 mg/l	0,001 mg/l
Total chromium III (as CrIII)	-	0,11 mg/l
Total chromium VI (as CrVI)	0,05 mg/l	0,02 mg/l
Total copper (as Cu)	0.01 mg/l	0,002 mg/l
Total iron (as Fe)	0.3 mg/l	0,3 mg/l
Total lead (as Pb)	0,01 mg/l	0,009 mg/l
Total mercury (as Hg)	0,005 mg/l	0,001 mg/l
Total selenium (as Se)	0,02 mg/l	0,02 mg/l
Total zinc (as Zn)	0.1 mg/l	0,05 mg/l
Faecal coliforms per 100 ml	1000 mg/l	1000 mg/l

The Department of Water Affairs DWS Water Quality Guidelines likewise makes arrangements for the release of industrial effluents. This reason necessitates that any individual who uses water for industrial purposes will refine or in any case treat such water as per prerequisites of DWA. The significant standards for release of acidic and sulfate-rich water are given in Table 2-2.

**Table 2-2: Discharge limits for mine wastewater (Masindi, 2016)**

Parameter	DWS Industrial	DWS Irrigation
pH	5.0-10.0	6.5-8.4
EC	0-250	>540
Na	-	430-460
K	-	-
Mg	-	-
Ca	-	-
Al	-	5.0-20
Fe	0.0-10	5.0-20
Mn	0.0-10.0	0.02-10.0
Cu	-	0.2-5.0
Zn	-	1.0-5.0
Pb	-	0.2-2.0
Co	-	0.05-5.0
Ni	-	0.2-2.0
SO <sub>4</sub> <sup>2-</sup>	0-500	-

Table 2-2 indicates that mine wastewater in South Africa are governed by dissolved Fe, Al, Mn, Ca, Na, Mg and traces of Cu, Co, Zn, Pb and Ni. The concentrations are far above the legal requirements and threaten the environment and human life.

## 2.4 SUMMARY OF LITERATURE REVIEW

The literature review identified areas of concern relating to the aims of this study. The excessive amounts of N and P should be prevented to avoid eutrophication in natural waters. The uncontrollable struvite precipitation which occurs under specific conditions, increase a hard scale deposit, and consequently lead to concerns for industries and wastewater treatment plants. Although the negative effects of struvite on equipment, it can be applied safely as fertiliser. There are several process parameters that govern the precipitation of struvite i.e. pH, molar ratios, temperature, agitation rate, and presence of co-existing ions. It is noted that pH level is viewed as the highly crucial variable influencing the precipitation of struvite, but agitation rate does not have a significant effect. It is also noted that morphology and crystalline phases of struvite are influenced greatly by divalent metal ions, such as  $\text{Cu}^{2+}$  and  $\text{Cd}^{2+}$ .

Various technologies exist for AMD treatment, though their implementation has not yielded desired results due to high cost, incorrect management procedures and production of further wastes which is detrimental to the environment and requires special disposal which increases maintenance costs. Magnesium based materials, particularly brucite have been applied successfully for AMD remediation, but the cost of manufacturing the material is a limiting factor. Magnesite does not raise the pH to the standard required by the water guidelines. Cryptocrystalline magnesite has been found to be efficient in neutralising AMD, as well as valorising wastewater to recover P and N as struvite. Therefore, this sparked the idea of using the struvite produced from using cryptocrystalline magnesite as a precursor, in the treatment of AMD, this is due to the presence of magnesium, brucite and periclase in the struvite. Based on the latter it is perceived that struvite will have the same neutralising effects as the other magnesium-based materials. Thenceforth, the notion that struvite is stable at alkaline media and very soluble in acidic condition justifies the feasibility of employing it for acid mine drainage treatment. This will play a critical role in the neutralization of acid mine drainage and attenuation of inorganic contaminants such as metals when the pH increases. The notable fraction of Ca in cryptocrystalline magnesite will also aid in the attenuation of sulfate as gypsum.

## **CHAPTER 3 MATERIALS AND METHODS**

### **3.0 INTRODUCTION**

The techniques and materials that were utilized in the study are discussed in detail in this chapter. These techniques present the composition of wastewater effluent and AMD and their impact on water security and the environment. The investigation, furthermore, proves the hypothesis that using waste material in a form of struvite from wastewater effluent and applying it to the treatment of AMD is feasible. Ethical standards were followed during the time spent collecting data. A full clarification of this investigation was given toward the North-West University through signing an ethics clearance form and performing a Hazard Identification and Risk Assessment (HIRA). To achieve the objectives of the research a variety of methods were utilized. The steps underneath evidently show the processes and methodology pursued to accomplish the research aims.

### **3.1 DESKTOP STUDY**

The desktop study included gathering literature from various sources locally and internationally. This likewise exhorts on which parameters are essential to analyse when it comes to wastewater effluents and acid mine drainage. It additionally gave the best techniques that can be utilized to accomplish the objectives of the study.

### **3.2 SAMPLES COLLECTION**

#### **3.2.1 Collection of municipal wastewaters**

Real untreated wastewater, rich in phosphate and ammonia, was collected from a Zeekoegat wastewater treatment works in Pretoria, South Africa. The treatment facility receives wastewater from several activities from the surrounding area. High-density polyethylene (HDPE) wide-mouth bottles were used for sample collection. Solids and debris were removed by filtration, using Macherey-Nagel filter papers (MN 615. Ø125mm), and the samples were used immediately thereafter. In the context of this work, the authentic wastewater was used with no dilution or pre-treatment.

#### **3.2.2 Collection of acid mine drainage**

AMD was collected from a coalmine in Mpumalanga, South Africa. The highly concentrated solution with high acidity and elevated levels of chemical species were collected in a toe seep from the stockpiled coal and tailings in a coal washing facility. High-density polyethylene (HDPE) wide-mouth bottles were used for sample collection. Solids and debris were removed by filtration,

using Macherey-Nagel filter papers (MN 615. Ø125mm), and the samples were used immediately thereafter. Authentic AMD was used with no dilution or pre-treatment.

### **3.2.3 Collection of cryptocrystalline magnesite**

Raw cryptocrystalline magnesite samples were collected from a run-down magnesite mine in Folovhodwe, Limpopo Province, South Africa. The collected raw cryptocrystalline magnesite was first milled into a fine powder, using a vibratory ball miller at 500 rpm for 15 min. Thence, the fine powder was calcined at 1,000 °C, using a furnace as reported in previous studies (Magagane et al., 2019, Mavhungu et al., 2019). Finally, and to acquire the desired material, the samples were milled again, under the same conditions, and then sieved through 32 microns perforated sieve. The thermally activated magnesite samples were then stored in safe containers until utilisation for the synthesis of struvite.

### **3.3 PREPARATION OF STRUVITE**

The collected municipal wastewater was used for the synthesis of high-grade struvite for AMD treatment. Struvite was synthesized via the typical crystallization and precipitation process as reported in previous studies (Mavhungu et al., 2019, Mavhungu et al., 2020, Mavhungu et al., 2020). To achieve that, 60 minutes of equilibration, 1g:100 mL of solid: liquid ratio, ambient temperature, and pH, and 500 rpm mixing speed were utilized for the synthesis of struvite. The product water was left to settle for 30 minutes. Thenceforth, the supernatant was decanted from the beaker and the sludge was taken to the oven for overnight drying at 105 °C. After drying, the samples were then milled into fine powder and kept into an air-tight container for utilization in AMD treatment.

### **3.4 OPTIMISATION STUDIES: TREATMENT OF ACID MINE DRAINAGE**

To obtain an in-depth understanding of the factors influencing the removal of contaminants from AMD, several operational parameters were evaluated. These include: i) contact time (i.e. mixing duration of the feed-wastewater solution); ii) feed dosage (i.e. the amount of struvite produced from mechano-thermo activated magnesite used during treatment); and iii) ambient temperature and pH were considered for optimization studies. Experiments were performed in 1L volumetric flasks, stirred at 300 rpm using an overhead stirrer. To gain in-depth insight onto influential parameters, the one-factor-at-a-time (OFAT) method was used, i.e. each time one parameter was varied while the others were fixed, as shown in Table 3-1.

**Table 3-1: Evaluated parameters for the treatment of acid mine drainage (AMD)**

Entry	Time	Dosage	pH and Temperature	Volume	Mixing speed
Units	minutes	grams	pH unit and °C	L	rpm
1	5 mins.	15g	Ambient conditions	1L	300 rpm
2	10 mins	15g	Ambient conditions	1L	300 rpm
3	15 mins	15g	Ambient conditions	1L	300 rpm
4	30 mins	15g	Ambient conditions	1L	300 rpm
5	45 mins	15g	Ambient conditions	1L	300 rpm
6	60 mins	15g	Ambient conditions	1L	300 rpm
7	45 mins	0.5g	Ambient conditions	1L	300 rpm
8	45 mins	1g	Ambient conditions	1L	300 rpm
9	45 mins	2.5g	Ambient conditions	1L	300 rpm
10	45 mins	5g	Ambient conditions	1L	300 rpm
11	45 mins	10g	Ambient conditions	1L	300 rpm
12	45 mins	15g	Ambient conditions	1L	300 rpm
13	45 mins	25g	Ambient conditions	1L	300 rpm

The effect of different operational parameters was evaluated using the highlighted conditions, Specifically, the factor to be evaluated was varied while the other factors were fixed to determine the effect of the parameter under study (Table 3-1). As part of quality control, a 4-decimal place analytical balance was used to calculate feed dosages. Finally, the temperature and pH were not evaluated but the ambient conditions of the feed solution were evaluated using the mother conditions. The effect of contact time was examined by agitating the AMD-feed solution at the time intervals specified in Table 3-1.

