

**Development of an acid mine drainage treatment
technology and recovery of minerals**

By

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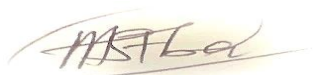
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Declaration

I, Albert Shumba (19023364), hereby declare that this thesis for the PhD Environmental Science Degree at the University of Venda, hereby submitted by me, has not previously been submitted for a degree at this or any other university, and this is my work in design and execution and that all reference materials contained therein have been duly acknowledged.



Signature.....Date...24/02/2024.....

Albert Shumba

Acknowledgment

I am forever obliged to the almighty God for granting me the power, knowledge, wisdom, and healthy life to make everything progress.

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Dedication

This work is dedicated to my creator, God Almighty, for keeping me alive and healthy during my studies.

Abstract

Acid mine drainage (AMD) is known to have negative environmental impacts due to low pH, high concentrations of toxic metals which can pollute freshwater sources. There is need for development of a technology which treats and recover beneficial minerals from AMD. Samples of AMD, water, sediments from the field and sludge from neutralization batch experiments were characterised for their chemical compositions using advanced research techniques. In designing the treatment method, hydrogeochemistry of decanting AMD from Mpumalanga was studied. Findings from this study revealed that decanting AMD continues to threaten the environment due low pH, high Electrical Conductivity (EC) and precipitation of secondary minerals. Simulated AMD prepared by choosing concentrations of worst-case scenario from Mpumalanga was used in batch experiment comparing flocculation and sonication techniques in treatment of AMD with calcined magnesite. Sonication technique was more effective in treatment of AMD because it raised pH faster and it enhanced precipitation of minerals than flocculation. Due to the superiority of sonication, it was used for recovery of metal oxides from AMD with calcined magnesite through sequential selective precipitation and recycling of metal enriched sludge over several cycles using filtration and pH adjustment. The technology enriched Fe -rich and Al-rich sludge up to cycle 3 while Mn-sludge up to cycle 2. Fe, Al, and Mn in product water were below the guidelines for irrigation water, while Ca, Mg, and SO_4^{2-} remained at higher levels. The technology may not be used for recovery of Mn due to co-precipitation with Mg. Future studies recommends the treatment of product water to recover portable water and salts and upscaling the technology to pilot for industrial applications. The high purity of recovered metals suggests their potential use for industrial applications such as catalysts, batteries, fertilizer, and pigment manufacturing.

Keywords: Acid mine drainage, hydrogeochemistry, flocculation, sonication, treatment, recovery of metal oxides.

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Chapter 1

1.1 Background

In South Africa, the mining of minerals such as coal, diamonds, gold, and platinum group metals are viewed as a foreign exchange earner and promotes socio-economic development because it contributes to education, health, and infrastructural development (Kefeni and Mamba, 2020; Sebogodi et al., 2020). However, mining leaves behind tailings and voids that contain sulphide minerals, which contribute to the formation of acid mine drainage (AMD) upon exposure to water and oxygen (eqn. 1.1) (McCarthy, 2011; Zhang et al., 2023).



Acid Mine Drainage is highly acidic with $\text{pH} < 3$ and has high amounts of Al, Mn, Fe, SO_4^{2-} and other trace elements (Gitari et al., 2011; Shingwenyana et al., 2021). This contributed to high total dissolved solids (TDS), high salinity, and high electrical conductivity (EC) in AMD (Masindi et al., 2016). Acid mine drainage must be treated according to the recommended guidelines before discharge to avoid environmental pollution due to its acidic nature. Available treatment techniques are either passive or active (Chen et al., 2021). Active treatment methods usually require alkaline chemicals to neutralize the pH, which results in the precipitation of metals (Kaur et al., 2018). Passive treatment methods consists of biological treatment, usually with wetlands, and chemical treatment with sulphate-reducing bioreactors and limestone drains (Favas et al., 2016). Both passive and active methods are driven by adsorption, ion exchange, and precipitation (Menzel et al., 2021).

Passive methods need much time to achieve the required results, while active methods are fast and can treat large volumes of AMD (Sebogodi et al., 2020). However, the active treatment method successfully decontaminates AMD and have of high SO_4^{2-} levels in product water and generation of sludge, which needs further purification (Shingwenyana et al., 2021). Acid mine drainage treatment wastes can be utilised by recovering metal oxides in the form of sludge. Water is a deficient commodity in South Africa, and water recycling and conservation is one of the options to solve water scarcity (Mzinyane, 2022). The reuse of water will convert AMD, a polluted resource, into a commodity, contributing to water availability in South Africa and promoting socio-economic development (DWS, 2016). Recently, there has been a paradigm

shift towards recovering valuable products from AMD to make the existing treatment methods sustainable (Naidu et al., 2019; Viadero Jr et al., 2020). The paradigm shift is driven mainly by three factors: reducing the amount of waste sludge and brines that require further handling and disposal, developing long-term sustainable AMD treatment plants, and generating revenues to supplement ongoing recovery and treatment costs (Matinde et al., 2018). Sulphur, sulphuric acid, electricity, alkali recovery, gypsum and cement, fertilizer, adsorbents for water treatment, and pigments are some of the valuable products that were recovered from AMD (Simate and Ndlovu, 2014). Recovery of H_2SO_4 from AMD produces water that is not dangerous to the ecosystem (Nleya et al., 2016).

Using selective precipitation, Wei et al. (2005) recovered Al and Fe from AMD. In another study, Fe^{3+} and Fe^{2+} compounds were well recovered at pH 3-4.5 and 8.5, respectively, from AMD using an oxidation-selective/fractional precipitation process, and they were further used for the preparation of magnetite, haematite, and goethite particles (Akinwekomi et al., 2020). Akinwekomi et al. (2020) synthesized goethite and haematite by heating ferric hydroxide-rich sludge at 70 °C and 700 °C, respectively. They further synthesized magnetite by mixing sludge rich in ferric and ferrous ions in the ratio of 2:1, respectively, at 100 °C at a pH of 10 with a small amount of sodium hydroxide. Alegbe et al. (2019) manufactured Fe nanoparticles from AMD and applied them to treat AMD. During the synthesis of iron nanoparticles, hydrogen peroxide was added to raw AMD to oxidize all ferrous to ferric iron; nitrogen gas was bubbled to eliminate the dissolved oxygen present. NaBH_4 was then added at room temperature to precipitate all the iron nanoparticles from the raw AMD. Their synthesized nanoparticles effectively removed toxic elements from AMD within sixty minutes. AMD treatment demand remained high and costly; therefore, there is room for further improvement (DWS, 2018). A more reliable and sustainable treatment technique is required, and it also considers integrating existing technologies with other technologies (Naidu et al., 2019).

Sustainability can be improved by the recovery of valuable products from AMD which can be sold to cater for treatment costs. A technique which reduces reaction time and increases reaction kinetics during treatment of AMD has the potential of improving sustainability. The introduction of sonication, which generates cavitations, can improve sustainability during the recycling and recovery of resources from AMD. The use of cavitations to initiate reaction kinetics were be utilised in the treatment of AMD with calcined calcined magnesite. Previous studies were done on the applications of cavitations in AMD treatment. Madzivire et al. (2013)

used a jet loop reactor to produce cavitations to reduce the quantity of fly ash needed to treat AMD. They showed low SO_4^{2-} removal in experiments with agitations rather than cavitations. In our work, cavitations were generated by ultrasound sonicators. Sonication increases the turbulence and kinetic energies of solid particles in the medium. With several collisions, the solid particles fracture, leading to a decrease in particle size and an increase in the reaction rate (Hagenson and Doraiswamy, 1998; Khavari et al., 2023). Magnesite is a liming agent easily accessible in South Africa, so it may replace limestone and lime, which are expensive. Magnesite is mainly composed of magnesium carbonate (MgCO_3), and its calcination results in the formation of magnesia (MgO) (Nobre et al., 2020). Several studies were done on the utilization of magnesite for AMD treatment, and XRF results of raw magnesite showed that it contains 82.095% MgO , 2.39% CaO , 6.09% SiO_2 , 0.71% Al_2O_3 , and 0.54% Fe_2O_3 (Masindi et al., 2016; Vhahangwele and Gitari, 2019). Masindi et al. (2016) evaluated the ability of magnesite to neutralize and remove metal elements from AMD. They showed that the reaction of AMD with magnesite increases the pH from 2.30 to greater than 10, mainly due to the reaction of magnesium carbonate with sulphuric acid and the reaction of periclase (MgO) with hydrogen ions from AMD. In another study, Letjiane et al. (2019) compared magnesite (MgCO_3) and MgO for pre-treatment of iron and sulphur-rich acidic effluents in the recovery of iron hydroxide for pigment synthesis. They observed that magnesium carbonate did not neutralize water rich in iron because magnesium carbonate first reacts with iron, forming a layer of iron carbonate (Fe_2CO_3) around magnesium carbonate particles and preventing further dissolution. They further observed that, MgO was effective in neutralizing iron-rich acidic water for the recovery of iron hydroxide. Calcining magnesite will produce magnesium oxide, neutralizing and recovering iron hydroxide from high-iron acidic water. This research aims to treat and recover resources from AMD by enhancing the neutralization of AMD with calcined magnesite using ultrasonication to generate cavitations

1.2 Problem Statement

Acid mine Drainage (AMD) is known to have negative environmental impacts due to low pH and high concentrations of toxic metals (Naidu et al., 2019). Acid Mine Drainage from abandoned coal and gold mines in Mpumalanga Province and Johannesburg area of South Africa led to pollution of nearby rivers, wetlands and underground waters, harming aquatic ecosystems (Ighalo et al., 2022, McCarthy, 2011). Acid Mine Drainage contamination can damage aquatic life, increasing safety risks, destroying natural herbs and negatively impacts the economy (Simate and Ndlovu, 2014). Heavy toxic metal loads may affect plant growth, damage infrastructure and degrade the quality of water, making it unfit for various uses (Xia et al., 2023). The South African government encourages treatment of AMD to achieve zero waste, however various AMD treatment methods are selective and leave behind wastes that needs further treatment (Mogashane et al., 2020). Furthermore, the treatment methods produce water that exceeds the department of water and sanitation (DWS) (formerly known as the Department of Waters and forestry affairs DWAF) guidelines. There is still a need and room for developing and improving AMD treatment technology that focuses on recovery of water and beneficial products from AMD (DWS, 2018).

It was observed that no uniformly applicable standard is available for any technology in AMD treatment (Xia et al., 2023). A more reliable and sustainable treatment technique that integrates reuse and resource recovery of beneficial products is needed (Naidu et al., 2019). A universal and suitable technology should be designed to produce zero waste and pure metal salts or hydroxides (de Almeida Silva et al., 2019; Kefeni et al., 2017). The results of this work will help in solving problems of AMD contamination by applying ultrasonication in enhancing treatment and recovery of mineral resources from AMD using calcined magnesite. It will also reveal conditions needed in developing a pilot plant using sonication in AMD treatment and recovery.

1.3 Research Aims and Objectives

1.3.1 Main Aim:

- The main aim of this work focuses on AMD treatment and recovery of metal oxides and associated minerals in AMD through the development of a treatment technology.

1.3.2 Objectives

- To determine hydrogeochemical characteristics of surface waters and sediments impacted by acid mine drainage in eMalahleni, Mpumalanga Province, South Africa.
- To compare the effectiveness of sonication and flocculation in the treatment of acid mine drainage using calcined magnesite.
- To evaluate sequential recovery of Fe, Al, and Mn minerals in Acid mine drainage adjusting pH with calcined magnesite and ultrasonic treatment
- To enrich the metal rich sludge with metals through treating more AMD over several cycles with calcined magnesite.

1.4 Hypothesis

- Acid mine drainage decanting from abandoned coal mines in eMalahleni affects surface water and sediment quality.
- Using ultrasonication is more effective than flocculation in treating and neutralizing AMD with calcined magnesite.
- The reactivation and recycling of used sludge to treat more AMD under ultrasonic conditions with calcined magnesite enriches the sludge with more metal oxides.

1.5 Limitations

Acid Mine Drainage is a worldwide problem despite the presence of other contaminants in surface water. Research had shown that clean or safe drinking water is scarce in most rural areas of the world including South Africa. Several studies were done focusing on AMD treatment using alkaline agents like magnesite. This study uses calcined magnesite in the treatment of AMD with sonication which increases reaction kinetics. The concept of this work is based on reuse of sludge for metal enrichment and recovery. The study used synthetic AMD prepared by simulating field AMD from Mpumalanga. Thus, limiting the representative of all

the field AMD from South Africa and world in general. This research was only limited to the use of ultrasonication at laboratory scale.

1.6 Significance and Novelty of the Study

The technology developed in this research will increase the efficiency in recovering valuable products from AMD. Findings from this study will contribute to the United Nations sustainable goal number 6 which aims to ensure clean water and sanitation for all by 2030. This will ensure that every South African have access to clean water in their households (NWRS-2013; NDP-2030). This work will also contribute to sustainable development goal number 12 which ensures sustainable consumption and production patterns by 2030. This goal can be achieved by more efficient disposal, reduction and recycling of toxic waste. In this study this goal will be achieved by confirming the possible recovery of metal/metal salts separately from AMD through metal recycling. For example, the successful recovery of minerals from AMD, such as iron, aluminum, and manganese oxides, will help curb treatment costs as they can be used for paint, catalysts, water treatment, and battery synthesis. The reuse of metal rich sludge in treating more AMD will improve the sustainability of the AMD treatment technology. Calcined magnesite and sonication have, to the best of our knowledge, never been applied in AMD treatment and recovery of minerals. The recycling of sludge over several cycles for metal enrichment and recovery is highly innovative in this work. The results from this work will help in developing a pilot plant with the purpose of upgrading to full operating plant. The success of this research will assist in protecting the ecosystem through the treatment and recovery of minerals from AMD.

1.7 Thesis Layout

This section covers the layout of the chapters

Chapter 1: This chapter covers the background of the work, bringing out the problem statement, Delimitations and the novelty of the work.

Chapter 2: The chapter covers literature review of impacts of AMD to environment, Its formation and treatment methods. The section highlights treatment methods that have been applied at pilot scale and at industrial level. The sections highlight the challenges of treatment methods and bring the need for further research that brings sustainability, such as ultrasonication and reuse and recycling of sludge.

Chapter 3: The work covers the hydrogeochemistry of AMD, impacted sediments and potential ecological of toxic metals in sediments in eMalahleni due to AMD decanting from abandoned mine. The results showed that AMD and impacted water was highly acidic and enhanced precipitation of secondary minerals at decant point and downstream of wetland

Chapter 4: This chapter covers the evaluation the effectiveness of sonication and flocculation in treatment and removal of pollutants from AMD using calcined magnesite. Sonication was more effective than flocculation. Sonication was more effective in raising pH, pollutant removal and enhance the precipitation of minerals than flocculation

Chapter 5: This chapter tackles the sequential recovery of Fe, Al and Mn from AMD in the form of sludge and it enhanced metal recovery through recycling and reuse of sludge. The elements Fe, Al and Mn were successfully recovered as metal hydroxyl oxides and hydroxyl sulphates at different pH. Reuse and recycling of metal rich sludge was observed to enrich sludge with metals.