#### **3.4.1 Effect of contact time**

AMD feed solution mixtures were equilibrated for 5, 10, 15, 30, 45, and 60 minutes at 300 rpm using overhead stirrer. After agitation, the mixtures were filtered through a 0.45 µm pore nitrate cellulose filter membrane. After filtration, each example was partitioned into two for anion and cation analysis by an ion chromatography (IC) - Metrohm make - Compact 930 AnCat Flex IC Chromatograph, and inductively coupled plasma–optical emission spectrometry (ICP-OES)- Agilent make - ICP OES 725. The pH was measured using the (HANNA instrument, HI9828) multimeter probe before and after agitation.

#### **3.4.2 Effect of dosage**

Experiments were carried out in glass beakers with a volume of 1L, varying dosages of 0.5g, 1g, 2.5g, 5g, 10g, 15g and 25g of struvite added to 1L of AMD and the mixtures were agitated with

the overhead stirrer. The mixing speed of 300rpm was used. The solution was left to settle for 30 minutes. The pH and metal content were evaluated as expressed in the previous section.

### **3.5 QUALITY CONTROL AND ASSURANCE**

Experiments were performed in triplicate, giving similar results, and are reported as mean average values. For quality control and assurance, ISO-accredited laboratories and NIST standards were used for sample analyses. To ensure reliable, accurate, and high precision results inter-laboratory analysis was also undertaken, i.e. for validation and verification purposes.

### **3.6 ASSESSING THE PERCENTAGE REMOVAL OF CONTAMINANTS**

The amount of contaminants removed from municipal wastewater and acid mine drainage was computed using equation (1), i.e.:

$$\% \text{ Removal} = \frac{C_0 - C_e}{C_0} \times 100 \quad (1)$$

Where,  $C_0$  is the initial concentration of AMD or any defined contaminant and  $C_e$  is the final concentration, after treatment, of AMD with struvite.

### **3.7 CHARACTERISATION OF FEED AND PRODUCT SAMPLES**

Different analytical techniques were used for the characterisation of liquid and solid samples generated from our laboratory experiments.

#### **3.7.1 Characterisation of solid samples**

The mineralogical properties were ascertained using X-ray Diffraction (XRD). Standardized Panalytical backloading system was used to prepare the samples, which stipulates approximately arbitrary dispersal of the particles. PANalytical X'Pert PRO-diffractometer equipped with Philips PW 1710 Diffractometer with graphite secondary monochromatic source was used to analyse the samples. A Pro powder diffractometer in  $\theta$ - $\theta$  configuration with an X'Celerator detector and variable divergence- and fixed receiving slits with Fe filtered Co-K $\alpha$  radiation ( $\lambda=1.789\text{\AA}$ ) was used. The mineralogy was determined by choosing the best suitable shape from the ICSD database to the measured diffraction pattern, using X'Pert Highscore plus software graphical representation. The comparative phase amounts (weight% of crystalline portion) were estimated using the Rietveld method (X'Pert Highscore plus software).

The Fourier transformed infrared (FTIR) spectroscopy was used to analyse for functional groups in transmission mode. A Perkin Elmer Spectrum 100 spectrometer was used to characterize the

spectra of each sample. The FTIR spectra of samples were obtained in the range of 550-4000  $\text{cm}^{-1}$ . 32 scans were co-added and averaged to achieve an acceptable signal-to-noise ratio. In all cases, spectra resolution was maintained at 16  $\text{cm}^{-1}$  and the gauge force at 150. Field Emission Scanning Electron Microscope (FESEM) equipped with Energy-dispersive X-ray spectroscopy (EDS), Auriga Cobra FIB-FESEM, Carl Zeiss FE-SEM, Germany. Elemental composition, X-ray fluorescence (XRF) analysis were done using the Thermo Fisher ARL Perform'X Sequential XRF instrument with Uniquant software. Those were the analytical techniques, which were utilized for the determination of the fate of contaminants post the treatment of AMD with struvite.

### 3.7.2 Characterisation of aqueous samples

Raw wastewater and AMD were analysed on continuous bases using a multi-parameter probe (HANNA instrument, HI9828). Chemical species concentrations were determined by means of Inductively coupled plasma mass spectrometry (ICP-MS), XSeries 2, ICP-MS, supplied by Thermo scientific, from Hanna-Kunath-Str. 11 28199 Bremen, Germany. The ICP-MS was coupled to ASX-520 Auto sampler. Inductively coupled plasma - optical emission spectrometry (ICP-OES), 5110 ICP-OES vertical dual view, Agilent technologies Australia, Made in Malaysia. The ICP-OES was coupled with Agilent SPS 4 Auto sampler. Ion concentrations such as Mg, Ca,  $\text{SO}_4^{2-}$ ,  $\text{PO}_4^{3-}$  and  $\text{NH}_4^+$  in the raw water samples were analysed by ion chromatography (IC) - Metrohm make - Compact 930 AnCat Flex IC Chromatograph, 725. The same analysis was conducted for the residual water to determine the concentration of the remaining ions in the water after struvite precipitation and after AMD treatment with struvite. Gallery plus photo spectrometer, Automated chemistry analyser, Supplied by Thermo Fisher scientific, Made in Vantaa, Finland. The listed equipment's were utilised inter-changeably depending on availability and characterisation needs.

## CHAPTER 4 RESULTS AND DISCUSSION

### 4.0 INTRODUCTION

The chapter describes the results obtained from using the various methods defined in the preceding chapter. The study aimed to use the supernatant from the anaerobic digesters at wastewater treatment works in the Tshwane Metropolitan municipality to produce struvite and test the by-product's (struvite) suitability to treat AMD and manage the negative impact caused by phosphate and ammonia as well as the discharge of acid mine drainage on the environment.

### 4.1 STRUVITE SYNTHESIS

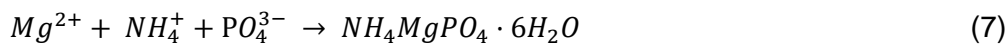
The results for chemical composition post the reaction of thermally activated magnesite with municipal wastewater to synthesize struvite are shown in Table 4-1. The feed and product water constituents for municipal wastewater are reported in Table 4-1.

**Table 4-1: The feed and product water constituents for treated municipal wastewater.**

Parameters	Units	SANS 241	Municipal effluents	Treated water
Ammonia Nitrogen	ppm	≤1.5	135	30
Calcium	ppm	≤150	200	0.2
Chloride	ppm	≤200	76	81
Chlorine (free)	ppm	≤5	0.07	0.04
Iron	ppm	≤0.3	0.015	<0.00088
Magnesium	ppm	≤100	1600	0.5
Monochloramine	ppm	≤3	0.03	<0.010
Nickel	ppm	≤0.07	0.017	0.013
Nitrate + Nitrite	ppm	≤1	1.5	1.3
Nitrate Nitrogen	ppm	≤11	1.4	1.3
Nitrite Nitrogen	ppm	≤0.9	<0.2	<0.2
pH	-	≥5 to ≤9.7	7.5	10.82
Phosphate	ppm	≤0.25	120	<0.001
Sodium	ppm	≤200	77	74
Sulfate	ppm	≤250	150	40
TDS	ppm	≤1200	2900	756

As shown in Table 4-1, there was an effective removal of pollutants from municipal effluents using a mechano-thermo-treated cryptocrystalline magnesite at optimised conditions. The optimised conditions by Mavhungu et al (2019) were used in the present study. Pollutants of concern were also removed from feed water, and this is evident in product water. The pH was observed to

increase from 7.5 to 10.8 hence indicating that there is a chemical reaction, which was taking place that led to an increase in pH. The reaction is depicted in equation (7):

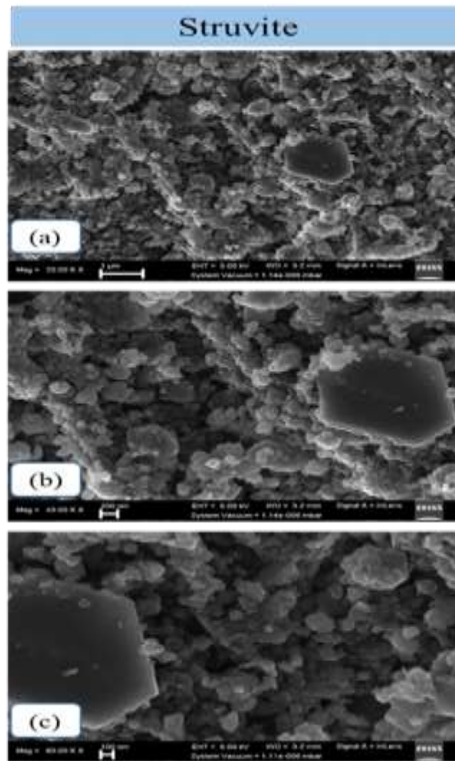


Total Dissolved Solids (TDS) was observed to decrease after contacting the pre-treated magnesite hence depicting that there was attenuation of pollutants from the aqueous media to sludge during the reaction period. Sulfate was also reduced from 150 to 40 mg/L thus suggesting a possible formation of gypsum. Phosphate was removed from 120 to 0 mg/L whereas ammonia was removed from 135 to 30 mg/L hence confirming a possible formation of struvite.

The levels of magnesium and calcium were also observed to have decreased significantly hence depicting a possible co-precipitation of MAP hence leading to the formation of struvite. This indicates that pre-treated magnesite would be a good candidate for the removal of phosphate and ammonia from aqueous medium. However, some contaminants were observed to be above the SANS 241 specifications hence suggesting that there is a need for a secondary treatment process unless the ultimate target is to discharge the treated water to nearby river. The synthesized struvite will then be employed for the treatment of AMD.

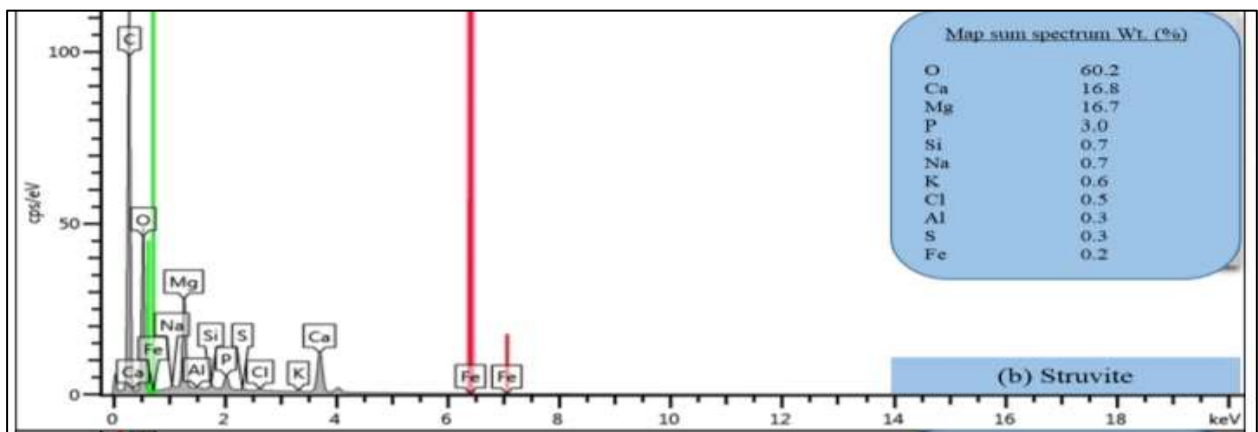
#### **4.1.1 Struvite characterisation**

The crystals were analysed by SEM-EDS to view the crystal morphologies and to find out the composition of the crystals. It is observed from the SEM results of  $MgCO_3$  in Figure 4-1 that the crystal shape is the basic struvite coffin-shaped or rod-shaped, the same results are reported in Liu et al (2013), the Rahman et al (2014) review and in Shaddel et al (2019).



**Figure 4-1: SEM micrograph of struvite crystals synthesised by using  $MgCO_3$**

The composition of the crystals is represented by Figure 4-2 below. It can be concluded that the crystals contain struvite because the percentage composition of its components, N, P and Mg is typical of what is found in struvite (Kumari et al., 2020).

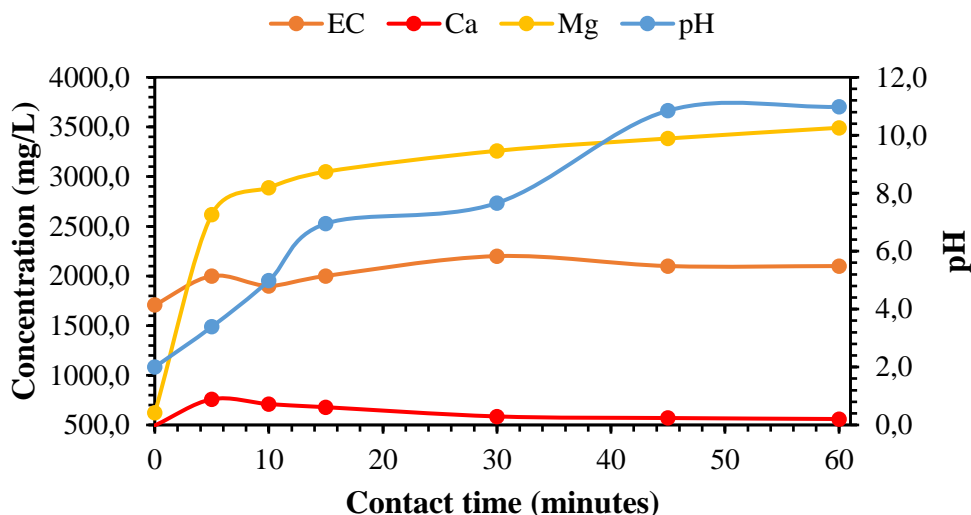


**Figure 4-2: EDS results of struvite synthesised by using  $MgCO_3$**

## 4.2 OPTIMISATION OF PARAMETERS FOR AMD TREATMENT

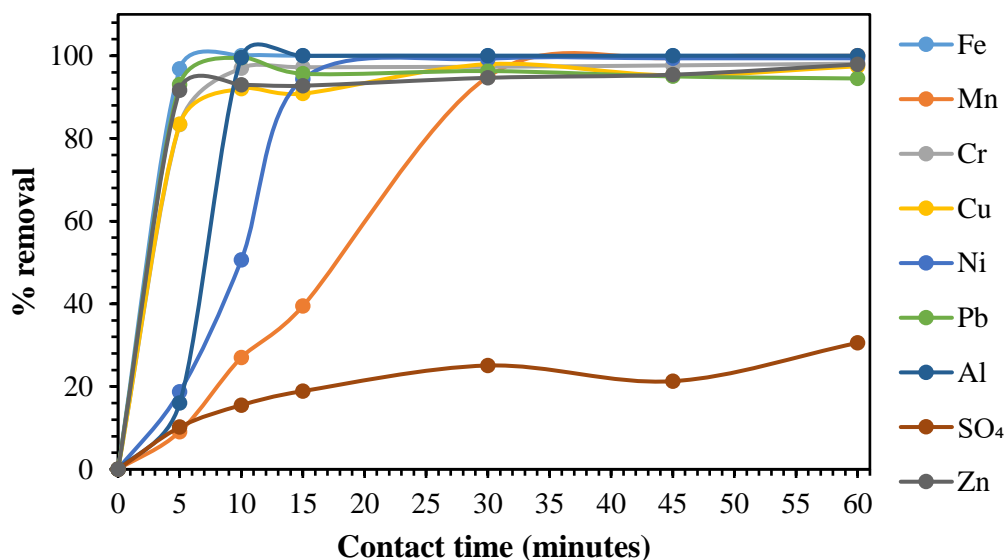
### 4.2.1 Treatment of AMD as a function of contact time

Variation in electrical conductivity (EC), pH, Ca and Mg with an increase in contact time during the treatment of AMD with struvite is shown in Figure 4-3.



**Figure 4-3: Variation in electrical conductivity (EC), pH, Ca and Mg with an increase in contact time during the treatment of AMD with struvite (conditions: room temperature and pH, 15 g of dosage in 1000 mL, and 300 rpm mixing speed).**

The effect of contact time, i.e. mixing duration, on electrical conductivity (EC) removal was examined by considering a wide spectrum of mixing durations, i.e. 0, 5, 10, 30, 45 and 60 min (Table 4-1). A slight increase in EC was observed from 0 to 5 min. Thereafter, only some relatively small fluctuations from the initial sharp increase were observed. This denotes that there is dissolution, which is related to the amount of chemicals precipitating. The pH of the solution was observed to increase with an increase in contact time, however, it was observed to stabilize after 45 minutes of mixing. There was a reduction in Ca level with an increase in contact time. This denotes the possibility of gypsum formation. Mg was observed to increase with an increase in contact time, this could be explained by a possible dissolution of struvite. Variation in percentage removal of chemical species with an increase in contact time during the treatment of AMD with struvite is shown in Figure 4-4.

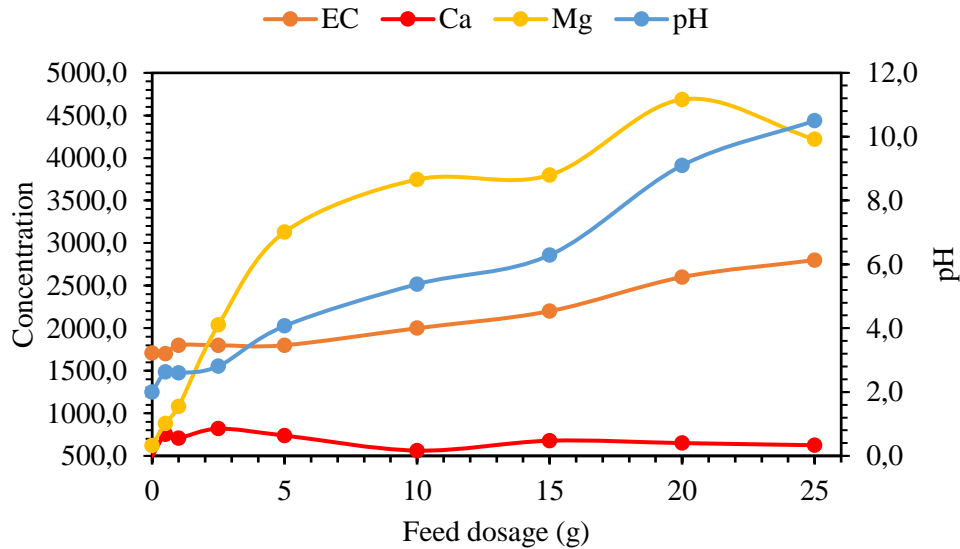


**Figure 4-4: Variation in the percentage removal of chemical species with an increase in contact time during the treatment of AMD with struvite (conditions: room temperature and pH, 15 g of dosage in 1000 mL, and 300 rpm mixing speed).**

As shown in Figure 4-4, there was a general increase in the percentage removal of different contaminants during the interaction of AMD with struvite as the time increases. A steep increase in the percentage removal of contaminants but this was aligned to different chemical species and their precipitation pH. Furthermore, the level of sulfate was observed to be inversely proportional to the Ca concentration. This further confirms the potential for gypsum formation. According to Figure 4-4, high removal efficacies (>90%) were observed at 10 minutes for Fe, Al, Zn, Cr, Cu and Zn whereas Ni and Mn were observed to attain higher removal efficacies at 30 minutes. This could be attributed to an increase in pH with time. The removal efficacy for sulfate was also observed to be gradually increasing with an increase in time. This could be linked to the concentration of Ca, which was reducing with an increase in time. As such, 30 minutes was taken as the optimum time for the removal of different contaminants from AMD and this will be utilized in our subsequent experiments.