Chapter 6: This section provides a summary of the findings of the thesis and recommendations for future studies

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Chapter 2

Literature Review

2.1 Introduction

Acid Mine drainage (AMD) is considered a significant water pollutant globally and the second environmental problem related to climate change by the USA Environmental Protection Agency (US-EPA) (Moodley et al., 2018; Zheng et al., 2023). The source of AMD in South Africa has been mining of Gold and Coal; some cases were reported in the Middelburg/Witbank area and the Witwatersrand basin (Abiye and Ali, 2022; McCarthy, 2011). To prevent AMD from entering nearby rivers, drainage plants were designed in the Witwatersrand basin and eMalahleni to treat AMD before discharging into rivers (McCarthy, 2011). This chapter will cover how AMD is formed, cases of AMD worldwide, various treatment methods, and piloted recovery techniques in South Africa.

2.2 Environmental Impacts of AMD

Acid Mine Drainage (AMD) has $\text{pH} < 3$, high concentration of Mn, Al, Fe, SO_4^{2-} and other trace elements (Abiye and Ali, 2022). Due to its acidic nature, AMD can dissolve the surrounding geology with oxide minerals such as calcite, bauxite, magnetite, pyrolusite, hematite, biotite, chlorite, cryolite, and many more; the metals in the ores will be part of AMD (Menzel et al., 2021). If carbonates and other alkaline minerals in the nearby geology cannot neutralize the generated acid, the surrounding surface water will remain acidic (Madzivire et al., 2013; Xia et al., 2023). Environmental impacts of AMD are grouped into four ecological classes (altering of habitats and food chain, loss of prey/ food sources), biological (reproductive problems, respiration, and mortality rates of organisms), chemical (increase of total acidity and toxic metal in the surrounding environment) and physical (reduction in penetration of light in affected water) (Ighalo et al., 2022; Xia et al., 2023). The environmental effects of AMD are summarized in Figure 2.1 (Ighalo et al., 2022). AMD discharged into the environment can affect the eco-environment as most plants do not survive in acidic environments due to high H^+ levels, which cause acid-base imbalances in soils, denaturing enzyme activity and restricting uptake of water and minerals salts by roots (Bell et al., 2001; Xia et al., 2023).

Besides affecting vegetation, water impacted by AMD has high levels of toxic metals and sulfate, making it undesirable for industrial and domestic use (Favas et al., 2016; Kefeni and Mamba, 2021). Some toxic elements, such as inorganic metal ions, preferentially accumulate

in fish's skin, muscles, liver, and grill, with the highest concentrations localized in the liver and gill tissues (Oberholster et al., 2010). The most abundant inorganic element in common AMD is Fe(II), whose oxidation decreases the amount of oxygen in aquatic systems (Favas et al., 2016). Oxygen decreases since Fe(II) will be oxidized and precipitate to ferric oxide, a yellow boy, which may harm aquatic species by affecting their visibility (Kefeni et al., 2017; Xia et al., 2023). Furthermore, an excess amount of Fe intake by humans damages cells and affects the functioning of the heart (Xia et al., 2023). Additionally, high amounts of sulphate in AMD are hazardous if consumed by humans as they may lead to vomiting and diarrhea at levels above 600 mg/L (Durand, 2012).

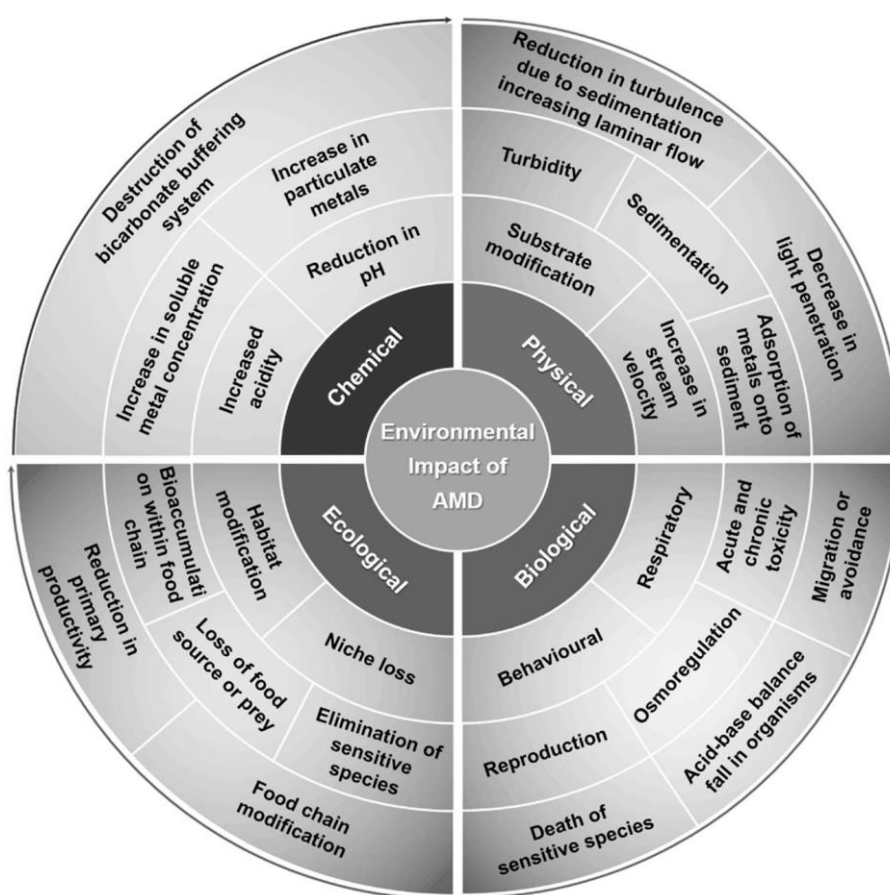
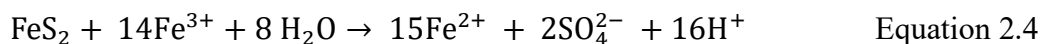
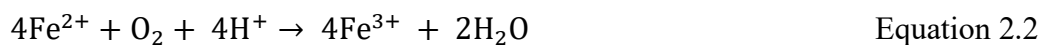
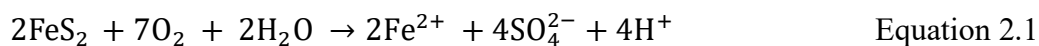


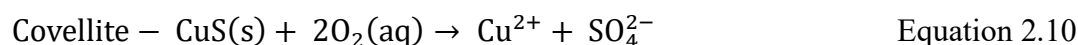
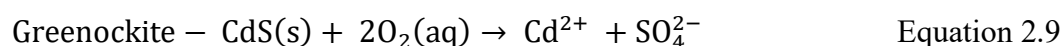
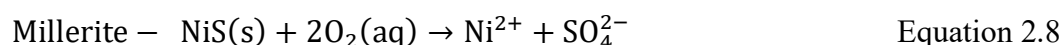
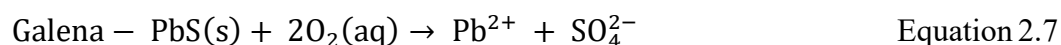
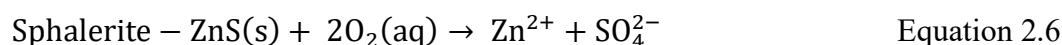
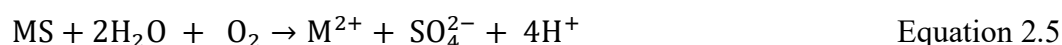
Figure 2. 1: Impacts of AMD on the environment (Ighalo et al., 2022).

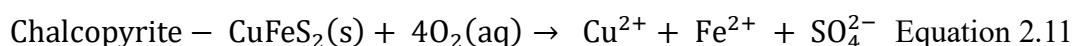
2.3 Occurrence Acid Mine Drainage

The generation of AMD occurs mainly due to the oxidation of pyrite and other associated minerals, such as covellite, chalcopyrite, and sphalerite, by water, oxygen, and sometimes microorganisms (Kefeni and Mamba, 2021; Menzel et al., 2021). Equations 2.1-2.4 show the oxidation of pyrite under different conditions (Jiao et al., 2023; Kefeni et al., 2017).



Pyrite forms Fe^{2+} and H_2SO_4 in the existence of water and oxygen eqn. (2.1). This is a key process in forming AMD. Microbial activity, the composition of minerals, and the availability of water and oxygen determine the rate at which pyrite and H^+ are oxidized and released, respectively. Fe^{2+} released in eqn (2.1) may be oxidized to Fe^{3+} in the proximity of necessary microorganisms such as bacillus ferro oxidants ($\text{pH} > 3.5$) eqn (2.2), and this is the slowest step, hence the rate-limiting step (Xia et al., 2023). At pH 2.2-3.5, Fe^{3+} forms precipitates of reddish-orange $\text{Fe}(\text{OH})_3$, releasing H^+ (eqn. 2.3). As the release of H^+ increases, pH will decrease gradually. $\text{Fe}(\text{OH})_3$ will be hydrolyzed again at $\text{pH} < 2$, forming Fe^{3+} to be released in solution and promoting pyrite oxidation (eqn 2.4). Waste rocks contain other metal sulphide minerals which can be oxidized, increasing the amounts of Cd, Zn, As, Cu, and Pb, contaminating ground and surface water eqn 2.5-2.11 (Kaur et al., 2018).





2.4 Acid Mine Drainage in Other Countries

Acid mine drainage (AMD) is a problem that affects the environment worldwide. In China, coal mining in Shanxi province was reported to increase SO_4^{2-} and Total Dissolved Solids (TDS) levels in Karst water systems, which supply Taiyuan city with water (Lu et al., 2023). Brazil's most significant coal mining companies are found in Santa Catarina. The mining tailings in this region are responsible for the low pH (less than 2) resulting in high iron sulphate water (Buzzi et al., 2013). Furthermore, the mining of pyrite and coal in Brazil caused mine water in the Figueira coal mine to be acidified (Zhang et al., 2023b). In Serbia, copper mining has been taking place for more than 100 years in the Bor area, resulting in tailing from the area producing acidic mine water that causes environmental problems in the Danube River (Masuda et al., 2019). Acid mine drainage problems were also reported in Australia, Russia, and USA. In Australia, more than 50 000 abandoned mining sites are believed to affect the environment with AMD, while about 4 200 mines are in Tasmania and 215 produce AMD. However, remediation is ongoing in the area, but it is recommended to implement passive treatment involving reuse and resource recovery (Moyo et al., 2023).

About 1000 ha of land in Quebec, Canada, is estimated to be covered by mining waste from abandoned mining wastes, which resulted in the formation of AMD, and about 150 million Canadian dollars is required for reclamation; this shows the significance of the problem (BussiÈre, 2010). AMD impacts on the environment was also reported in the USA in Pennsylvania, where it's stated that AMD impacts over 8 849.5 km of Pennsylvania surface waters (Hassas et al., 2022). AMD has been a major environmental problem in Russia, mainly due to abandoned coal mines. Cases were reported in the Kizel coal basin, where mining began more than 200 years ago. It ceased in 1990, causing the interaction of AMD with surrounding rocks upon its discharge, resulting in the dissolution of toxic metals and increasing their concentration in surrounding rivers, some of which were water sources for humans in the area (Khayrulina et al., 2016).

In the Levikha group of copper pyrite deposits found in the Middle Urals of Russia, mining occurred from 1927 to 2003. AMD decanting started in 2007, and it was then pumped from the

basin and neutralized with lime before being disposed of in the Tagil River (Rybnikova et al., 2023). Tinto River in Spain is viewed to be heavily impacted by AMD due to extremely low pH and elevated concentration of toxic metals, and the basin is part of the Iberian Pyrite Belt, which has mineral reserves of about 1700 million tonnes of sulphides ores (Amaya-Vías et al., 2019). About 4800 ha of the belt is occupied by substantial mining wastes such as tailings dams, waste dumps, open pits, and abandoned mining facilities, which produce acidic leachates that continue to pollute the basin and also the Odiel River basins (Amaya-Vías et al., 2019). Acid Mine Drainage was reported in Chile due to the treatment of sulphide minerals during Cu production (Menzel et al., 2021). In Colombia, 38 % of mining activities is coal production, with 3.087 million tonnes generated for use in metallurgical and thermal areas, which led to the generation of AMD characterized by low pH and high concentration of Sulphate toxic metals (Blanco-Zuñiga et al., 2022).

2.5 Methods of Treating AMD

Acid mine drainage treatment technologies consist of abiotic and biological methods, further grouped into passive and active treatment methods (Chen et al., 2021; Jiao et al., 2023). Passive methods basically attain precipitation of metal sulphides by generating reducing states and make use of organic material as neutralizing agents while active methods often make use of alkaline agents to enhance AMD to meet regulated standards (Naidu et al., 2019).

2.5.1 Active Methods

Active treatment methods involve adding chemicals to elevate AMD's pH to precipitate metal as insoluble hydroxides. Generally used chemicals include lime, magnesium hydroxide, and sodium hydroxide (Xia et al., 2023). These chemicals generate sludge that requires further treatment. These methods include adsorption, neutralization, flocculation, and ion exchange (Naidu et al., 2019).

2.5.1.1 Adsorption

The adsorption process involves the removal of pollutants by the interaction of different functional groups from adsorbent molecules and pollutants (Jiao et al., 2023). Recently, research has moved from ordinary adsorbents to cheap, efficient, and ecologically friendly adsorbents in AMD treatment, some of which are high molecular polymers, natural mineral materials, and nanoparticles (Jiao et al., 2023). Shrimp shells were successfully used as

adsorbents for remediation and removing excess pollutants from AMD (Nunez-Gomez et al., 2019). In another study, Moreroa-Monyelo et al. (2022) tried to ameliorate the adsorption requirements of naturally occurring attapulgite clay by modifying it with BaCl_2 and evaluating its effectiveness for removing SO_4^{2-} from AMD. They observed that about 70.8 % of SO_4^{2-} could be removed. An organic mixture (wheat straw, peat, and soil) was evaluated in the adsorption of toxic metals from AMD and emerged as a good adsorbent (Levio-Raiman et al., 2021). Kefeni and Mamba (2020) assessed the ability of charcoal ash from Namibian hardwood to remove pollutants from AMD, and they showed that charcoal ash removes pollutants using adsorption and precipitation. In another study, Wibowo et al. (2022) developed biochar and biochar clamshell composites and successfully removed Al from AMD under the implemented conditions. Many adsorbents can remove dissolved toxic metals from solutions but have the disadvantage of poor adsorption at low pH, difficulties with adsorbent regeneration, high capital, and inability to trace levels, which has limited their implementation in removing toxic metals from low pH mine water (Mzinyane, 2022).

2.5.1.2 Neutralization/ Precipitation Method

The neutralization method entails the precipitation of metal hydroxides, which is achieved by using alkaline agents (Kefeni et al., 2015). Metal ions in AMD precipitate as insoluble metal hydroxides are removed as solids (Kefeni et al., 2015; Xia et al., 2023). Alkaline chemicals, including lime, limestone, caustic soda, slaked lime, magnesium hydroxide, ammonium hydroxide, and ammonia, may be used. The main reaction mechanism for the reaction is (when Ca(OH)_2 is used) (eqn 2.12) (Xia et al., 2023).