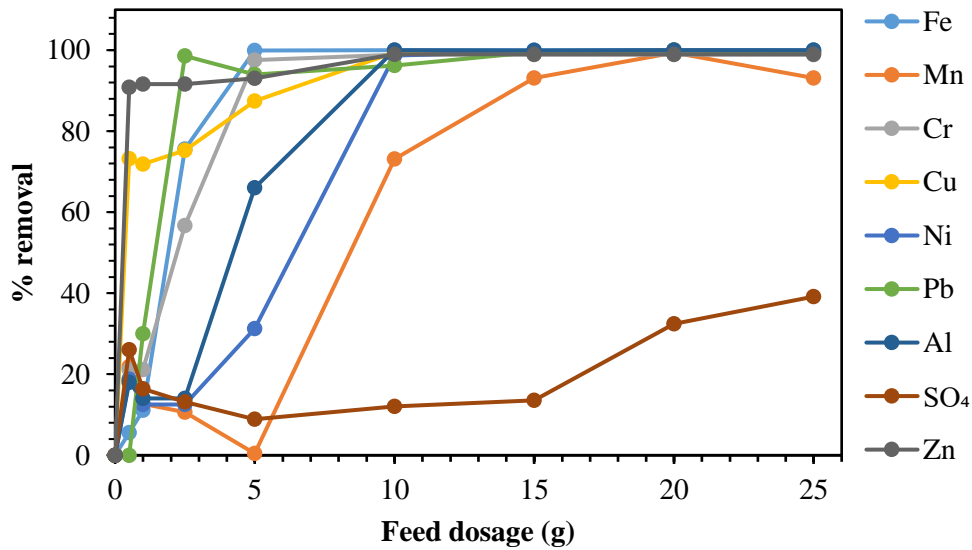
#### 4.2.2 Treatment of AMD as a function of dosage

Variation in electrical conductivity (EC), pH, Ca and Mg with an increase in struvite dosage during the treatment of AMD with struvite is shown in Figure 4-5.



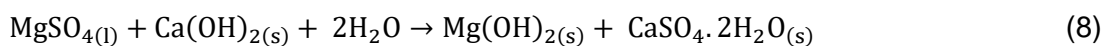
**Figure 4-5: Variation in electrical conductivity (EC), pH, Ca and Mg with an increase in struvite during the treatment of AMD with struvite (conditions: room temperature and pH, 15 g of dosage in 1000 mL, and 300 rpm mixing speed).**

The effect of feed dosage, on electrical conductivity (EC) removal was examined by varying the dosages of struvite (Table 1). As shown in Figure 4-5, the EC was observed to increase with an increase in feed dosage. This could be attributed to an increase in mineral phases that are dissolving in water when struvite is introduced. Similarly, the pH of the solution was observed to increase with an increase in feed dosage. There was a reduction in Ca level with an increase in struvite dosage. This denotes the possibility of gypsum formation due to the reaction of struvite embedded Ca and sulfate from AMD. Mg was observed to drastically increase with an increase in feed dosage, this could be explained by a possible dissolution of struvite leading to the enrichment of water with Mg fractions. Variation in percentage removal of chemical species with an increase in struvite dosage during the treatment of AMD with struvite is shown in Figure 4-6.



**Figure 4-6: Variation in the percentage removal of chemical species with an increase in struvite dosage during the treatment of AMD with struvite (conditions: room temperature and ambient pH, 45 minutes and 300 rpm mixing speed).**

As shown in Figure 4-6, there was a general increase in the percentage removal of different contaminants during the interaction of AMD with struvite as the time increases. A steep increase in the percentage removal of contaminants but this was aligned to different chemical species and their precipitation pH. Furthermore, the level of sulfate was observed to be inversely proportional to the Ca concentration. This further confirms the potential for gypsum formation as denoted by the following equation (8) (Zarga et al, 2013, Masindi, 2016b):



The presence of Mg lead to the formation of  $\text{MgSO}_4$  which then lead to the formation of gypsum and brucite after the interaction of CaO in the matrices of struvite with  $\text{MgSO}_4$  complex. Furthermore, 5 g was adequate for the removal of Zn, Pb, Fe, Cr and Cu whereas 10 g was adequate for the removal of Al and Zn, and lastly, 15 g is adequate for the removal of Mn from aqueous solution. As such, 15 g was taken as the optimum dosage for the removal of different contaminants from AMD and it will be used in subsequent experiments.

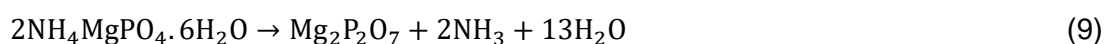
#### 4.2.3 Treatment of AMD at optimised conditions

The feed and product water qualities for raw and treated AMD are reported in Table 4-2.

**Table 4-2: The feed and product water qualities for treated AMD at optimized conditions.**

Elements	Units	Standards Limits	AMD	Treated AMD	% Removal
Fe	mg/L	≤ 2	2000	0.031	100.0
Mn	mg/L	≤ 0.4	76	0.034	100.0
Cr	mg/L	≤ 0.05	0.7	0.01	98.6
Cu	mg/L	≤ 2	0.2	0.04	74.7
Ni	mg/L	≤ 0.07	1.3	0.014	98.9
Pb	mg/L	≤ 0.01	0.2	0.012	94.0
pH	pH units	≥ 5.00 to ≤ 9.70	2.63	9.7	-
Al	mg/L	≤ 0.03	410	0.035	100.0
EC	mS/m	≤ 170	1700	2200	-29.4
SO <sub>4</sub>	mg/L	≤ 250	14900	13166	11.6
Zn	mg/L	≤ 5.0	0.11	0.08	27.3
P	mg/L	≤ 10	2.60	0.74	71.5
Ca	mg/L	≤ 300	751	737	1.9
Mg	mg/L	≤ 100	882	3638	-312.5

As shown in Table 4-2, there was an effective removal of pollutants from AMD using struvite at optimised conditions. Specifically, contaminants of concern were removed from feed water, and this is evident in product water. The pH was observed to increase from 2.6 to 9.7 hence indicating that there is a reaction which was taking place that prompted a rise in pH. Alkalinity of the resultant water was seen to have increased after contacting the struvite hence indicating an enrichment of water bodies by base metals. Specifically, an increase in pH is mainly attributed to the following chemical reactions (9-11):



The EC was observed to increase after the interaction of AMD and struvite at optimized conditions. This could be attributed to dissolution of different chemical species such as Mg and Ca during the attenuation of metals and sulfate from the aqua sphere. The presence of elevated levels of Fe and sulfate denotes that the genesis of this AMD is a result of weathering of pyrite (FeS) which was also associated with traces of other sulfide bearing minerals such as ZnS, PbS, CuS and NiS amongst others. This could be confirmed by the presence of those chemical species. Albeit major chemical species were observed to be Al, Fe, Mn and sulfate. Notable levels of Mg and Ca were also observed to be present in AMD interface. The assessed chemical species and parameters were out of the limits as stipulated in SANS 241 specifications. However, after the interaction of AMD and struvite, major chemicals such as Al, Fe and Mn were completely removed

from the AMD interface to the product sludge. The levels of pH, EC and Mg were observed to have increased after the treatment of AMD with struvite. Heavy metals were also reduced in the product water, and they were also observed to be below the SANS 241 limits for drinking water. Metals' removal efficiency was  $\geq 90\%$  for metals and  $\geq 95\%$  for heavy metals. This can be represented by the following chemical reaction (12):



Moreover, the Ca and Mg levels were a bit high, and they were also observed to be above the prescribed limits. This could also lead to elevated hardness of the product water. Thenceforth, the system managed to remove 12% of sulfate from AMD as reported in product water. This could be linked to the level of Ca and its removal efficacy since gypsum is the main route of sulfate attenuation during the treatment of AMD. Considering the obtained results, polishing of product water for drinking purposes might be required to reduce sulfate and Mg levels from the aqueous solution. This could be done using lime, softeners, and reverse osmosis (RO) to polish the water to required standards as stipulated in different water quality guidelines, requirements, specifications, and standards.

### 4.3 CHARACTERISATION OF PRODUCT MATERIALS

#### 4.3.1 X-ray fluorescence (XRF) analysis

The elemental composition of calcined magnesite, struvite and AMD-struvite are shown in Table 4-3.

**Table 4-3: The elemental composition of calcined magnesite, struvite, and AMD-struvite**

	STANDARD		Calcined magnesite	Struvite	Struvite-AMD
	BHVO-1 STD	BHVO-1 Analysed			
SiO <sub>2</sub>	49.94	48.17	1.81	0.49	1.83
Al <sub>2</sub> O <sub>3</sub>	13.8	17.33	0.29	<0.01	6.33
MgO	7.23	5.96	81.84	61.03	24.48
Na <sub>2</sub> O	2.26	2.94	<0.01	<0.01	<0.01
P <sub>2</sub> O <sub>5</sub>	0.273	0.308	0.04	18.29	3.33
Fe <sub>2</sub> O <sub>3</sub>	12.23	10.98	0.18	0.01	32.10
K <sub>2</sub> O	0.52	0.565	<0.01	0.21	0.03
CaO	11.4	10.82	6.08	1.93	2.56
TiO <sub>2</sub>	2.71	2.5	<0.01	<0.01	<0.01
V <sub>2</sub> O <sub>5</sub>	0.0566	0.0588	<0.01	<0.01	<0.01
Cr <sub>2</sub> O <sub>3</sub>	0.0422	0.0402	<0.01	<0.01	<0.01

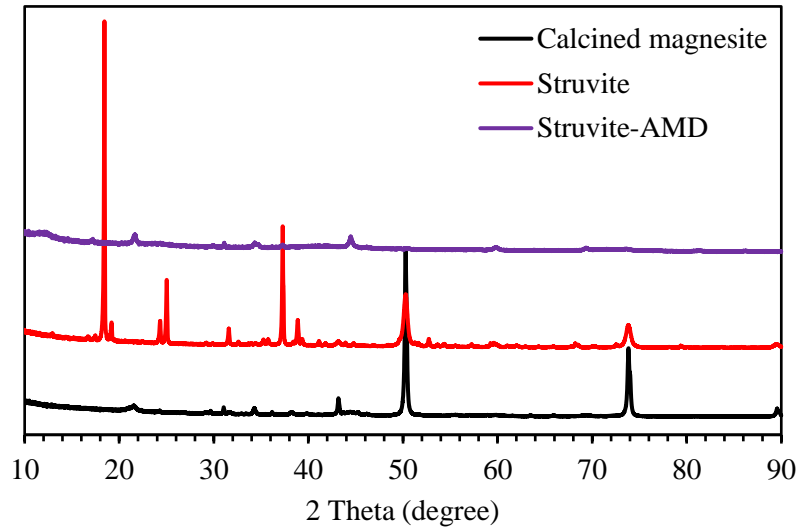
MnO	0.168	0.165	0.01	0.01	0.27
NiO	0.0154	0.0145	<0.01	0.03	<0.01
CuO	0.017	0.0163	<0.01	<0.01	<0.01
ZrO <sub>2</sub>	0.0242	0.0245	0.02	<0.01	<0.01
SO <sub>3</sub>	-	0.0066	0.51	0.04	0.91
Nb <sub>2</sub> O <sub>5</sub>	-	-	0.02	<0.01	0.03
CO <sub>3</sub> O <sub>4</sub>	-	0.0151	<0.01	<0.01	0.05
ZnO	-	-	<0.01	0.01	0.02
SrO	-	0.0443	0.09	<0.01	0.02
Y <sub>2</sub> O <sub>3</sub>	-	-	<0.01	<0.01	<0.01
LOI	-	-	9.06	17.90	27.99
TOTAL	100.6864	99.9583	99.94	99.95	99.95

As shown in Table 4-3, calcined magnesite was characterised of MgO and CaO as major elements with traces of Fe, Si and S. The loss if ignition (LOI) was also observed to be high but this could be attributed to organic matter and carbonates in the matrices of calcined magnesite. The presence of Mg and Ca will aid in the removal of phosphate and ammonia from municipal wastewater as struvite. After interacting calcined magnesite with municipal wastewater led to the enrichment of product sludge with phosphate as shown in the XRF results. This could be attributed to the formation of struvite during the interaction of Mg, P and NH<sub>3</sub>. This is basically called MAP, i.e. Magnesium Ammonium Phosphate, a product popularly known as struvite.

These results could be attested by the reduction in phosphate and magnesium level at municipal wastewater. Thenceforth, the resultant sludge, i.e. struvite, was used for the treatment of acid mine drainage (AMD). As shown in Table 4-3, there is elevated levels of Fe, Al, Mn and Sulfate, which are present in elevated concentration. The main elements were Fe and Mg, intermediates elements were Al, Si, Ca, S, P and Mn, and traces of other elements such as Zn and Co amongst others. This is evident enough that the product sludge is acting as a sink of chemical species in AMD. The obtained results corroborate the water quality results.

#### 4.3.2 X-ray diffraction (XRD) analysis

The mineralogical properties of calcined magnesite, struvite and AMD-reacted struvite were ascertained using X-ray Diffraction (XRD) and are shown in Figure 4-7.



**Figure 4-7: The mineralogical properties of calcined magnesite, struvite, and AMD-reacted struvite.**

As shown in Figure 4-7, calcined magnesite comprises periclase, brucite, and calcite, in addition to substantial amount of amorphous fractions. This shows that the material comprises MgO as intermediate mineral phase, CaO and Si as intermediates minerals and traces of other impurities such as Fe. Thenceforth, after contacting calcined magnesite and municipal wastewater, the product mineral was found to contain struvite, periclase, and brucite. Of which, struvite comprises 51% of the material and a combination of brucite and periclase was 45%. This is an indication that phosphate and ammonia are adsorbed by the feed and form struvite, as denoted in equation (13):



Precisely, the obtained peaks at 21, 23, 31, and 34, 2theta degrees for struvite corroborates what have been reported by Li et al. (2017) and Gao et al. (2018). Furthermore, the results confirm that the interaction between calcined magnesite and municipal effluents led to the formation of struvite as a by-product. Practically, the presence of Mg and Ca in the feed contributes towards increasing the pH value of the wastewater and generating  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$ . This is shown in eq. (14-15):

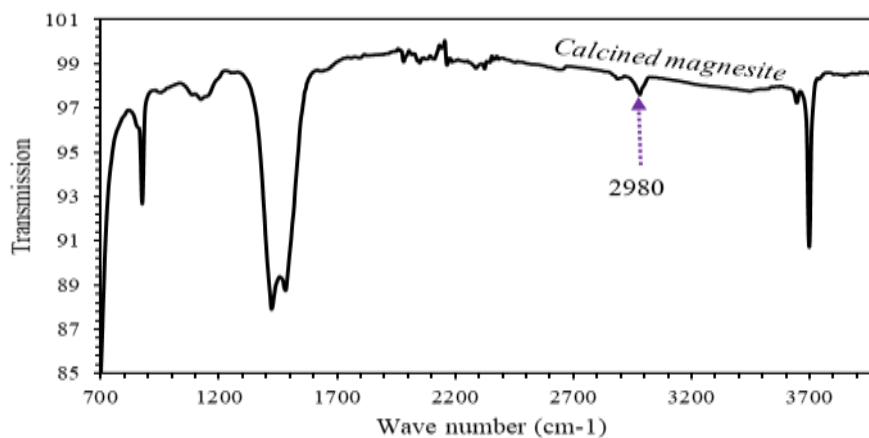


Specifically,  $\text{Mg}^{2+}$  will then scavenge the  $\text{NH}_4^+$  and  $\text{PO}_4^{3-}$  to form a complex, as denoted in equation 13. The very same principle will be employed for the treatment of AMD since the key components

that are suitable for pH increase are crystal Mg and Ca, and they are embedded into the matrices of struvite. This could be used for AMD neutralization and chemical species attenuation. Thenceforth, the presence of Ca denotes the feasibility of gypsum formation. The synthesized struvite was then employed for the treatment of AMD, the resultant sludge was observed to be amorphous in nature with few crystal peaks that could be assigned to Fe-hydroxide, gypsum, and quartz. This confirms that struvite can be a sink of metals from AMD. However, there are secondary processes such as the co-precipitation of metals and co-adsorption including surface complexation of constituents in AMD. For instance, phosphate has high affinity to  $\text{Fe}^{3+}$  and  $\text{Al}^{3+}$ , thus, it could be presumed that they bind to each other and eventually precipitate. Higher pH could result in stripping of ammonia and co-adsorption, thus, leading to the reduction in the levels in the product water.

#### 4.3.3 Metal functional groups

The metal functional groups of calcined magnesite, struvite and synthesized struvite were ascertained using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectrum of calcined magnesite, their distinguished metal functional groups, their wavenumber ( $\text{cm}^{-1}$ ) and references for relevant studies dealing with the known metal functional groups are shown in Figure 4-8. and Table 4-4

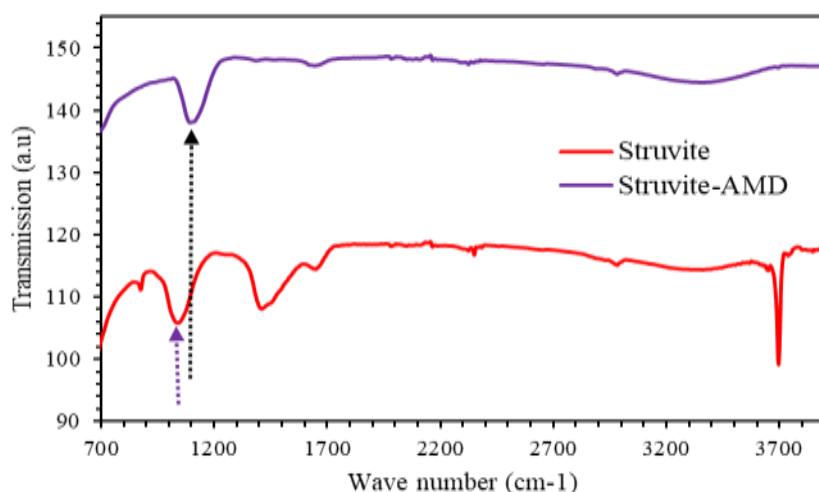


**Figure 4-8: The metal functional groups of calcined magnesite.**

**Table 4-4: The identified metal functional groups of the calcined magnesite.**

Mineral	Wavenumber (cm-1)	Metal functional	References
Calcined magnesite	850	MgO	(Magagane et al., 2019,
	1400	CO <sub>3</sub>	Mavhungu et al., 2019,
	3700	-OH (Water)	Mavhungu et al., 2020c)

As shown in Figure 4-8 and Table 4-4, the metal functional groups of calcined magnesite were carbonates, hydroxyl groups and MgO, which will be influential for struvite synthesis and crystallization. The FTIR findings also substantiate the ones found by the XRD and XRF studies and technique. Moreover, the presence of hydroxide (-OH) in the calcined magnesite propose the probability of brucite being available, which was affirmed by the XRD results shown above. In addition, the carbonates, i.e. magnesite, will show residual minerals as shown in XRD. In Figure 4-9, the FTIR spectrum of struvite and AMD-reacted struvite are shown, while Table 4-5 records the distinguished metal functional groups, their wavenumber (cm-1), and references for applicable studies managing the identified metal functional groups.