M-divalent metal ion

Most of the chemicals for precipitation are produced commercially and are costly to acquire (Naidu et al., 2019). These neutralizers produce high amounts of sludge, which causes secondary pollution because they are difficult to reuse and recycle, causing treatment to be more expensive (Jiao et al., 2023; Xia et al., 2023). Recently, researchers have been interested in looking for cheap ways to treat AMD. For example, naturally accessible resources, by-products from industries, magnetic nanoparticles, and organic materials have recently emerged as cheap AMD treatment substitutes (Kefeni and Mamba, 2020; Kefeni et al., 2017). These

treatment options appeared to be cheap and eco-friendly. Some of these cost-effective AMD treatment materials include coal fly ash, metallurgical slugs, mine tailings, tree bark, tealeaves, charcoal ash nanoparticles and charcoal ash leachate, magnesite and cryptocrystalline magnesite (Gitari et al., 2006; Kefeni and Mamba, 2020; Kefeni and Mamba, 2021; Masindi and Gitari, 2016).

The ability to remove pollutants from charcoal ash nanoparticles was evaluated (Kefeni and Mamba, 2020). The authors observed that charcoal ash nanoparticles completely remove metals at lower pH except for Na, Mg, Ca, K, and SO_4^{2-} . Metallurgical slugs which are cheap compared to other liming methods were investigated for treating AMD and could reduce acid, iron and sulphur concentration (Name and Sheridan, 2014). The neutralization potential of coal fly ash was investigated and was found to remove metal ions from AMD (Gitari et al., 2006). In another study, coal fly ash reduced sulfate to levels below the South African water quality guidelines for portable water (Madzivire et al., 2011). Masindi et al. (2016) evaluated the use of locally available magnesite as an AMD neutralizing agent and observed a rise in pH from 2 up to 10. They further showed a drop in the amount of Fe, Mn, Zn, Al, Ca, and SO_4^{2-} in treated water, indicating the formation of new mineral phases.

2.5.1.3 Ion Exchange

Ion exchange is a finely established process for generating pure water from water with low concentrations of dissolved solids (Feng et al., 2000). The principle of ion exchange entails the transfer of ions from a solution to a solid material with the simultaneous transfer of hydrogen and hydroxyl ions from a solid material to the solution (Feng et al., 2000). Several ion exchange resins were developed to remediate AMD. A study by Gogoi et al. (2021) developed a biosorbent anion exchanger animated peat (PG-peat) using polyethyleneimine and glycidyltrimethyammonium chloride. It evaluated its column mode and batch in removing sulphate from AMD. The adsorbent was observed to be effective in removing SO_4^{2-} from field AMD. Vecino et al. (2021) proposed integrating ion exchange and selective precipitation in recovering valuable metals from AMD. The authors recovered Fe and Al in schwertmannite and basaluminite at pH 3.7 and 4.8, respectively. They further observed the best extraction of Zn (II) (> 96 %) at pH 2.7 using impregnated resin, VP1026, and extraction of greater than 99 % for Cu (III) using cation IX resin, TP107 at pH 3-4. Ion exchange has several advantages, such as resin regeneration, which can treat large amounts of AMD and recover toxic metals

(Feng et al., 2000). However, they have several disadvantages, such as being expensive if large volumes are to be treated and resin replacement over time is required (Feng et al., 2000).

2.5.1.4 Membrane Technologies

The principle membrane technologies encompass the use of a membrane barrier that separates charged ions from clean water; in the process, they leave behind a solution with a high concentration of dissolved solids (Jiao et al., 2023). Reverse Osmosis, forward Osmosis, nanofiltration, membrane distillation, and Electrodialysis are some of the membrane technologies used in AMD treatment (Jiao et al., 2023). One or more mechanisms during membrane technologies include size rejection, adsorption, and Donnan rejection (Abdullah et al., 2019). The mechanism of removal of membrane distillation is shown in Figure 2.2.

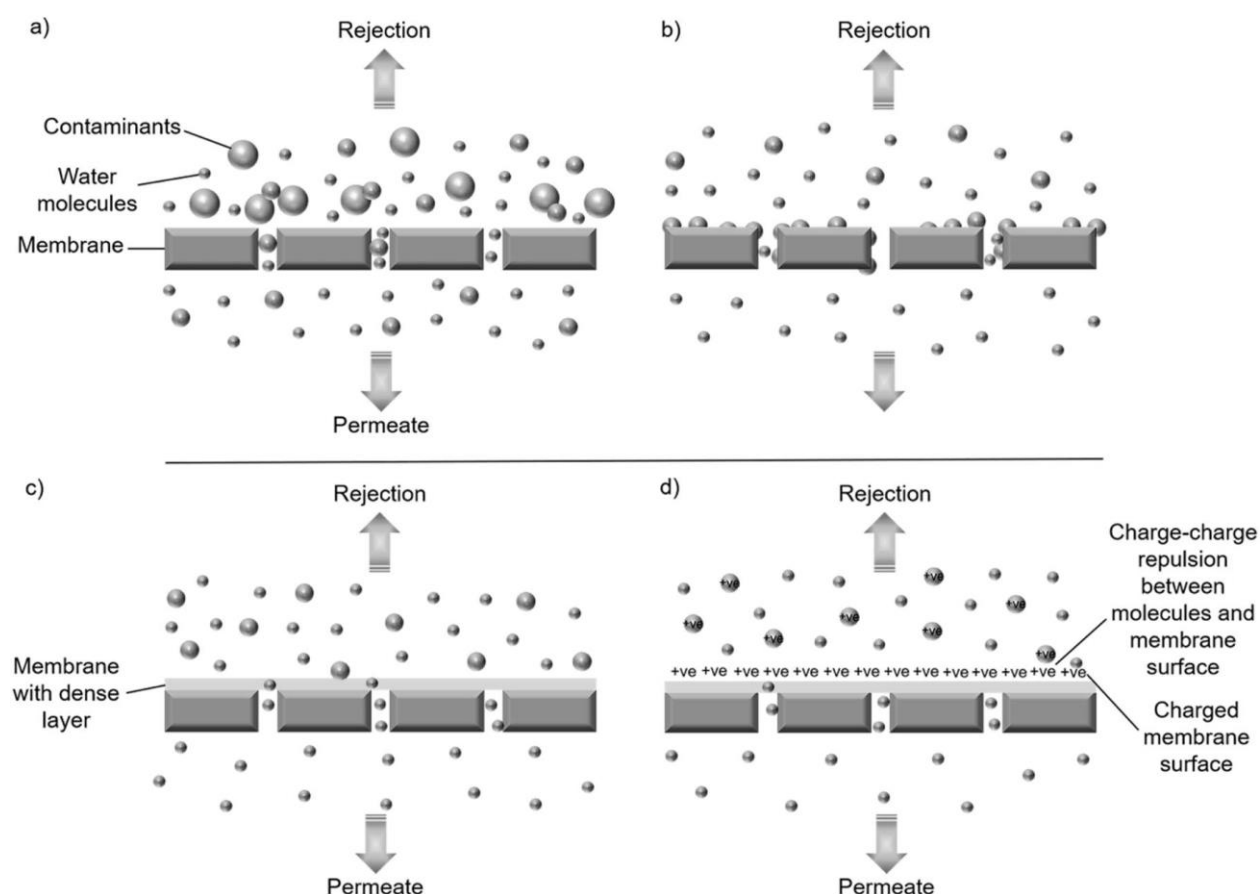


Figure 2.2: Removal mechanisms of membrane processes (Abdullah et al., 2019).

2.5.1.6 Reverse Osmosis (RO)

Reverse osmosis (RO) is when pressure is applied across a semi-permeable membrane, resulting in water molecules moving opposite to natural osmosis (Qasim et al., 2019). RO has

been used to remove dissolved solids from brackish (Saline) feed water, producing good-quality water. During RO, lime has been used for pre-treatment to precipitate metal ions, followed by ultrafiltration, which generates force to move water through a semipermeable membrane, leaving behind ions (Dama-Fakir et al., 2017). The behavior of the RO process in wastewater treatment from mining activities in Australia was evaluated, and there was a significant improvement in the quality of permeate from wastewater as indicated by a significant decrease in levels of toxic metals and Total Dissolved Solids (TDS) (Samaei et al., 2020). Clean water and brines are produced, and RO removes bacteria, sugars, dyes, and proteins. RO has the advantage of producing water with a low concentration of TDS. However, it is expensive and produces brine that has to be treated further (Dama-Fakir et al., 2017). Reverse osmosis performs well with integrated systems that overcome fouling, remove scaling agents, and treat the brine produced.

2.5.1.7 Forward Osmosis (FO)

The process of forward osmosis (FO) entails a low-energy membrane system that utilizes osmotic pressure instead of hydraulic pressure. In the FO process, the difference in osmotic pressure is generated when a low-concentrated feed and highly concentrated solutions are placed through a semi-permeable membrane, causing fresh water to be drawn from the feed to draw the solution (Cabrera-Castillo et al., 2021; Naidu et al., 2019). Vital et al. (2018) used draw solutions NaCl and NH_4HCO_3 with FO membrane (Thin film composite) to treat AMD from a Cu mine in Chile. The authors observed that when NaCl is used as a draw solution, there are higher rejection levels for most of the ions in AMD than when using NH_4HCO_3 , which was not favored as a draw solution due to scaling. Cabrera-Castillo et al. (2021) also applied 1M NaCl as a draw solution in treating AMD with FO under continuous assay at 60 °C temperature and achieved a 50 % water removal. This indicates that NaCl can be used as a draw solution. However, there is a need for alternatives. Another study (León-Venegas et al., 2023) used selective precipitation mixed with membrane technologies, RO, and osmotically assisted RO in recovering water and metals from sludge. Their results showed possibilities of recovering 80 % water, more than 95 % recovery of Fe as hematite at pH 3, more than 95 % recovery of Al at pH 4.5 as diasporite, $\text{Cu}(\text{OH})_2$ at pH 6.3, and recovery of 99 % and 94 % of Zn and Mn hydroxides at pH 8.5. The disadvantage of FO, which has spurred the development of the integrated system, is its lack of appropriate membranes and suitable draw solutions (Naidu et al., 2019).

2.5.1.8 Nanofiltration (NF)

The process of nanofiltration has the same principle and pre-treatment as RO, but it allows the passage of monovalent ions and only allows the separation of multivalent ions (Ighalo et al., 2022). The ability of NF270 (nanofiltration membrane) to recover water and concentration of Cu and how NF can be coupled with solvent extraction in Cu recovery from AMD was evaluated (Pino et al., 2020). They observed that NF and solvent extraction had the potential to recover 80 % water and 97 % Cu. However, the capacity of the membrane to concentrate metals and recover water was limited by gypsum scaling, and fouling of the NF membrane in AMD treatment was investigated. Their results showed that the main composition of AMD is inorganic compounds, which cause membrane fouling, causing a decrease in water permeability by 60%. Integrating Membrane technologies with systems that overcome fouling may help in AMD remediation.

2.5.1.9 Electrodialysis (ED)

Electrodialysis is a technology that utilizes the electric current to separate and purify substances (Jiao et al., 2023). It consists of a cell comprising a sequence of cation and anion-exchange membranes between the cathode and anode to make cells (Buzzi et al., 2013; Jiao et al., 2023). When a direct electrical current is passed through the cells, cations move to the cathode, and anions drift to the anode; this results in two streams, one with pure water and the other one with brine (Buzzi et al., 2013; Dama-Fakir et al., 2017). ED has been successfully applied to recover water and sulphuric acid from AMD (Buzzi et al., 2013; Martí-Calatayud et al., 2014). It suffers from several drawbacks, such as highly concentrated brines needing to be treated further; they don't have industry standards, scaling salts may cause precipitation of salts on the membrane, and regular maintenance and cleaning improves the stability of the ED treatment system (Jiao et al., 2023).

2.5.1.10 Membrane Distillation (MD)

Membrane distillation technology consists of an integrated thermal membrane technology that uses the difference in vapor pressure as its driving force (Jiao et al., 2023; Naidu et al., 2019). The difference in vapour pressure is generated due to variations in temperature between the distillate side and the membrane feed. The hydrophobic membrane enables water vapor to be

transported only through membrane pores (Naidu et al., 2019). Water gap MD and air gap MD were used to evaluate the performance of MD during the treatment of AMD from Tinto River. The authors observed electrical conductivity (EC) rejection values above 99 % in permeate from all experiments and higher permeate fluxes, which were even higher than those obtained from seawater RO and FO (Amaya-Vías et al., 2019). They further observed no membrane fouling when using air and water gap MD. Ryu et al. (2020) evaluated the potential of increasing the concentration of Cu while recovering water from AMD using direct contact MD. Overall, direct contact MD successfully concentrated Cu and was effective for the recovery of high-quality water. MD has the advantages of using lower operating pressure, energy efficient, sustainable, and portable; hence, it can be applied in remote areas (Amaya-Vías et al., 2019).

2.5.2 Passive Methods

Passive treatment methods focus on the reduction of environmental impacts by using alkaline agents to neutralize AMD, using permeable reactive barriers, microorganisms, artificial wetlands, or phytoremediation (Delgado et al., 2023; Menzel et al., 2021). These methods have cheap maintenance and operational costs, and the sludge generated is stable. However, they require more time to produce the targeted results and may suffer from passivation due to the formation of metal precipitates (Delgado et al., 2023; Menzel et al., 2021).

2.5.2.1 Artificial Wetlands

These form part of the ecology and utilize biological processes in AMD remediation. They are associated with mechanisms such as adsorption and ion exchange of metals, sulfate reduction, and precipitation of sulfates and metal hydroxides (Blanco-Zuñiga et al., 2022). Two types of artificial wetlands are aerobic and anaerobic.

2.5.2.2 Aerobic Wetlands

These consist of a shallow large pond with limestone, soil, organic matter, and planted wetland flora. Its depth is often less than 30 cm, and limestone provides alkalinity for removing metals via precipitation reactions such as hydroxides and oxides (Nguegang et al., 2022; Yang et al., 2023b). Plant wetlands remove metal toxicity from solutions through phytoextraction and rhizo-filtration (Daraz et al., 2023). During phyto-extraction, plants extract toxic metals and store them in different plant parts, and during rhizo-filtration, plants adsorb, precipitate, and concentrate toxic metals in the plant rhizosphere. This system requires the transportation of

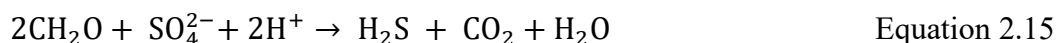
oxygen from the ground to the rhizosphere by plants to increase oxidation and surface area for the precipitation of metals.

2.5.2.3 Anaerobic Wetland

This method uses the organic material of spent mushroom composites, sawdust, clay, different manure, and sometimes limestone to generate alkalinity (Blanco-Zuñiga et al., 2022). The Organic material must contain sulfate-reducing bacteria, which converts sulfates into hydrogen sulfide, generating alkalinity as indicated by the reaction (Blanco-Zuñiga et al., 2022). The limestone increases the pH of AMD to about 6, favoring the growth of SRBs, and during the process, calcite dissolves, releasing calcium and carbonate in the presence of H^+ (Blanco-Zuñiga et al., 2022). The released bicarbonate will then react with H^+ , releasing carbon dioxide and water (eqn 2.13 & 2.14).



The SRBs convert sulphates to sulphides under anaerobic conditions (reaction 2.15).



Toxic metals are precipitated as metal sulfides with hydrogen sulfide as in reaction 2.16.