**Figure 4-9: The metal functional groups of synthesized struvite and AMD-reacted struvite.**

As shown in Figure 4-9 and Table 4-5, the metal functional groups of the recovered struvite, it was observed to contain  $PO_4^{3-}$ , N-H and MgO (Table 4-5), which affirms that through the proposed technology struvite is developed. Hydroxide alongside carbonates was likewise noticed to be present at the recovered sludge. As stated above hydroxide propose the presence of brucite, while the carbonates may emanate from magnesite, as signified by the XRD results. At last, aside from proposing that brucite may be available, hydroxide likewise recommends that the synthesized struvite is hydrated.

Furthermore, the interaction of struvite and AMD led to the formation of new minerals phases and metals functional groups. This could be explained by the precipitation of different metals and metalloids from the aqueous interface of AMD to the resultant sludge. Precisely, the Fe-OH group was observed, and this denotes the precipitation of Fe<sup>3+</sup> from AMD. This has been confirmed by other techniques such as XRF, and XRD. The water quality results further attest to that finding. Furthermore, the presence of SO<sub>4</sub> group (Table 4-5) could be explained to the formation of gypsum from the reaction of Ca and SO<sub>4</sub> in AMD. The presence of carbonates and hydroxyl group denotes the formation of hydroxides, oxy-hydrosulfates and carbonates post the interaction of AMD with chemical components in struvite. This further certifies that struvite can act as a sink of chemical species from AMD. This has been confirmed by different analytical techniques such as XRF, XRD and ICP-MS. The identified metal functional groups of synthesized struvite and AMD-reacted struvite are shown in Table 4-5.

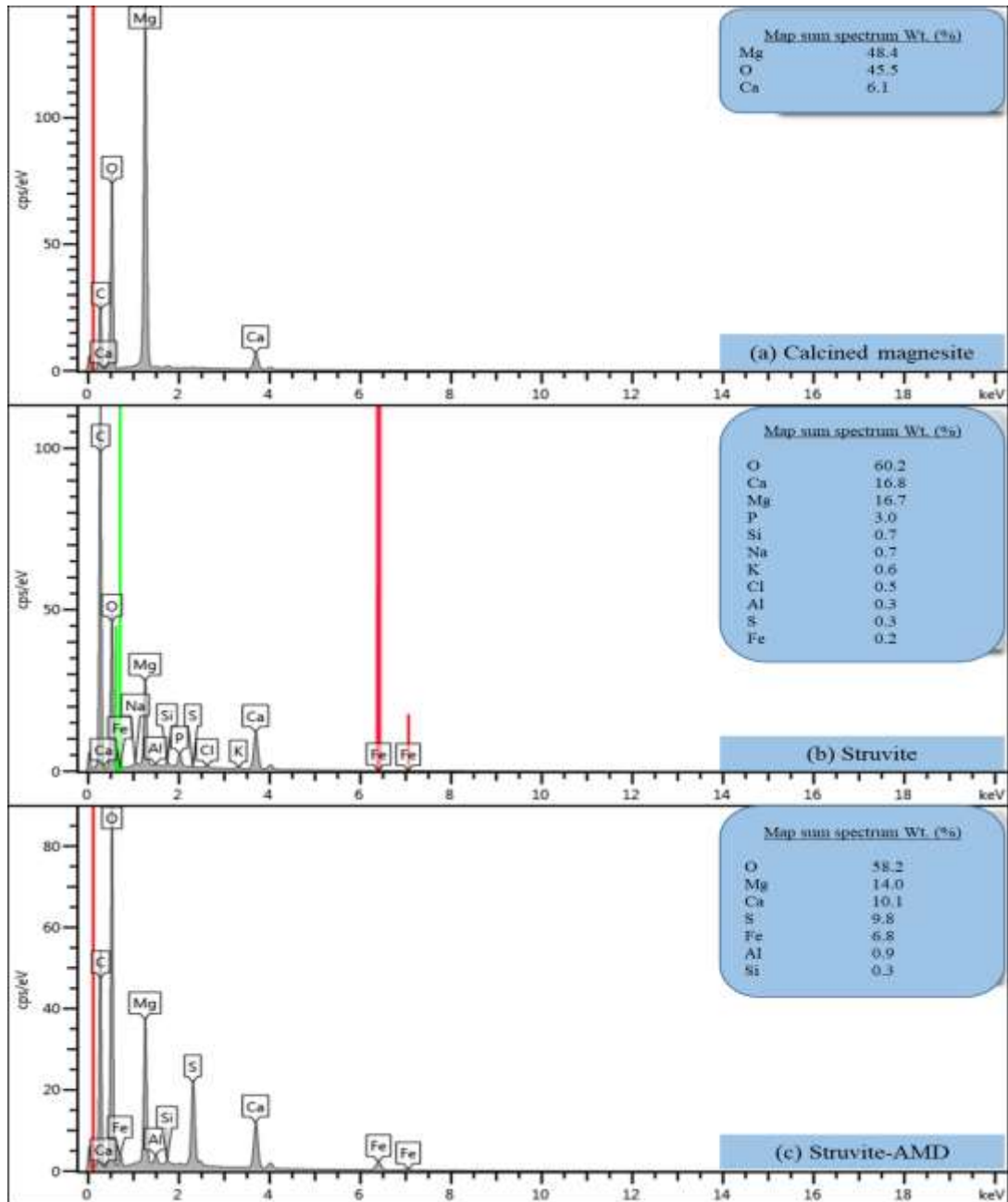
**Table 4-5: The identified metal functional groups of synthesized struvite and AMD-reacted struvite.**

Mineral	Wavenumber (cm-1)	Metal functional	References
Struvite	850	MgO	(Cahil et al., 2007, Heraldy et al., 2017, Wang et al., 2017, Mavhungu et al., 2019, Shu et al., 2019, Wei et al., 2019)
	1005	PO <sub>4</sub> <sup>3-</sup>	
	1200	PO <sub>4</sub> <sup>3-</sup>	
	1400	CO <sub>3</sub>	
	1690	N-H	
	3000	-OH (Water)	
	3700	-OH (Water)	
AMD-struvite	1100	Fe-OH group	(Slavov et al., 2010, Yahya et al., 2017, Mavhungu et al., 2020b)
	1500	SO <sub>4</sub> -group	
	1600	CO <sub>3</sub> -group	
	3000	-OH (Water)	
	3400	-OH (Water)	

The obtained results confirm that the interaction of municipal wastewater with calcined magnesite led to the formation of struvite and the product sludge (struvite) could be used for the treatment of AMD.

#### 4.3.4 Elemental composition using EDS

As mentioned above, the HR-SEM was equipped with an Energy-dispersive X-ray spectroscopy (EDS) detector, which was used in identifying the elemental properties of calcined magnesite, struvite, and the AMD-reacted struvite.



**Figure 4-10: Elemental composition of calcined magnesite (a), synthesized struvite (b), and AMD-reacted struvite (c).**

As shown in Figure 4-10 (a), calcined magnesite was characterised of MgO and CaO as major elements. The presence of Mg and Ca further confirms that this will aid in the removal of phosphate and ammonia from municipal wastewater hence forming struvite as the by-product. After interacting calcined magnesite with municipal wastewater (Figure 4-10b) led to the enrichment of product sludge with phosphate as shown in the XRF results.

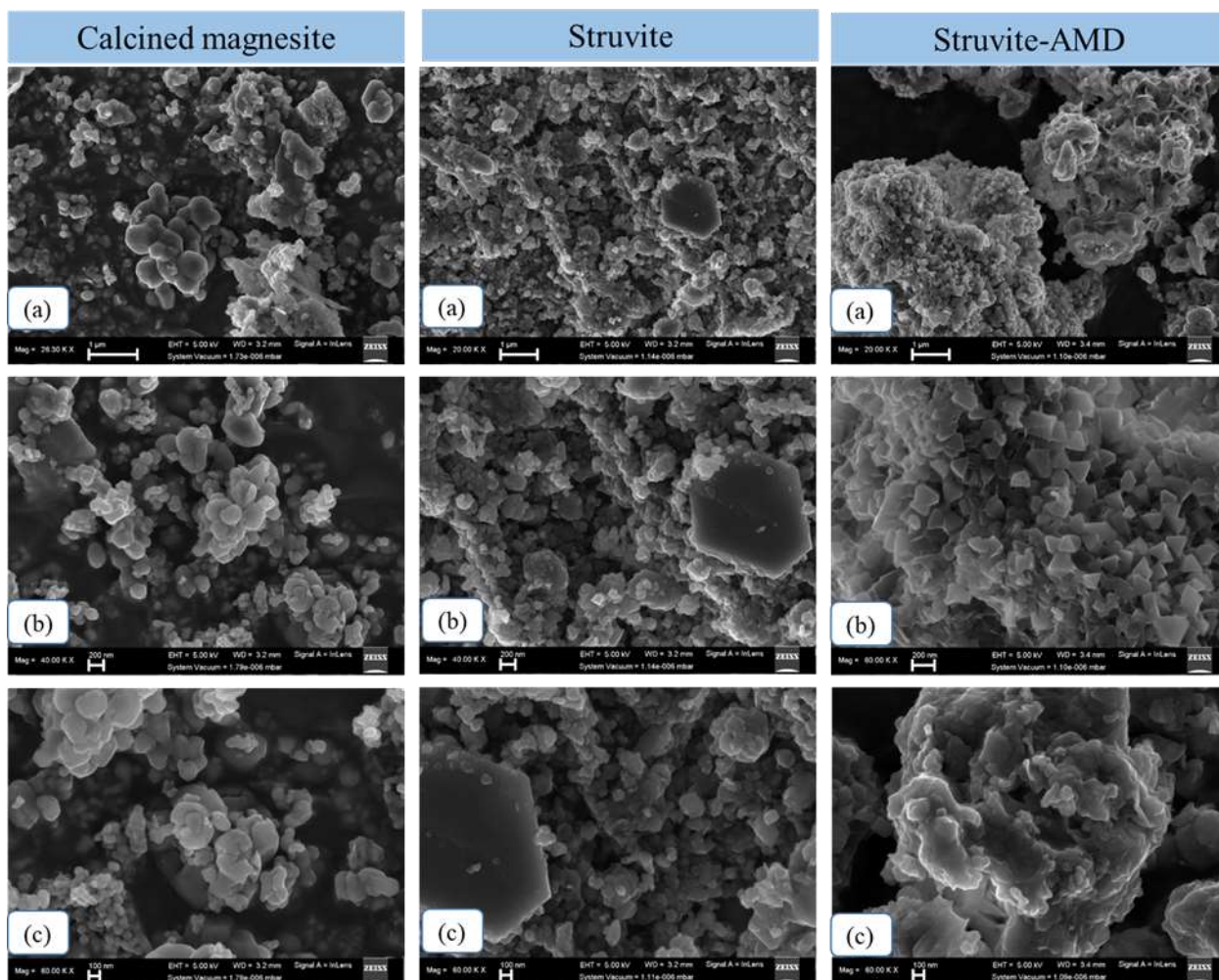
This could be attributed to the formation of struvite during the interaction of Mg, P and NH<sub>3</sub> in municipal wastewater and magnesite. Predominant elements were observed to be O, Ca, Mg and P. This is basically called MAP, i.e. Magnesium Ammonium Phosphate, a product popularly known as struvite, albeit, ammonia cannot be detected in the EDS. Thenceforth, the results could be attested by the reduction in the levels of phosphate and magnesium in municipal wastewater. Traces of other impurities were observed but these could be attributed to other chemicals that were embodied in municipal wastewater and calcined magnesite matrices.

Furthermore, the resultant sludge, i.e. struvite, was used for the treatment of acid mine drainage (AMD). Specifically, as shown in Figure 4-10(c), there is elevated levels of Fe, Al, Mn and Sulfate, which are present in elevated concentration. The main elements were Fe and Mg, intermediates elements were Al, Si, Ca, S, P and Mn, and traces of other elements such as Zn and Co amongst others. This is evident enough that the product sludge is acting as a sink of chemical species in AMD. The obtained results corroborate the water quality results. These results are also consistent to what has been reported in XRF, XRD and FTIR.

#### **4.3.5 Morphological characteristics**

The morphology of calcined magnesite, struvite and AMD-reacted struvite are shown in Figure 4-11. A high-resolution Focused Ion Beam Scanning Electron Microscope (HR-FIB FESEM) device was utilized to distinguish the morphological characteristics. In Particular, an Auriga Cobra HR-FIB FESEM was employed in this work, which can be additionally applied for SEM imaging. Thenceforth, clear, high resolution, and low electrostatically distorted pictures were explored using the HR-FESEM function. The obtained results showed the morphology of the minerals studied.

As shown in Figure 4-11, it can be observed that calcined magnesite comprises asymmetrical sheets, which are evenly dispersed throughout its surface. Additionally, the morphological properties of the calcined magnesite surface were observed to remain the same irrespective of the different amplification applied, i.e. from 1µm to 100 nm. It is also implied by the FESEM results that calcined magnesite is a nanomaterial with octagonal structures. However, post struvite synthesis, the morphology of struvite was observed to have changed to compact hexagonal structures. This could be attributed to the fact that struvite synthesis led to the formation of new phases, which recommends that a reaction occurred to form MAP.



**Figure 4-11: The HR-FESEM images showing the changes in morphological properties of calcined magnesite, synthesized struvite and the synthesized struvite and AMD-reacted struvite from lower to higher magnification, i.e. a) 1  $\mu\text{m}$ , b) 200 nm, and c) 100 nm.**

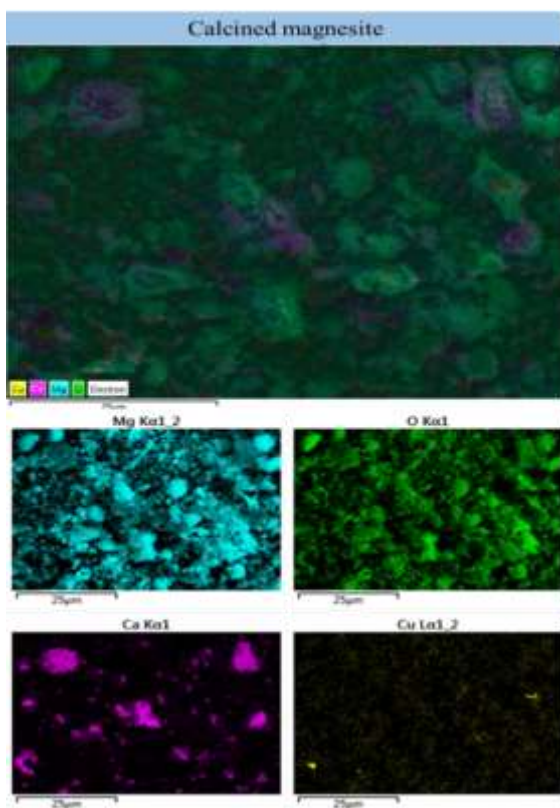
Finally, after the struvite is synthesized, this was discovered to be rich in round nanosheets as well as coffin structure. Similar findings were reported by Mavhungu et al (2019) and numerous groups. Herald et al. (2017) detailed that struvite can be available in various morphologies, for example, coffin-shaped, pyramid type, prismatic sort, needle type, and feather-shaped, among others, and this is unequivocally reliant on development parameters and synthesis conditions, amongst others. Comparable results were reported by Chauhan and Joshi (2013). Also, other Mg-based minerals, aside from MgO, might have impacted the morphology of the synthesized struvite, alongside contaminations associated inside the magnesite matrices and micelles that would have been co-accumulated with struvite during the synthesis process. Lastly, Figure 4-11 (a-c), demonstrated triangular sheets with homogenous arrangement onto the surface of AMD-reacted struvite. The sheets also comprised leafy-like structures. This result further confirms the

development of new mineral phases on the matrices of each mineral, which was generated in different phase of the reaction.

#### 4.3.6 Spot analysis using HR-SEM

To further substantiate the elemental composition of calcined magnesite, synthesized struvite and AMD-reacted struvite, spot-analysis, by means of Auriga Cobra FIB- FESEM instrument, which consist of an EDS detector, was utilized. The morphological spot-analysis are shown in Figure 4-12 to 4-14.