Chang et al. (2022) developed an aerobic constructed wetland system for treating AMD by utilizing walnut shell and its associated biochar product and supplementing external carbon with plant straw broth and sucrose. They observed that metals were efficiently removed except Fe, even when sulfidogenic activity was not properly developed. Biochar had a higher metal retention capacity and supported a higher abundance of sulphate-reducing bacteria. They concluded that the developed constructed wetland was promising as an ecological option for AMD treatment. Anaerobic wetlands are more efficient when treating small volumes of AMD with limited acidity (Blanco-Zuñiga et al., 2022). Generally, artificial wetlands have several

advantages, which include easy operation, little energy consumption and investment, low cost of operation, and easy management. However, they have a slow flow of water in the wetland, and the generation of large quantities of sludge decreases their operation efficiency (Blanco-Zuñiga et al., 2022). However, they also need large areas of land, are unable to treat large amounts of AMD and suffer from seasonal variations (Yang et al., 2023a).

2.5.2.4 Limestone Passive Treatment System

These use limestone to neutralize AMD, comprising open limestone channels, anoxic drains, oxic limestone drains, and stabilization beds (Yang et al., 2023a). The disadvantage of limestone is its tendency to be passivated by precipitates of metal hydroxides, known as armoring, which will reduce the dissolution of limestone, thus reducing its efficiency (Turingan et al., 2020).

2.5.2.5 Anoxic Limestone Drains (ALD)

These consist of crushed limestone buried underground, sealing it from air, and as AMD moves through limestone, it produces CO₂ (Skousen et al., 2019). Figure 2.3 shows an anoxic limestone drain being constructed.



Figure 2. 3: Anoxic limestone drains (Skousen et al., 2017).

From Figure 2.3, it can be observed that the oxidation of Fe occurs under anaerobic conditions without the precipitation of ferric hydroxide (Daraz et al., 2023). Generally, the system works by preventing atmospheric oxygen and promoting the generation of CO₂ (Rambabu et al., 2020).

2.5.2.6 Oxic Limestone Drain (OLD)/ Oxic Limestone Channels (OLC)

These are used for the remediation of AMD in the presence of air. In OLD, AMD flows through the drain that contains limestone, while in OLC, AMD percolates on the surface of the reactive material (Mehdaoui et al., 2023). In both methods, sulfates and metal hydroxide precipitation occurs due to oxidation and neutralization of AMD (Mehdaoui et al., 2023).

2.5.2.7 Open Limestone Channels

These are limestone channels covered with iron, and aluminum hydroxide is used in the system to reduce the breaking of limestone (Daraz et al., 2023).

2.5.2.8 Alkaline leach Beds

These are different from open limestone channels. They are smaller ponds constructed with limestone (Skousen et al., 2017). Their principle involves the continuous dissolution of limestone, generating alkalinity until passivation occurs (Skousen et al., 2019). Due to passivation, they are used to treat low pH and metals-free AMD. However, steel slag can enhance alkalinity (Skousen et al., 2019).

2.5.2.9 Dispersed Alkaline Substrate (DAS)

These are reactive materials composed of coarse material that is highly porous (Chips of wood) and neutralizing agents made of small grains (CaCO₃, MgO) (Rakotonimaro et al., 2016). This technique was developed specifically for AMD, which is highly contaminated and whose dissolution of its neutralizers delays passivation (Mehdaoui et al., 2023). The DAS system can be integrated into singular units, MgO-DAS, CaO-DAS, WS-DAS, and Limestone-DAS reactors (Rakotonimaro et al., 2016). Orden et al. (2021) obtained high treatment efficiency of highly contaminated AMD Mina Esperanza (SW Spain) for two and one third years after successfully implementing a limestone-DAS reactor.

2.5.2.10 Pyrolusite Limestone Beds

These consist of shallow limestone beds inoculated with aerobic microorganisms (Berghorn and Hunzeker, 2001). Pyrolusite beds are constructed to remediate AMD with a high concentration of manganese. During the remediation, microorganisms generate oxygen, which facilitates hydrolysis of Mn^{2+} to insoluble pyrolusite, as shown by equation 17 (MnO_2) (Taylor et al., 2005a).



2.5.2.11 Limestone Diversion Wells (LDW)

This underground well comprises a metal or concrete tank filled with crushed limestone (Taylor et al., 2005a). Figure 2.4 shows a diagram of a limestone diversion well (LDW). LDW has a pipe that enters vertically through its center, carrying acidic water from a dam with a hydraulic head. The water exits the well near the bottom under high pressure and flows back through the limestone, agitating and fluidizing the beds. The acidic water generates alkalinity by dissolving limestone, and the water currents flush it to the top of the well (Skousen et al., 2017).



Figure 2.4: Limestone diversion walls (Skousen et al., 2017).

2.5.2.12 Permeable Reactive Barriers (PRB)

These can be called vertical flow wetlands and are composed of reactive material buried underground to help with the in-situ treatment of AMD (Nguegang et al., 2022a). The reactive

material can be limestone, organic matter, or zero-valent iron (Rambabu et al., 2020; Taylor et al., 2005a). Organic material promotes the reduction of sulfates to H₂S and HS⁻ which will form metal sulfides with metals from AMD. The bacteria consume Organic material, leaving voids that the metal precipitates will fill. PRB may be limited by the availability of reactive material mass and the volume of pore space availability of the barrier (Rambabu et al., 2020; Taylor et al., 2005a).

2.5.3 Biological Treatment Methods

The principle of these methods is based on the biological action for water treatment according to recommended guidelines (Yang et al., 2023a). Biological treatment methods consist of phytoremediation and microbial treatment methods.

2.5.3.1 Sulphate Reducing Bacteria (SRB)

The SRB uses organic carbon, which reacts with sulfate to form insoluble metal sulfite precipitates by binding to metal ions eqns 19 & 20 (Hu et al., 2022a). Alkalinity and pH increase, and the concentrations of metals and sulfate decrease in product water after treatment with SRB (Yang et al., 2023a). The remediation efficiency of SRB can be enhanced by mixing carbon sources such as yeast extract, composite manure, etc., with salts like calcium carbonate, calcium chloride, ammonium chloride, etc. (Yang et al., 2023a).

2.5.3.2 Phytoremediation

Phytoremediation involves growing plants that survive in an acidic medium to absorb toxic metals from AMD to reduce environmental pollution (Yang et al., 2023a). The plants are grouped into accumulators, excluders, and hyperaccumulators depending on their ability to absorb metals from the impacted environment (Thomas et al., 2022). Phytoremediation can be integrated with sustainable land use in the mining industry. Plants may be used in phytomining, extracting commercially valuable minerals from hyperaccumulators (Thomas et al., 2022). One of the commonly used plant species for phytoremediation is vetiver grass (*Vetiveria zizanioides*) because of its efficiency in the uptake of toxic metals released from AMD and its ability to easily adapt to rocky, dry and chemically contaminated areas (Girmay, 2019). Nguegang et al. (2022) assessed the treatment of AMD using horizontal flow with *Vetiveria zizanioides* in artificial wetlands. The authors reported significant removal of selected pollutants over 30 30-day retention time. However, they recommended integrating the method with other effective methods to meet effluent discharge guidelines.

2.6 Combined Process and Resource Utilization of Acid Mine Drainage

Using a single technology in treating AMD has limited effectiveness because it may not meet the required treatment guidelines. In contrast, using two or more technologies may help overcome the weakness of a single AMD treatment technology (Chen et al., 2021). Integrating AMD treatment processes will help offset treatment costs associated with handling waste material, as existing treatment technologies don't meet the cost of sustainability (Chen et al., 2021). To manage residues and wastes, the paradigm shifted from conventional to sustainable (Naidu et al., 2019). Valuable resources recovered from AMD through sustainable treatment include water, sulphuric acid, metals, and critical elements (Kefeni et al., 2017; Naidu et al., 2019).

2.6.1 Recovery of Sulphuric Acid

Acids are used for various applications, such as metal and chemical industries, for various treatments; recently, demand for sulphuric acid for leaching in copper-cobalt oxide, uranium, and nickel laterites industries was observed (Nleya et al., 2016). Several techniques, like crystallization, solvent extraction, distillation, diffusion dialysis, and ED, have been applied to recover acids from wastewater (Nleya et al., 2016). Amongst these techniques, ED is most preferred due to its ability to produce highly concentrated and purified acid (Simate and Ndlovu, 2014). A study by Martí-Calatayud et al. (2014) recovered sulphuric acid from AMD in an anodic compartment of an ED cell with an ion exclusion technique. The researchers also observed that the ED cell, consisting of three compartments, enabled the increase in sulphuric acid concentration from AMD. They further observed that the performance of ED cells decreased due to precipitation of Fe(III), which was being removed simultaneously with sulphuric acid. Furthermore, freeze crystallization and membrane distillation technologies are promising for recovering pure acids (Naidu et al., 2019). However, the acid recovery process is complex. Thus, sulphuric acid recovery with these technologies needs to be researched further. Additionally, Nanofiltration (NF) is one of the recent techniques that offers a good chance of recovering acids from AMD (López et al., 2019). However, the separation is influenced by the active layer's membrane chemistry and the feed's composition.

2.6.2 Recovery of Metals

As alluded earlier, AMD have elevated amounts of toxic metals that are non-biodegradable, hence pose environmental pollution. Thus, there is a need for their efficient removal from AMD in an efficient way that supports environmental sustainability to enhance recycling (Chen et al.,

2021). Bioelectrochemical and electrochemical methods are promising techniques in sustainable metal recovery from AMD. (Leon-Fernandez et al., 2021). Delgado et al. (2023) coupled electrodialysis with bioelectrochemical processes (Microbial electrolysis cell and microbial fuel cell) to enhance the recovery of metals by increasing their concentration in AMD. They recovered Cu as Cu⁰ throughout microbial fuel cell operation. They further recovered Ni²⁺, Fe²⁺, Cd²⁺, and Zn²⁺ as mixed metal masses during the subsequential operation of the microbial electrolysis cells. Hence, it was impossible to recover metals using their techniques selectively. In another study, a combination of Fe pretreatment recovery, Cu pretreatment recovery, and S pretreatment recovery from AMD was evaluated by oxidation with hydrogen peroxide, reduction with sulfate-reducing bacteria (SRB), and oxidation with sulfur-oxidizing bacteria (SOB) (Hu et al., 2022c). Hu et al. (2022) showed that the removal % of Total Fe, Mn²⁺, Mg²⁺, and Cu²⁺ was 99.46 %, 99.10 %, 84.08%, and 99.66 %, with average Fe content of 27.53 %, 13.8 % of Mn, 32.2 % of Mg and 35.6 % of CuS respectively in sludge. The conversion rate of elemental S was above 90 % at pH ranges of 8.34-9.11.

2.6.3 Rare-Earth Elements (REE)

Rare-earth elements are classified as heavy (Gd, Y, Dy, Tb, Er, Ho, Tm, Lu and Yb), light (La, Eu, Sc, Pr, Ce, Sm and Nd), and critical (Y, Nd, Tb, Eu, Dy, Y and Er), recently these elements have found applications in energy storage, high-tech industry, and green initiatives (Hassas et al., 2023). China is one of the biggest producers of REE in the world, accounting for approximately 80 % of the total world production from 2015 to 2016; however, due to export regulations imposed by China, importer countries began to search for alternative means of producing REE due to increases demand (Royer-Lavallée et al., 2020). Therefore, research has shifted towards the recovery of REE from other sources, such as AMD. Hassas et al. (2022) selectively precipitate REE from AMD by pre-treating AMD to pH 4 and 5 to remove Fe and Al, respectively. They further treated the product water to pH 7 with Na₂CO₃ to recover REE. The total REE recovered was 5.2 %, with 5.74 % Al as the main impurity. Hassas et al. (2022) further improved the purity and concentration of REE by redissolving the precipitates and repeating the staged precipitation process twice. They observed that the total REE increased to 17 % and 47 % in the second and third precipitation stages, respectively, representing the best compared to the literature. Yang et al. (2023b) successfully removed REE from AMD using a biosynthetic adsorbent, green-reduced graphene oxide (G-rGO). However, they recommended further research on the performance of the adsorbent. From the above literature, it is difficult

to recover REE from AMD using one technique; therefore, integrating AMD treatment management technologies offers a possible solution.

2.7 Piloted Active Treatment Methods in South Africa

2.7.1 The Savmin Process

This process was designed by Smith and Kalch (1999) and used at Stillfontein plant and was able to remove SO_4^{2-} to concentrations below 200 mg/L. Figure 2.5 shows a scheme diagram of the Savmin process. In the process, metal hydroxides and SO_4^{2-} are removed in different stages. During the first stage, metal hydroxides are removed by raising pH to about 12 using lime (Chatla et al., 2023; Smith and Kalch, 1999). In the second stage, the remaining liquid solution reacts with lime forming gypsum and part of this solution is returned to act as seed for gypsum precipitation while the rest is removed. The third stage is when $\text{Al}(\text{OH})_3$ is added to the feed from stage two forming ettringite as shown by eqn (Chatla et al., 2023; Smith and Kalch, 1999).

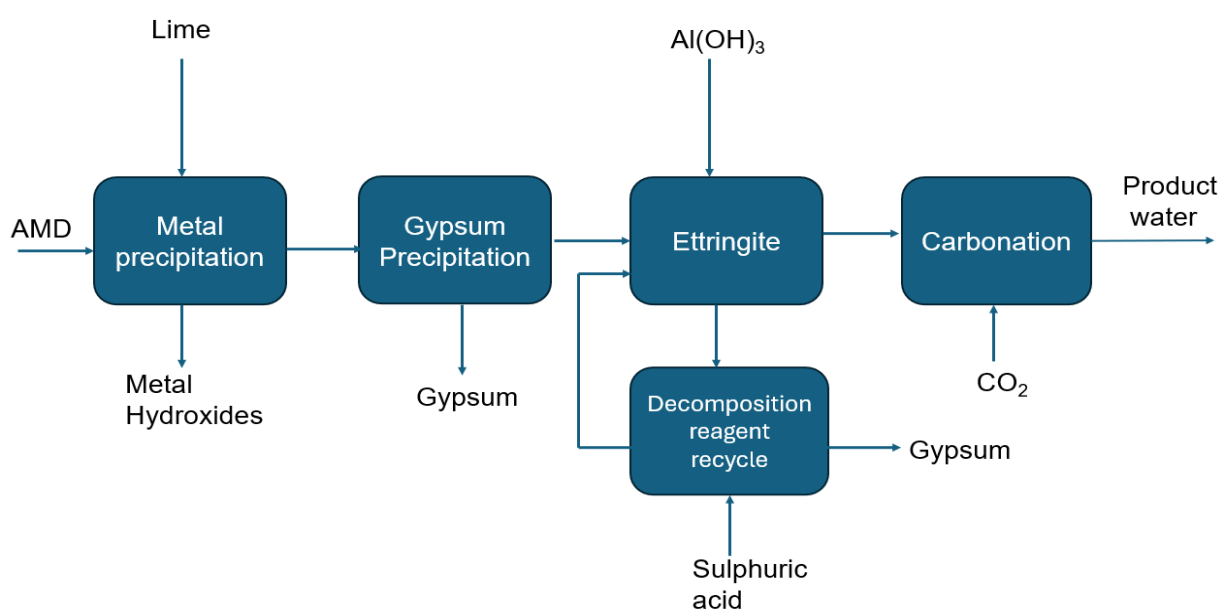
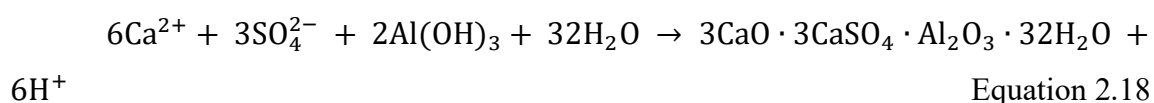


Figure 2.5: The SAVMIN process (Chatla et al., 2023).