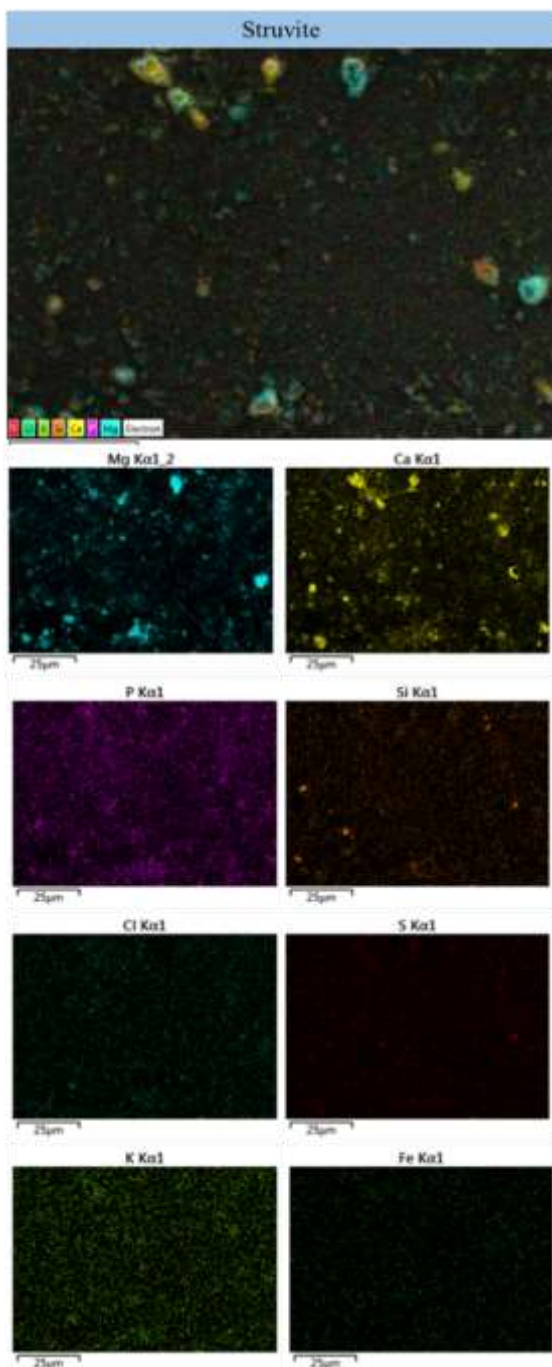
As shown in Figure 4-11, calcined magnesite is dominated by octagonal structures on its surface. Elemental analysis further showed that the prevalent elements are Mg and O, as well as traces of Ca. The EDS spot analysis findings are also in accord with the XRF, XRD and FTIR results for calcined magnesite. Additionally, the identified Ca might be helpful in increasing the pH of the raw wastewater effluent. Mg and O were predominant elements on the surface of the material. Scattered distribution of Ca was also observed on the surfaces of calcined magnesite. Cu was primarily from the coating material hence it could be the background mineral.



**Figure 4-12: The SEM-EDS results of calcined magnesite showing the spot analysis image and relevant EDS spectra.**

Figure 4-12 shows the elemental distribution properties of the synthesized struvite. It is indicated from the figure that crystal clear sphere-shaped and even crystals were noticed in the synthesized struvite. Moreover, it was discovered that the synthesized struvite is dominated by Mg, P and Ca, while traces of Cl, S, K, Fe and Si were similarly observed. More significantly, the presence of P was recognized, which affirms the synthesis of struvite. The distribution of P and Mg were consistent through-out the surface. It should be observed that only the dissolvable part of calcined magnesite will contribute to the synthesis of struvite and the rest will stay in the solution. Furthermore, the availability of Mg and P confirms the synthesis of struvite.

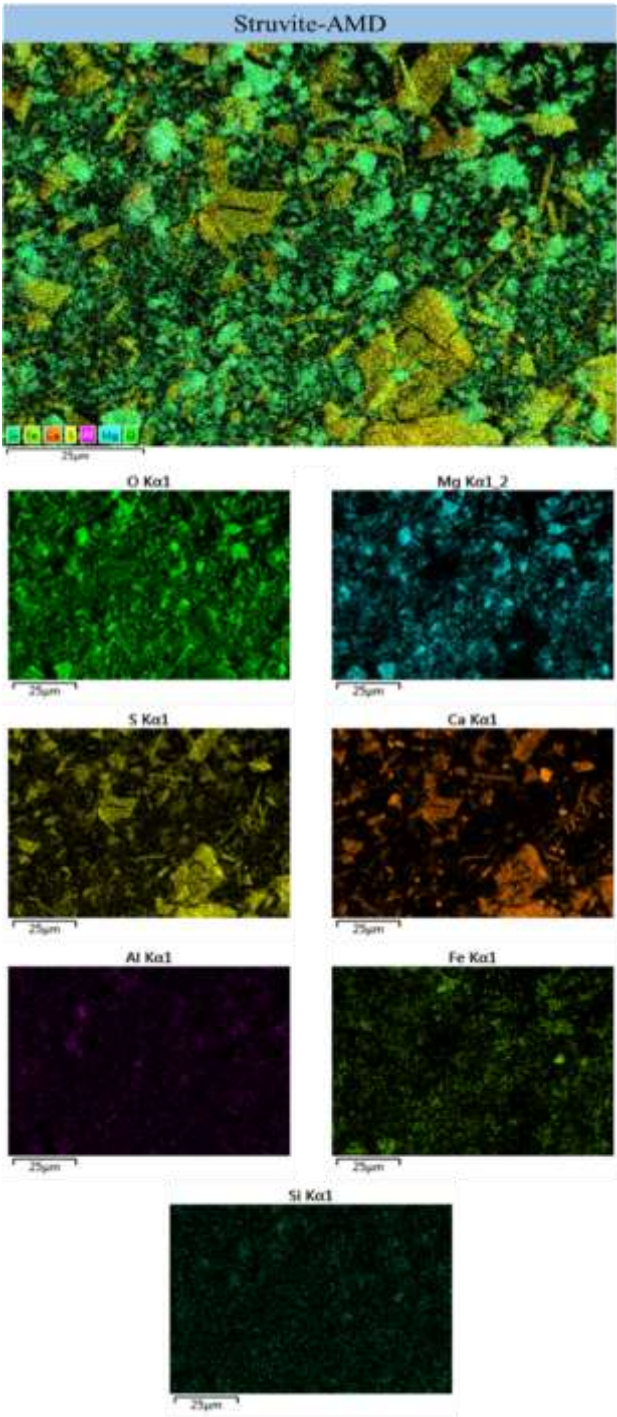
Finally, the availability of Si and Ca suggests the co-precipitation of struvite with those impurities. The findings are supported by the ones from XRD and FTIR analysis.



**Figure 4-13: The SEM-EDS results of the calcined raw magnesite showing (a) the spot analysis image and (b) to (f) the relevant EDS spectra.**

The elemental distribution properties of the AMD-reacted struvite are shown in Figure 13.

**Figure 4-14: The SEM-EDS results of AMD-reacted struvite showing the spot analysis image and the relevant EDS spectra.**



As shown in Figure 4-14, triangular-like and rod-like structures were observed on the matrices of the AMD-reacted struvite. It is apparent that the rod-like structure denotes a combination of Ca and S, thus implying the possibilities of synthesizing gypsum in the product mineral. This could further allude the attenuation of sulfate from AMD to the product sludge. The XRF, XRD, FTIR and EDS techniques further confirmed the results. The presence of Mg and O confirm the presence of brucite and periclase on the matrices of product minerals. Al, Fe and Si were also observed to be present post the treatment of AMD with struvite. The presence of these chemical species certifies the removal of contaminants from AMD to the product sludge. This will further confirm that struvite can act as a sink of chemical species from AMD and any metalliferous drainage.

## CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

### 5.1 CONCLUSION

This feasibility study was designed with an effort to achieve the following objectives relating to the application of struvite synthesized from wastewater effluents for neutralisation of acidity and removal of chemical species concentration from gold mine waters.

- To determine the physicochemical properties of municipal effluents
- To synthesize struvite from municipal effluent using pre-treated cryptocrystalline magnesite as the precursor.
- To determine the physicochemical properties of acid mine drainage and optimize conditions that are suitable for the removal of contaminants in acid mine drainage using the synthesized struvite.
- To compare the quality of product water with different water quality guidelines and specifications.

Struvite was synthesized at 1 g: 100 mL of activated magnesite and municipal wastewater, respectively. The mixtures were mixed for 60 minutes at 300 rpm. XRD confirmed the synthesis of struvite, which was additionally confirmed by elevated concentration of phosphate in XRF results. Struvite was then used for AMD treatment. Treatment of acid mine drainage using struvite has provided promising results at laboratory-scale. The one-factor-at-a-time (AFAAT) initiative was used to evaluate contact time (mixing time) and feed dosage. Contact of AMD with struvite led to an increase in pH, high removal efficiencies (>90%) were observed at 10 minutes for Fe, Al, Zn, Cr, Cu and Zn whereas Ni and Mn were observed to reach higher removal efficiencies at 30 minutes. Increase in feed dosage led to an increase in pH of the solution. There was a general increase in the percentage removal of different contaminants during the interaction of AMD with struvite. Hence, the optimum conditions were observed to be 30 minutes of equilibration and 15 g of dosage in 1L at 300 rpm of mixing speed. Interaction of struvite with AMD led to 99% removal efficacy for Al, Fe, Mn and other metals except for sulfate, which demonstrated close to 12% removal efficacy.

Additionally, it can be confirmed that the product mineral was effective enough for the removal of metals from AMD. The pH was observed to be  $\geq 9.7$  and this was suitable for attenuation of all the chemicals except for sulfate. The formation of oxy-hydrosulfates was also deduced in EDS results. The removal of chemical species from municipal wastewater and acid mine drainage subsequently was observed to be technically viable. Thus, this technology could valorise struvite

synthesized from municipal wastewater effluents and open new horizons for the effective and sustainable management of wastewater effluents and AMD. Further research is required to prove the efficacy and lifecycle analysis. This technology could minimize the footprints of acid mine drainage and municipal wastewater on different spheres of the environment. Struvite treatment brought about water that met some of the water quality guidelines.

## **5.2 RECOMMENDATIONS**

The application of struvite for AMD treatment showed promising results and the product water nearly met the DWAF Water Quality Guidelines standards. Even though, more research studies are required in this area to ensure application of this technology on a larger scale. Therefore, numerous research areas could be pursued:

- Considering the above conclusion, future research should focus on the use of life cycle assessment tools to measure ecological footprints of this initiative.
- Employ geochemical modelling to substantiate this technique, this will further enhance the techno-viability of this technology.
- Investigate the effectiveness of struvite on AMD from different sources
- Economic feasibility to encourage the adoption of this technology

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# APPENDICES



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ENG-REC ethics  
screening checklist\_