Stage four is the addition of CO_2 and precipitation of CaCO_3 , which was removed by filtration, and finally, ettringite is decomposed in H_2SO_4 for $\text{Al}(\text{OH})_3$ regeneration. The resulting sulfate and calcium ions are contacted with gypsum to crystallize the calcium sulfate, which is removed by thickening/filtration (Chatla et al., 2023; Smith and Kalch, 1999). Due to their good quality, the SAVMIN process produces by-products such as gypsum, calcine, and metal hydroxides with good resale value. However, it has large amounts of sludge that need further disposal (Baloyi et al., 2023).

2.7.2 Rhodes-Biosure Process

The Biosure process was briefly explained and designed by (Rose, 2013) and its novelty is in utilizing organic wastes like sewage sludge as a carbon or electron donor source to reduce biological sulphate under anaerobic reactions. A pre-commercial plant was assembled at the Grootvlei Gold Mine, close to an operating lime high-density sludge (HDS), removing metals from AMD. The primary sewage sludge was a carbon source for neutralized feed water. Sulphate was reduced from around 1 500 mg/L to 300 mg/L. The advantage of this process is that it offers the disposal option of waste treatment sludge. However, the plant ceases operation due to the availability of sludge (Mogashane et al., 2020).

2.7.3 Alkali-Barium Calcium Process (CSIR-ABC).

The Alkali Barium Carbon process was developed by Council for Scientific and Industrial Research (CSIR) for resource recovery from AMD using calcium carbonate, barium carbonate, coal, and lime as the main raw materials (Mulopo, 2015; Rukuni et al., 2012).

The scheme diagram of the CSIR-ABC process is shown in Figure 2.6. The technology consists of three steps: neutralization, sulphate removal with barium carbonate and sludge processing (Mulopo, 2015; Rukuni et al., 2012). During neutralization, limestone is mixed with acidic water to raise the pH to 5.5 – 6.5. Lime is then added to the partially neutralized water in the gypsum reactors to raise the pH to 11.5 for precipitation of $\text{Mg}(\text{OH})_2$ and SO_4^{2-} associated with magnesium as gypsum. Carbon dioxide is introduced to the water from gypsum reactors to reduce pH from 11.5 to 9.0 before being pumped to barium reactors, where barium carbonate is added to remove Ca and SO_4^{2-} as CaCO_3 and barite precipitates. Barite and calcium carbonate from the sludge (Obtained from barite clarifier) are converted to barium sulphide and calcium oxide respectively. After this process, the BaS and CaO are slurred with water, BaS dissolves completely, and CaO forms a precipitate of $\text{Ca}(\text{OH})_2$. The filtrate which contains barium

sulphide reacts with carbon dioxide to form H_2S gas and BaCO_3 . Generally, the ABC method lowers toxic metal and SO_4^{2-} concentrations below the South African guidelines for irrigation water (Mogashane et al., 2020). BaCO_3 is a poisonous compound. It may be harmful if it enters the product water (Van Rooyen et al., 2021).

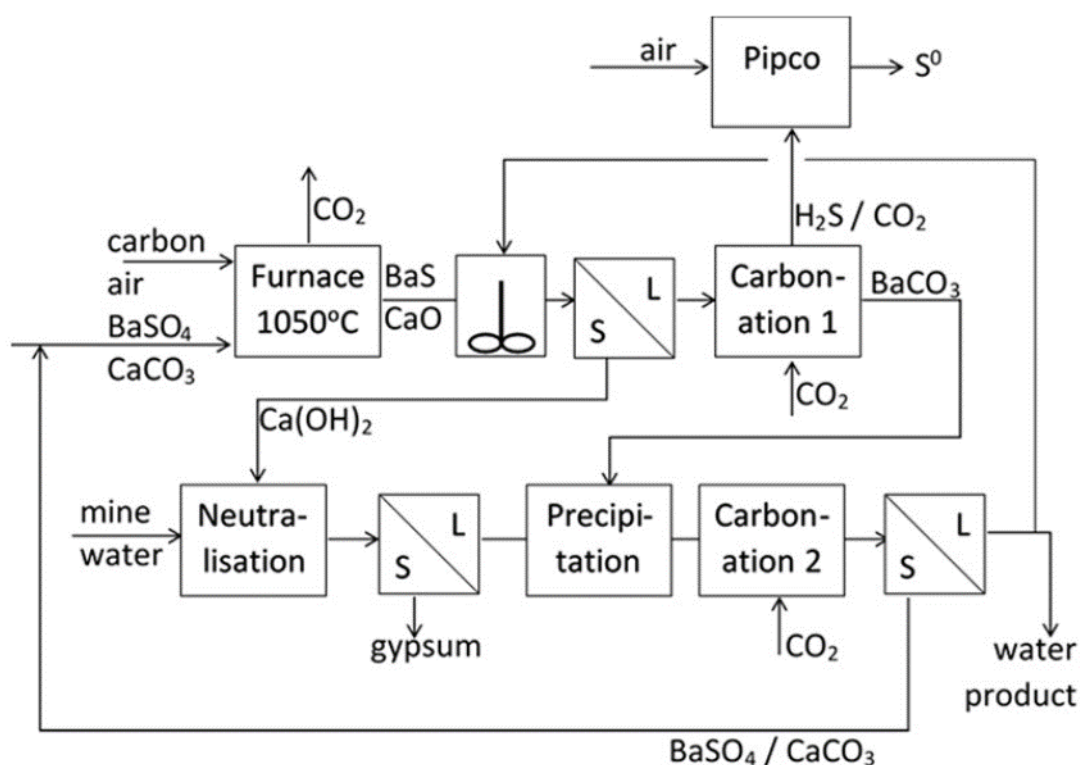


Figure 2.6: CSIR- Alkali Barium Carbon (ABC) process (Mulopo, 2015).

2.7.4 High Recovery Precipitating Reverse Osmosis (HiPRO) Process

Three AMD treatment plants were built in South Africa 2005 to solve the upper Oliphant River water challenges (Mogashane et al., 2020). This process has three phases: pretreatment, ultrafiltration, and reverse osmosis, as shown in Figure 2.7 (Karakatsanis and Cogho, 2010; Mogashane et al., 2020). During the pre-treatment step, limestone is applied to remove total Fe, Al^{3+} , and H_2SO_4 at eMalahleni, where pH values are low. Mn, Fe^{2+} , and other toxic metals that remained at low levels are removed by lime. At optimum colliery, where low levels of Mn and Fe were observed, ozone is used to remove such metals. The sludge is removed in stage 1 clarification after dosing with anionic polymer flocculant to promote agglomeration. Stages 2 and 3 pre-treatment differs from stage 1 due to removing $\text{Mg}(\text{OH})_2$ and gypsum.

Hydrocyclones attract large sludge particles, while small ones are introduced in stages 2 and 3. UF is the last stage for the removal of solids before RO.

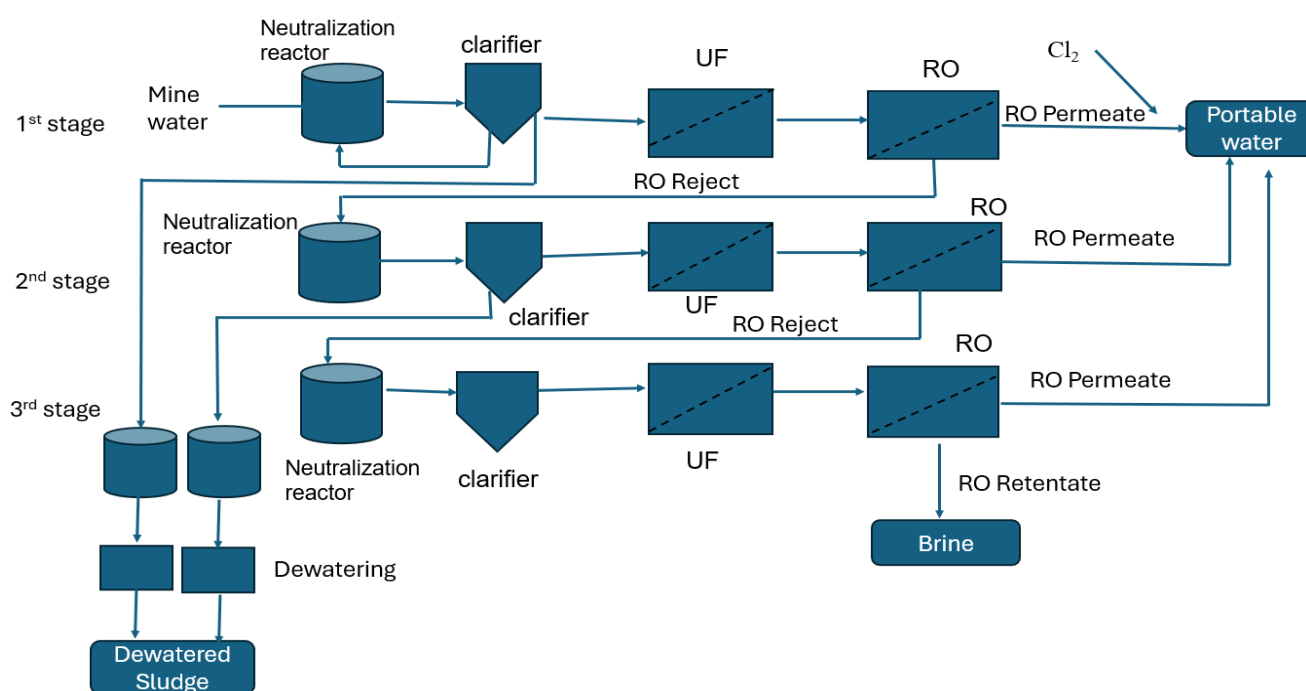


Figure 2.7: High Recovery Precipitation Reverse Osmosis (HiPRO) (Hutton et al., 2009).

Each UF skid has 38 modules that are regularly backwashed to remove entrained solids. H_2SO_4 and antiscalant are added in small amounts upstream of UF in stage 1 to prevent gypsum scaling on RO membranes. For stages 2 and 3, due to high pH after pre-treatment, antiscalant acid is added after UF and H_2SO_4 to correct pH. RO is the last stage aimed at the recovery of water. The CaSO_4 saturated feed water from stage 1 produces about 90-95 %; however, the CaCO_3 precipitation limits recovery. Stage 2 and 3 RO brines aimed at recovering 65 to 60 % of water due to high levels of CaSO_4 in feed water. Product water from each RO skid is collected in common tanks while the reject from each stage is pumped to the following stage. Sludge, brines, and gypsum become waste solids, and about 98 % of water is recovered. However, the brines and sludge waste streams from reverse osmosis must be disposed of longer because they are harmful and highly concentrated with dissolved salts (Dama-Fakir et al., 2017).

2.7.5 GYP-CIX Process

The process uses the principle of cation and anion exchange resins for the adsorption of SO_4^{2-} and Ca^{2+} from AMD by exchanging them with H^+ and OH^- ions (Baloyi et al., 2023; Robertson et al., 1994). In the process, the pilot plant is fed with limed AMD water from the underground

mine, which moves into the cation loading section with strong acid resins, where it moves due to the force of gravity through up-flow fluidized bed stages. Water is moved into the weak base anion resin comprising six fluidized stages. The product water has a neutral pH with low concentration of calcium, sulphate ions and other metal ions. The novelty of this process is in the resin regeneration and the production of gypsum as solid waste. Cation exchange resin is regenerated using sulphuric acid, which contains gypsum seeds, while anion resin is regenerated using lime, which contains gypsum seeds. Gypsum seeds in cation and anion exchange resins allow removing gypsum crystals from the solution. The advantage of this process is the generation of Ca and SO_4^{2-} that can be reused. However, much sludge is produced during ion exchange resin renewal (Baloyi et al., 2023). Furthermore, iron, silica, and organic compounds cause fouling to the resin, causing additional costs and limiting plant desalination (Robertson et al., 1994).

2.7.6 HybridICETM Technology

In the process, a solution is cooled to its eutectic temperature, forming pure ice crystals that leave behind more concentrated salt. Figure 2.8 shows the diagram of the eutectic freeze crystallization process. In this technology, pure water will be separated from salt according to density, and ice will float on top of the salt solution and can be separated easily (Dama-Fakir et al., 2017). Eutectic freeze recovers pure salts from brine mixture and TDS water (Dama-Fakir et al., 2017).

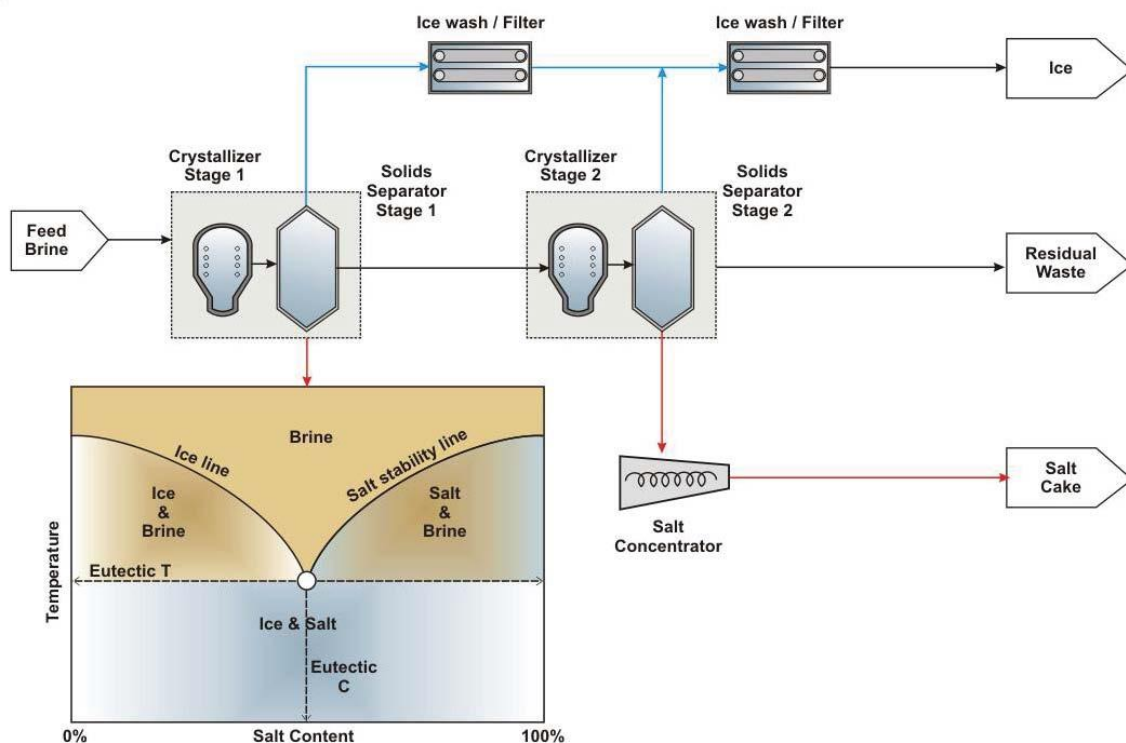


Figure 2.8: Eutectic freeze crystallization (Dama-Fakir et al., 2017).

2.8 Cavitation

Cavitation is a phenomenon of microbubbles' formation, growth, and collapse in an aqueous phase (Ručigaj et al., 2022). Ultrasound may produce cavitations, defined as the sound of a frequency range between 20 kHz and 500 MHz. Sonochemistry is a non-classical method that enhances the reaction rate (Azarpour et al., 2019). The irradiation of ultrasonic waves to a liquid medium generates microbubbles, which expand during the rarefaction and contract during the compression, as shown in Figure 2.9 (Leong et al., 2011). The bubbles will continue to grow until they reach an unstable size and collapses violently during the compression stage (Leong et al., 2011; Wang et al., 2023). Bubbles formed are either stable or transient cavities; in the former, bubbles oscillate steadily and last for about one cycle, and in transient cavitation, there is fast growth and enormous release of energy, and it lasts for less than a cycle (Dehane et al., 2021).

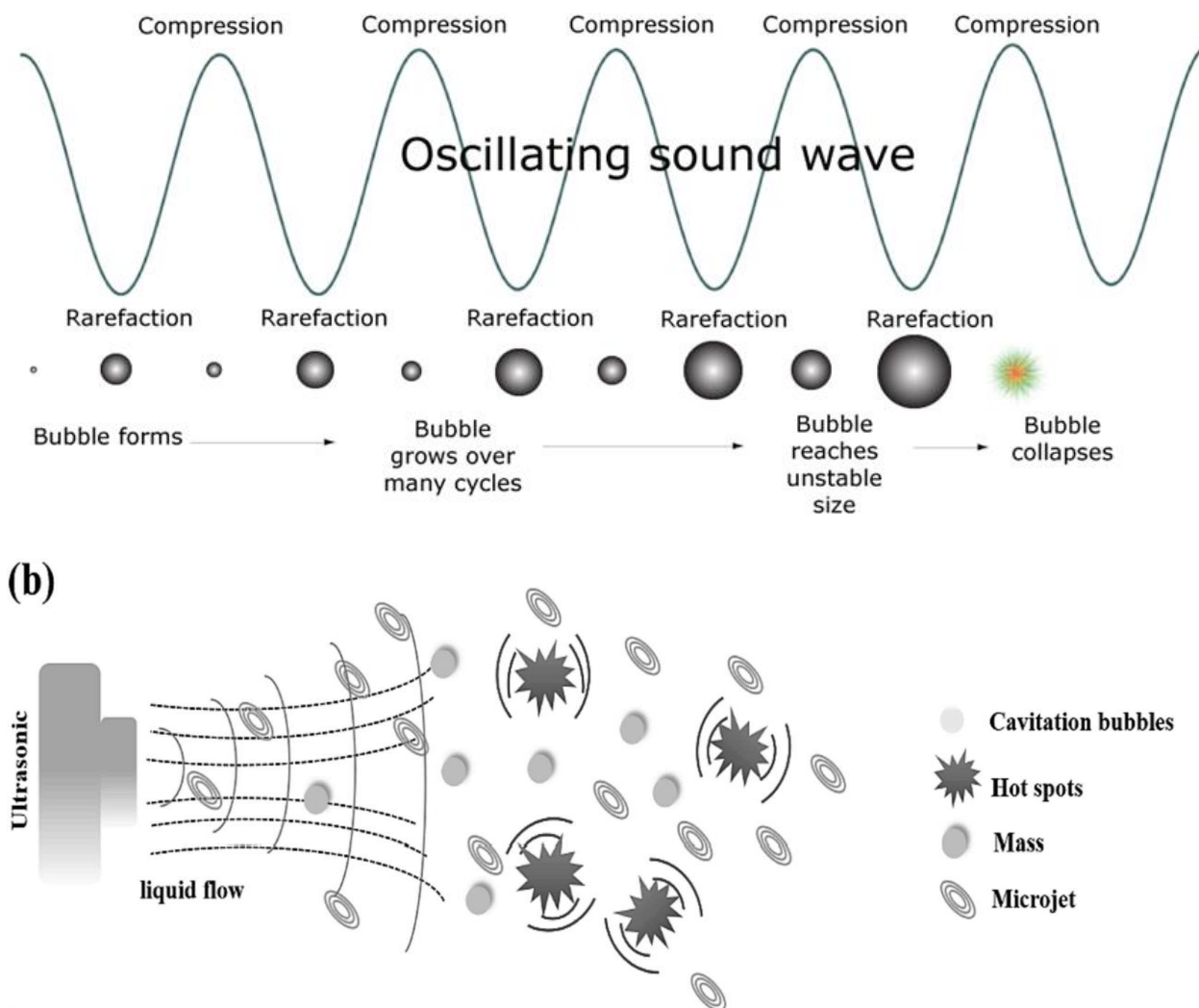
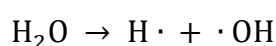
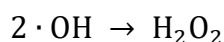


Figure 2.9: (a) Bubble formation, bubble growth, and collapse during rarefactions and contractions in acoustic cycles (Leong et al., 2011) (b) microfluidic phenomenon (Wang et al., 2023).

The sudden burst or collapse of microbubbles produces a high amount of energy, causing localized hot spots characterized by high pressure and temperature of 500 atmospheres and 5000 K, respectively (Wang et al., 2023). Local hot spots formed after bubble collapse last for microseconds, followed by quenching of the surrounding liquid; thus, bubbles with high amounts of energy may serve as microreactors where radicals and ions take part in chemical reactions (Wang et al., 2023). During sonolysis of water, high reactive radicals such as $\cdot\text{OH}$ and $\cdot\text{H}$ may be formed, which will further interact with each other to form H_2O_2 (eqns 2.19-2.20) (Dehane et al., 2021; Leong et al., 2011; Wang et al., 2023).



Equation 2.19



Equation 2.20

Sonication can be used in heterogeneous reactions such as solid-liquid to improve the efficiency of chemical reactions. The advantages of this include improved nuclei for cavitation and bubble collapse (Wang et al., 2023). Bubble collapse, which occurs during this phenomenon, is asymmetrically near the solid surface, resulting in violent microjets and shock waves (Wang et al., 2023). This results in increased turbulences and shear forces that can facilitate mass transport in chemical reactions, for example, increases in kinetic energy of solid powders in solution and microfluidic effects, resulting in several collisions such that particles fracture (figure b) (Hagenson and Doraiswamy, 1998; Leong et al., 2011). This effect of cavitation may be applied in surface cleaning of solid materials and mass transfer reactions (Hagenson and Doraiswamy, 1998). Very few studies have reported the application of cavitation in AMD treatment. Musyoka et al. (2012) used mine waters and fly ash directly to synthesize zeolite A, employing ultrasound to enhance the dissolution of fly ash in mine water and boost the crystallization process. Musyoka et al. (2012) observed that applying ultrasound during the aging step before hydrothermal treatment reduced the time needed to synthesize single-phase zeolite A from two hours to one hour and enhanced the zeolite's crystallization process. Ileri and Sanliyuksel Yucel (2020) modified fly ash with ultrasonication and evaluated its metal removal capacity from AMD. The authors observed cracks and pits on the surface of modified fly ash and a reduction in contact time and dosage when using modified fly ash than fly ash during the treatment of AMD. They also observed the effectiveness of ultrasound in the removal of metals as compared to fly ash during the reuse of sludge. Cavitation effectively enhances the removal of pollutants and lowers reaction time and dosage in treating AMD with coal fly ash and magnesite (Kalombe et al., 2020; Madzivire et al., 2013).

2.9 Conclusion

This chapter covers the formation, global cases, treatment methods, and environmental impacts of AMD, focusing on South Africa. AMD causes significant water pollution and other environmental impacts. Several AMD treatment methods include adsorption, precipitation, ion exchange, reverse osmosis, and electrodialysis. Amongst these methods, precipitation is most preferred since it allows the recovery of valuable products. However, the use of 2 or more techniques in AMD treatment is considered a better option for AMD treatment. Some of the piloted AMD treatment methods which focused on recovery of resources in South Africa include the Savmin Process, Rhodes-Biosure Process, the HiPRO, and ABC. The generation of sludge and brines remained a challenge. There is still a need to develop an AMD treatment technique to address these challenges. The treatment technique should be more efficiency and sustainable. Such technique should enhance treatment and recovery of metals from AMD by reducing contact time and dosage. Furthermore, the technique should allow the recycling of metal rich sludge to increase concentration of minerals.

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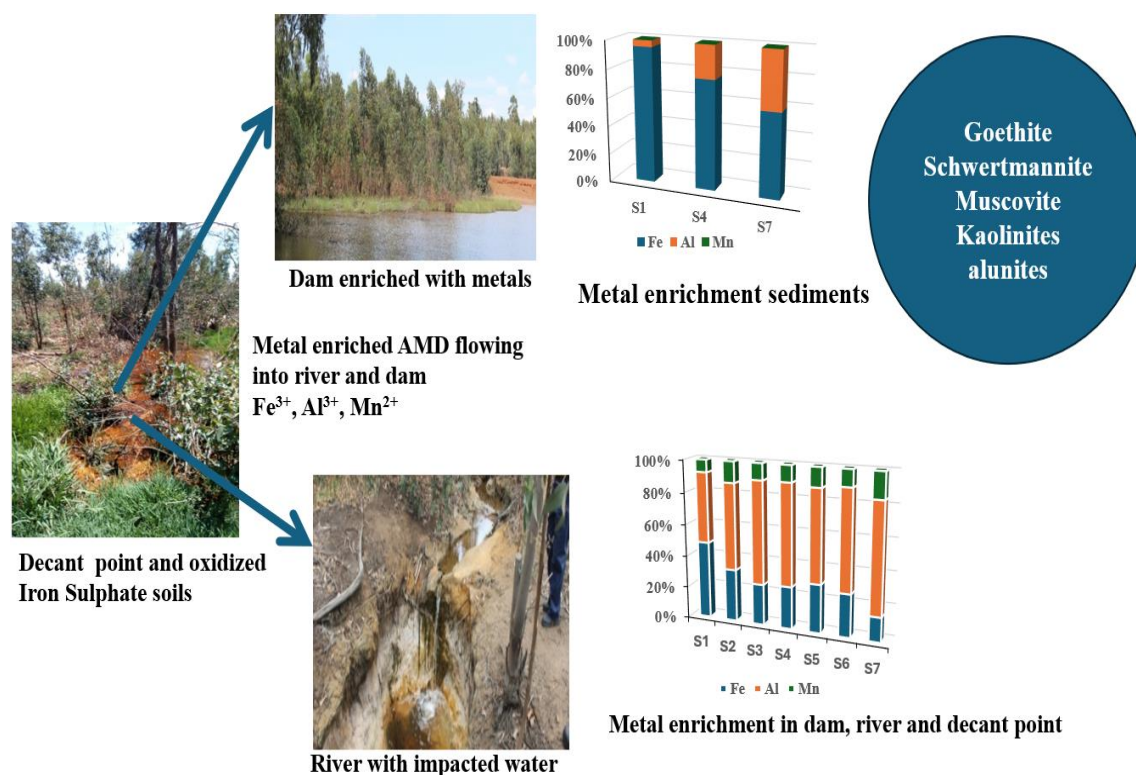
Chapter 3

Hydrogeochemical characteristics of surface waters and sediments impacted by acid mine drainage: Case of eMalahleni, Mpumalanga Province, South Africa

Highlights

- Surface water in eMalahleni is impacted by Acid Mine Drainage (AMD) which decant from abandoned coal mines
- Hydrogeochemistry, mineralogy and potential ecological impact of AMD in water and sediments was evaluated respectively
- AMD was highly acidic, and pyrite and silicate weathering were major processes controlling water chemistry.
- Most metals were above recommended guidelines in AMD and most toxic metals cause potential ecological risks in sediments.
- Design of a sustainable AMD treatment process was recommended

Graphical Abstract



Abstract

This study focused on evaluating the hydrogeochemical characteristics of acid mine drainage (AMD), surface water, sediments, and the associated ecological impacts. Samples were collected from seven distinct locations in EMalahleni, South Africa. Physicochemical parameters of water samples were measured in the field, while chemical and mineralogical analysis was done in the laboratory. The results showed that AMD was characterised by low pH (2.69 to 3.30) and high Electrical Conductivity (EC) (1863-3110 $\mu\text{S/cm}$), Fe (20-56 mg/L), Al (51-89 mg/L), Mn (9-21 mg/L) and other toxic metals which were above South African guidelines for wastewater discharge. The hydrogeochemical facie revealed the dominance of the Ca-Mg-SO₄-Cl water type. PHREEQC geochemical modelling showed that alunite was oversaturated at the decant point. At the same time, silicates containing minerals such as K-feldspar, k-mica, and kaolinite were undersaturated. Sediment characterization showed the presence of goethite while at decant points and downstream of the wetland; precipitation of amorphous Fe(oxy)hydroxides and schwetmannite was observed. The geo-accumulation index (I_{geo}) indicated extreme pollution in sediments obtained from the decant point with (Cd, As, and Zn), the stream with (As), and those from downstream of the wetland (Pb). The potential ecological risk index (RI) showed low ecological risk for the presence of toxic metals in the

stream and downstream of the wetland and very high risk at the decant point. Cd was observed to contribute to the highest contamination levels at the decant point. Sediment quality indices showed that AMD was likely to cause an impact on sediments. Acid mine drainage from decant points contaminates sediments, rivers, and dam water due to its low pH and continued pyrite oxidation. Innovative treatment approaches are recommended to alleviate the environmental impacts caused by AMD.

Keywords: Acid mine drainage, sediments, geochemical model, Hydrogeochemistry

3.1 Introduction

The mining of coal exposes iron sulphides to oxygen and water, leading to the generation of acid mine drainage (AMD), which can cause serious environmental impacts by increasing SO_4^{2-} , metals, and acidity to ground and surface water (Chen et al., 2021; McCarthy, 2011). Environmental impacts of AMD from abandoned coal mines have necessitated the understanding of hydrogeochemistry to provide important information to water management authorities (Tran et al., 2020). The hydrogeochemistry of AMD has been reported worldwide (Galhardi and Bonotto, 2016; Neogi et al., 2017; Tran et al., 2020). A study by Neogi et al. (2017) observed that hydrogeochemical facies, Mg-SO_4 and Ca-Mg-CO_3 were controlling the geochemistry of trace and major elements of AMD from North Karanpura coal fields, India, due to sulphide oxidation and carbonate weathering. Studies from the Ruhr coal mining area in Germany confirmed that mine water was weakly acidic to neutral due to water-rock interaction (Tran et al., 2020). Furthermore, AMD impacts the quality of natural water, and changes in hydrogeochemistry due to seasonal variations have been studied in Brazil (Galhard and Bonotto, 2016). Galhard and Bonotto indicated that AMD effluents originated from coal mining activities, causing the dissolution and leaching of chemical species from tailings dumps into the surrounding aquifers. They recommend further studies that help understand AMD's impacts on surface water that humans use for consumption to help alleviate environmental protection.

Several studies have been conducted in South Africa focusing on the hydrogeochemistry of AMD decanting from abandoned coal mines (Gomo and Masemola, 2016; Gomo and Vermeulen, 2014; Kgari et al., 2016). Gomo and Masemola (2016) studied the impacts of AMD and hydrogeochemical processes that control groundwater chemistry in a rehabilitated coal mine in the Karoo Basin within the Vryheid of South Africa in Free State Province. They reported higher Total dissolved solids (TDS) and water hardness due to dolomite dissolution, which prevented the leaching of metals and AMD formation. In another study, Gomo and Vermeulen (2014) investigated the hydrogeochemistry of an underground coal mine flooded with water in Witbank, Mpumalanga province in South Africa, and its ability to contaminate groundwater and observed a Ca-SO_4 hydrogeochemical water type evolving from buffering of the AMD due to calcite and dolomite minerals. A study by Kgari et al. (2016), analyzed water from discharge points from the surface impacted with AMD obtained from abandoned coal mines in the Witbank area. The authors found high concentrations of Cl^- , SO_4^{2-} , Na, Mg, Al,

Ca, and K, indicating leaching of surrounding geology and sulphide minerals. Most of these studies focused on the environmental impact of AMD in the water from the area. However, they neglected to focus on the hydrogeochemical and mineralogical characteristics of impacted sediments and the potential ecological risk of metal in impacted sediments.

Smith et al. (2022) indicated that disused coal mines in eMalahleni pose a significant environmental risk due to the potential discharge of AMD to surface water. Remediation of AMD prevents further pollution of local surface water. Through the South African Government, the Department of Water and Sanitation proposed the option of re-using AMD to improve water availability and recover beneficial industrial products in conformity with the circular economy. The design of a proper and efficient remediation technique needs an appropriate understanding of the hydrogeochemistry of AMD water and the re-use of treated AMD for agricultural purposes and domestic uses (Smith et al., 2022). To understand AMD impacts from decant points to the surface water chemistry and surrounding sediments, AMD from abandoned coal mines, dams, rivers, wetlands, and associated sediments in the study area were collected and analyzed. Objectives of this work were: (1) to identify chemical and mineralogical transformations taking place in sediments impacted by AMD at decant point, dam, and river, (2) to evaluate pollution and ecological risk of toxic metals in sediments, and (3) to evaluate the hydrogeochemical processes of the AMD from the decant points as it flows into recipient dams, rivers, and wetlands

3.2 Materials and Methods

3.2.1 Study Area

This study was performed in eMalahleni in Mpumalanga Province, South Africa. Figure 3.1 shows a map of sampling points where AMD, surface water, and sediments were collected. The climatic condition of the area consists of dry winters, moderate summers, and average annual rainfall between 624 mm and 713 mm from October to April (Ódri et al., 2022). The mining of coal in the Witbank area commenced in 1889 with four mines, namely, Douglas Mine, Brugspruit Adit, Maggies Mine, and Steenkoolspruit (Falconer, 1990). The Coalfields are found on the northern part of the Main Karoo Basin with an estimated area above 568,000 ha, which extends for about 90 km from West to East (Hancox and Götz, 2014). There are basement rocks within the area that includes metamorphic, volcanic, and dolomite rocks of the Neoproterozoic Supergroup and Palaeoproterozoic Group (Hancox and Götz, 2014).

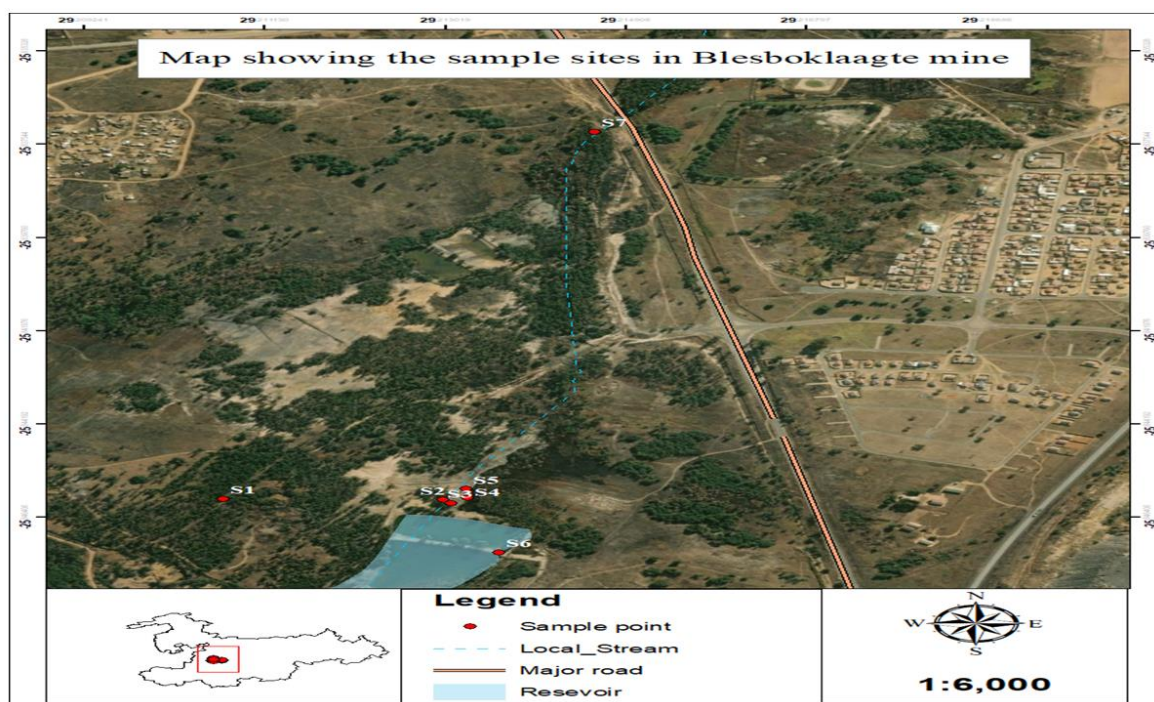


Figure 3. 1: Map showing the location of sampling points in the eMalahleni region of Mpumalanga Province, South Africa.

3.2.2 Sampling and Sample Preparation of Sediments

Sediments were scooped with a stainless-steel pan at an old, abandoned AMD decant point (S1), collection of decant points (S2), outlet from a dam (S3), streams (S4, S5), dams (S6) and downstream of the wetland (S7) (Figure 1). Control sediment samples were collected in the Upper Olifants River, about 125 km from eMalahleni. The samples were put inside zip-lock

plastic bags and ferried to the laboratory in cooler boxes preserved with ice. Upon arrival in the laboratory, sediments were dried in air to remove water before being oven-dried for 8 h at 85°C. Thereafter, sediments were milled using a ball mill to obtain a fine powder (<32 µm). The Hydrochloric acid-nitric acid-hydrofluoric acid (H-N-HF) digestion method was applied to sediments (Gallelo et al., 2022). Briefly, 30 mL of 37 % HCl was mixed with 5 g of the sediments and heated for one hour while covered with a lid. 50 mL of 55 % HNO₃ was added, and the mixture was heated for 15 minutes. A volume of 30 mL of 49 % HF was added and further heated for 15 minutes. Thereafter, the lid was removed, and heating continued to apparent dryness. The sample was cooled, rinsed with 10 mL 2% diluted HNO₃, and heated for about two minutes. The sample was cooled in an open space before filtering with a 0.45µm membrane.

3.2.3 Assessment of Sediments Based on Ecological Risk Index

Sediments were assessed by calculating the potential ecological risk index (RI) proposed by Hakanson (1980). The method consists of contamination factor (C_f^I), toxic response factor (T_r^I) potential ecological risk index of one element (E_r^I) and the sum of RI estimated by eqn 3.1 and 3.2.

$$E_r^I = C_f^I \times T_r^I \quad \text{Equation 3.1}$$

$$RI = \sum_{i=1}^n E_r^I \quad \text{Equation 3.2}$$

Hakanson defined C_f^I as the ratio of the levels of metals in sediments to the background concentration and provided values for T_r^I (T_r^I for Hg, Cd, Pb, As, Cu, Cr, and Zn, Ni is 40, 30, 5, 10, 2, 1, 5, and 5). The classification of E_r^I and RI in evaluating metal pollution in sediments is shown in Table 3.1.

Table 3. 1: E_r^I and RI risk index grades of metal pollution (Rostami et al., 2021).

E_r^I	RI value	Risk index
$E_r^I < 40$	$RI < 150$	Low risk
$40 \leq E_r^I < 80$	$150 < RI < 300$	Moderate risk
$80 \leq E_r^I < 160$	$300 < RI < 600$	Considerate risk
$160 \leq E_r^I < 320$	$RI \geq 600$	High risk
$E_r^I \geq 320$		Very High Risk

3.2.4 Assessment of Sediments Based on Geo-accumulation Index (I_{geo})

The geo-accumulation index (I_{geo}) quantifies certain toxic metal pollution in sediments and soil by comparing it with the toxic metal background value (Marove et al., 2022). Mathematically, I_{geo} is expressed as follows (eqn 3.3) (Muller, 1969). C_n shows concentration of elements, B_n shows background levels. The value 1.5 was applied to minimize changes in the background usually caused by lithogenic effects. Calculated I_{geo} of metals were classified as background values ($I_{geo} \leq 0$), unpolluted ($0 < I_{geo} \leq 1$), unpolluted to moderately polluted ($1 < I_{geo} \leq 2$), moderately polluted ($2 < I_{geo} \leq 3$), moderately to highly polluted ($3 < I_{geo} \leq 4$), highly polluted ($4 < I_{geo} \leq 5$) and excessively polluted ($I_{geo} \geq 6$) (Singovszka et al., 2016).

$$I_{geo} = \log_2 \frac{C_n}{1.5B_n} \quad \text{Equation 3.3}$$

3.2.5 Sampling of AMD and Water

Water and AMD samples were collected from points S1 to S7, as depicted in Figure 3.1. Samples were collected using 1 L high-density polyethylene containers that were thoroughly washed and rinsed using 3 % nitric acid and ultrapure water. Geochemical parameters {pH, Total Dissolved Solids (TDS), Electrical Conductivity (EC), redox potential (Eh), Salinity, and Dissolved oxygen (DO)} were measured at sampling points with an Orion Star A 34 pH multi-meter. The samples for analysis were filtered through a 0.45 μm pore cellulose nitrate membrane. Samples were collected in pairs (1. acidified with 3 M nitric acid for cation analysis, 2. Unacidified for anion analysis). The samples were preserved with ice and ferried to the laboratory for refrigeration at $< 4^\circ\text{C}$ before analysis.

3.2.6 Analysis of Solid and Aqueous Samples

X-ray diffraction (XRD D2 Phaser Brucker AXS, Germany) and Scanning Electron Microscopy equipped with Energy Dispersive Spectroscopy (SEM-EDS Thermo Fisher Nova NanoSEM, Holland) were used to identify minerals and morphology, respectively. Inductively Coupled Plasma Mass Spectrometry (ICP-MS Agilent 7900, USA) and ion chromatography (850 Professional Ion Chromatography, Metrohm, Switzerland) were used for cation and sulphate analysis, respectively. Total acidity was determined using the hot peroxide treatment method (APHA, 1999). Briefly, 50 mL of AMD and water were placed in a 500 mL beaker, and 5 drops of 30 % H₂O₂ were added. The mixture was boiled for 3 minutes and allowed to cool to room temperature. Five drops of Phenolphthalein indicator were added, and the solution was titrated with 0.02N NaOH until the endpoint. The endpoint was observed by the appearance of the permanent pink color. Acidity was calculated and reported as mg/L CaCO₃ (eqn 3.4).

$$\text{Acidity} = \frac{\text{mg}}{\text{L}} \text{CaCO}_3 = \frac{([A \times B] - [C \times B]) \times 50\,000}{\text{ml sample}} \quad \text{Equation 3.4}$$

The hydrogeochemical composition for AMD and acidic water was plotted using the Geochemist WorkBench Student Edition on trilinear piper diagrams. Pearson correlation analysis was carried out using IBM SPSS Statistics Data Editor. Scatter plots were also used to determine the hydrogeochemical characteristics of AMD and acidic. The PHREEQC geochemical model with a WATEQ4 database to calculate saturation indices (SI). If SI = 0, it shows equilibrium; if SI < 0, it shows undersaturation; if SI > 0, there is supersaturation. The cation/anion balance values were ≤ 10 % for sampling points S1-S7.

3.3 Results

3.3.1 Hydrogeochemistry of AMD and Water Samples

3.3.1.1 Chemistry of Water and AMD Samples

Table 3.2 shows the hydrogeochemical characteristics of AMD and impacted water. The pH values ranged from 2.69-3.30, which is typical of AMD. The pH values were below the Target Water Quality Range (TWQR) (Table 3.2) for wastewater discharge into surface water, which was established by the Department of Water, Forestry and Fisheries (DWAF, 2004).

Table 3.2: Physicochemical composition of AMD and impacted water at selected sites (concentration is in mg/L except pH, salinity, EC, and Eh).

Parameter	S ₁	S ₂	S ₃	S ₄	S ₅	S ₆	S ₇	(DWAF, 2004)
pH	3.30	2.76	2.69	2.71	2.74	2.75	2.95	5.5-9.5
Eh (mv)	214	245	250	249	248	247	235	
EC (μS/cm)	1863	2594	2704	2660	2605	2617	3110	1000
TDS	913	1272	1325	1304	1278	1283	1524	
Salinity (psu)	6	1.39	1.45	1.43	1.39	1.40	1.67	
DO	3.65	5.96	8.15	7.73	7.87	7.73	7.67	
Total Acidity	1160	700	750	800	842	930	980	
CaCO ₃								
SO ₄ ²⁻	993	1190	1321	1321	1230	1310	1818	
Cl ⁻	60.3	81.8	81.0	67.0	77.7	62.4	161	0.25
Al	51	66	75	74	72	72	89	
Mn	9	16	12	12	15	12	21	0.1
Fe	56	40	30	31	38	31	20	0.3
Sr	0.33	0.48	0.52	0.51	0.50	0.52	0.74	
Ni	0.5	0.5	0.7	0.7	0.6	0.7	0.8	0.2
Ca	124	136	139	141	144	139	199	
Mg	60	59	71	72	67	72	99	
Zn	1.92	1.80	1.91	1.90	1.93	2.09	2.41	0.1
Na	63	73	79	78	93	76	133	
K	5.1	4.9	6.8	6.7	5.9	6.5	8.9	
Si	49.3	39	55.3	55.4	46.6	55.8	30.6	
As	0.003	0.006	0.007	0.007	0.006	0.006	0.018	0.02
Pb	0.004	0.004	0.012	0.012	0.007	0.015	0.004	0.10
Co	0.0004	0.0005	0.0006	0.0006	0.0006	0.006	0.009	
Cd	0.004	0.004	0.003	0.005	0.004	0.004	0.008	0.005
Se	0.0001	0.001	0.0006	0.0016	0.0006	0.005	0.0001	0.02
Cr	0.008	0.002	0.0017	0.017	0.021	0.012	0.037	0.05
Cu	0.007	0.028	0.013	0.026	0.045	0.018	0.030	0.01
Ba	0.002	0.009	0.03	0.027	0.014	0.024	0.009	

Low pH was due to the oxidation of sulphidic minerals at the decant point, leading to the formation of sulphuric acid. Low pH corroborates with high acidity (700-1160 mg/L CaCO₃). The high acidity of AMD is enhanced by a deficiency of carbonate minerals required to neutralize excess acidity generated during the oxidation and hydrolysis of pyrites (Madzivire

et al., 2011). In the study area, the pH of AMD outflows at S1 (pH= 3.30), decreases as it flows downwards to S2 (pH=2.76), S3 (pH=2.69), S4 (pH=2.71), S5 (pH 2.74) and S6 (pH=2.75), due to dissolution of aluminosilicates minerals which releases significant concentrations of Al, in addition to Fe which can be hydrolyzed to provide additional acidity (Espan˜a et al., 2005).

From Table 3.2, site S1 indicated high concentrations of Al (51 mg/L), which increased as AMD from the decant point mixes with river water (S5, 74 mg/L), dam (S6, 72 mg/L) and downstream of wetland S7 (89 mg/L). High concentrations of Al downstream of the wetland are attributed to the dissolution of silicate minerals, which are associated with coal seams (Bell et al., 2001). High Si content was also observed in all the points with a minimum of 30.6 mg/L to 55.8 mg/L, indicating active weathering of Silicate minerals (Ren et al., 2021).

The levels of Fe ranged from 20 to 56 mg/L, which were above wastewater discharge limits (DWAF, 2004) (Table 3.2). High concentrations of Fe observed at S1 were due to oxidation and hydrolysis of iron pyrites from decant points, which occurs very fast after contact with atmospheric oxygen (Chikanda et al., 2021). Dissolved Fe concentration decreased downstream (31 mg/L at S6 to 20 mg/L at S7). This can be ascribed to hydrolysis and precipitation of Fe-(oxy)hydroxides in the wetland. From Table 3.2, there are increasing concentrations of Co, Cd, As, and Ni with increasing SO_4^{2-} concentrations from the dam to downstream of the wetland. This indicates the progressive dissolution of pyritic ores at decant points. The Eh value at the source S1 was (214 mV) and began to increase as AMD mixed with the dam (250 mV) and river water (247 mV) (Table 3. 2). This could be explained by underground AMD decanting and coming into contact with atmospheric oxygen, consequently decreasing pH and increasing Eh (Hancox and Götz, 2014). The hydrolysis and oxidation of metal hydroxides also explain the increase in Eh. The change in Eh corroborated with dissolved oxygen levels of < 5 mg/L at S1 compared to other sampling points (S2-S7) downstream of the decant point, which had values > 5 mg/L. Table 3.2 shows that EC ranged from 1163-3110 $\mu\text{S}/\text{cm}$, above the DWAF for wastewater disposal (DWAF, 2004). Higher levels of EC and TDS from S1 to S7 indicate oxidation and subsequent dissolution of pyrite, increasing salinity and SO_4^{2-} levels in local surface and underground water (McCarthy, 2011). From Table 3.2, the highest and lowest concentrations of SO_4^{2-} were at S7 (1818 mg/L) and S1 (993 mg/L), respectively. High levels of SO_4^{2-} , which accounted for about 60% of the total AMD compositions, are ascribed to sulfide mineral oxidation (Affandi et al., 2018).

3.3.1.2 Geochemistry and Hydrogeochemical Facies

Figure 3.2 depicts the Piper diagram on which the hydrogeochemical composition of AMD was plotted.

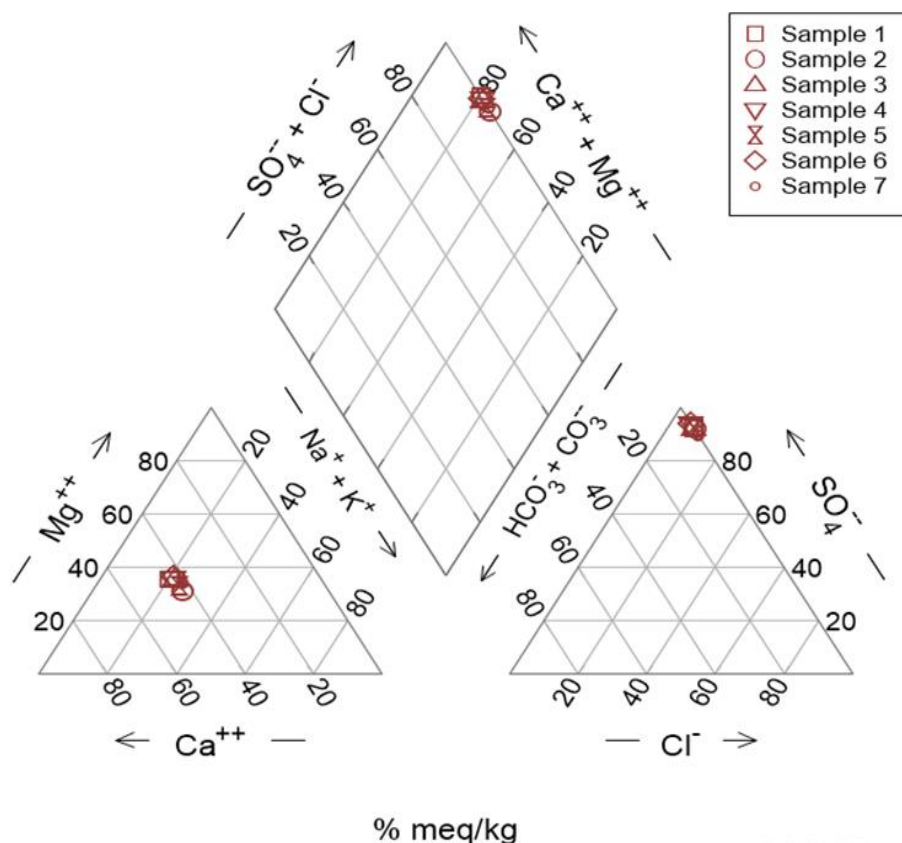


Figure 3. 2: Trilinear Piper diagram of AMD, river, and dam water from sampled area.

From Figure 3.2, the AMD and water samples showed characteristics of Ca-Mg-SO₄-Cl type. The Ca-Mg-SO₄ hydrogeochemical facie is highly influenced by AMD (Equeenuddin et al., 2010). The Ca-Mg-Cl hydrogeochemical facie indicates water-rock interaction within the aquifer (Mohanty et al., 2018). Carbonate rocks, which are present in the local stratigraphic area, could be controlling high concentrations of Ca and Mg; however, due to low pH and high concentration of metals, which depict oxidation and hydrolysis of sulfide minerals, neutralization of AMD becomes difficult (Campaner et al., 2014; Ódri et al., 2022).

The correlation coefficients between geochemical parameters and selected major elements are shown in Table 3.3.

Table 3.3: Correlation matrix of geochemical parameters and selected major elements in acidic mine water

	pH	Ec	TDS	Al	Mn	Fe	Ni	Ca	Mg	Na	K	SO ₄ ²⁻	Cl ⁻	Pb	Si
pH	1														
Ec	-0.6*	1													
TDS	-0.6	1**	1												
Al	-0.5	1/0**	-0.5	1											
Mn	-0.2	0.8*	-0.2	0.8*	1										
Fe	0.61	-1.0**	0.5	-1**	-0.7	1									
Ni	-0.4	0.8*	-0.4	0.9**	0.4	-0.9**	1								
Ca	-0.03	0.8*	-0.1	0.8*	0.9**	-0.8	0.7	1							
Mg	-0.05	0.8*	-0.2	0.9*	0.7	-0.8*	0.9**	1*	1						
Na	-0.07	0.8*	-0.3	0.8*	0.9**	-0.7	0.7	1*	0.92*	1					
K	-0.15	0.8*	-0.3	0.9**	0.6	-0.9*	1*	0.9*	0.98*	0.9*	1				
SO₄²⁻	-0.2	0.9**	-0.3	0.9**	0.8*	-0.9**	0.9*	0.9*	0.97*	0.9**	0.95**	1			
Cl⁻	0.07	0.7	-0.1	0.8	0.9**	-0.6	0.6	1	0.87*	0.9**	0.79*	0.9**	1		
Pb	-0.6	0.1	0.1	0.2	-0.5	-0.3	0.4	-0.3	-0.07	-0.4	0.09	-0.07	-0.5	1	
Si	-0.3	-0.4	-0.2	-0.4	-0.9*	0.2	-0.04	-0.7	-0.48	-0.7	-0.33	-0.54	-0.9*	0.84*	1

The pH negatively correlates with Ca, Mn, Ni, Al, Mg, K, and EC (Table 3.3). This is ascribed to the competition for adsorption sites on clay minerals between metals and H^+ leading to decreased metal removal from AMD (Esmaeili et al., 2019). Sulphate (SO_4^{2-}) shows a strong correlation with EC (0.89), salinity (0.89), Al (0.94), Mn (0.81), K (0.95), Na (0.94), Mg (0.97), Ca (0.89) and Ni (0.86). A positive correlation of SO_4^{2-} with these metals shows the formation of SO_4^{2-} compounds at low pH. Sulphate (SO_4^{2-}) shows a strong negative correlation with Fe (0.9). The relationship between SO_4^{2-} and Fe may be elaborated by understanding the kinetics during AMD formation. Fe^{3+} can be hydrolysed to form $Fe(OH)_3$ and H^+ (eqn 3.5) (Dold, 2017).



This reaction can cause the depletion of Fe without the depletion of SO_4^{2-} (Campaner et al., 2014). A positive correlation of Al with Mn, Ni, Ca, Mg, and Pb shows that these metals possibly come from the same source (Malakooti et al., 2015).

Table 3.4 shows major ions, and the ratio of major ions found in AMD and impacted water. The dominance of $Ca^{2+} + Mg^{2+}$ (8.94-18.8 meq/L) was much greater than that of $Na^+ + K^+$ (2.81-6.01 meq/L) in all the water samples.

Table 3.4: Major ions and the ratio of major ions in AMD sampled from eMalahleni (units are in meq/L except for Na^+/Cl^- with no units).

Sample ID	$Ca^{2+} + Mg^{2+}$	Na^+	Cl^-	K^+	$Na^+ + K^+$	Na^+ / Cl^-
S1	11.2	2.76	1.71	0.13	2.89	1.61
S2	8.94	4.06	2.3	0.125	4.19	1.76
S3	12.9	3.43	2.28	0.174	3.6	1.5
S4	13.03	3.37	1.88	0.171	3.54	1.79
S5	12.87	4.07	2.14	0.151	4.21	1.9
S6	12.91	3.30	1.75	0.167	3.46	1.88
S7	18.18	5.77	4.518	0.228	6.01	1.277

This points to the dissolution of silicate minerals as one process that releases Ca^{2+} and Mg^{2+} (Tran et al., 2020). Table 3.2 shows an increase in Ca, Mg, Na, and K from S6 to S7, indicating the dissolution of abundant aluminosilicate minerals within the wetland. From Table 3.4, the Na^+/Cl^- ratio ranged from 1.50 to 1.9, with an average of 1.67. This points to the dissolution of silicate minerals as the major source of Na^+ because the $Na^+ / Cl^- > 1$ (Zhang et al., 2020). Besides silicate weathering, elements such as Na^+ come from halite dissolution. Figure 3.3 shows a plot of $Na^+ + K^+$ versus Cl^- with R^2 of 0.90, indicating halite dissolution might also contribute to Na^+ and Cl^- sources in AMD.

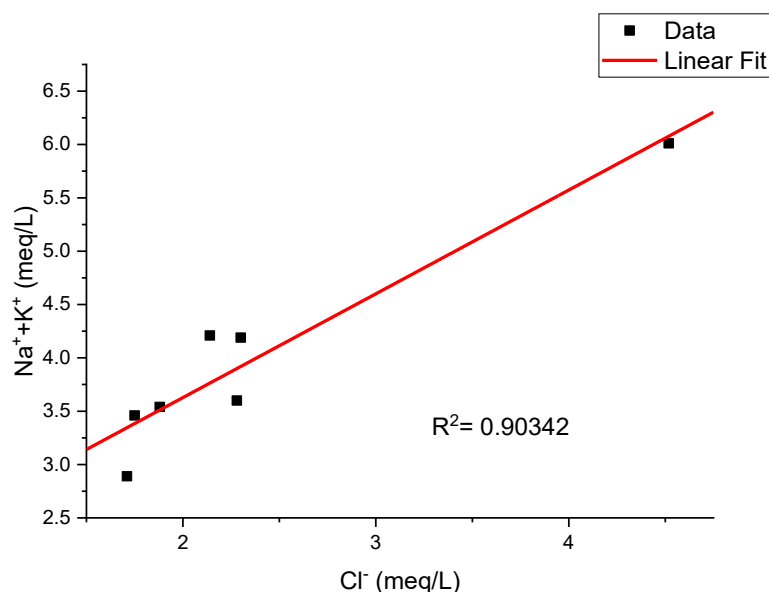


Figure 3. 3: Plot of (a)Na +k vs. Cl of AMD and AMD-impacted water from the sampled area.

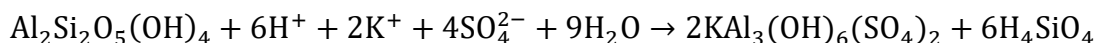
3.3.1.3 Geochemical Modelling

Table 3.5 shows saturation indices of various minerals likely to precipitate from AMD and AMD-impacted water.

Table 3.5: SI values mineral phases for AMD and AMD-impacted water samples.

Sampling point	S1	S2	S3	S4	S5	S6	S7
pH	3.3	2.76	2.69	2.71	2.74	2.75	2.95
Al(OH) ₃	-4.94	-7.55	-6.82	-6.52	-6.44	-6.44	-5.88
Anhydrite (CaSO ₄)	-1.02	-0.58	-0.81	-0.94	-0.95	-0.94	-0.72
Barite (BaSO ₄)	3.01	3.01	3.29	3.26	2.95	3.21	2.82
Schwertmannite (Fe ₈ O ₈)(OH) ₆ SO ₄	-55.79	-66.50	-67.44	-65.09	-64.12	-64.75	-61.06
Fe(OH) ₃ (a)	-7.80	-9.55	-9.54	-9.20	-9.07	-9.16	-8.64
Gibbsite (Al(OH) ₃)	-2.27	-4.86	-4.13	-3.83	-3.75	-3.75	-3.19
Goethite (FeOOH)	-1.91	-3.66	-3.65	-3.23	-3.18	-3.26	-2.75
Gypsum (CaSO ₄ :2H ₂ O)	-0.8	-0.36	-0.59	-0.72	-0.73	-0.72	-0.51
Hausmannite (Mn ₃ O ₄)	-39.97	-44.01	-43.93	-43.08	-42.65	-42.91	-40.43
Pyrolusite (MnO ₂ :H ₂ O)	-25.16	-26.49	-26.56	-26.14	-26.00	-26.09	-13.2
Pyrochroite (Mn(OH) ₂)	-12.78	-14.13	-14.06	-13.84	-13.7	-13.08	-33.47
Manganite (MnOOH)	-16.02	-17.36	-17.36	-17.04	-16.90	-16.99	-16.04
Kaolinite (Al ₂ Si ₂ O ₅ (OH) ₄)	-1.9	-7.25	-6.55	-4.96	-4.96	-4.81	-4.19
Hematite (Fe ₂ O ₃)	-1.82	-5.30	-5.29	-4.63	-4.36	-4.52	-3.49
Alunite (KAl ₃ (SO ₄) ₂ (OH) ₆)	0.19	-4.29	-3.21	-2.60	-2.53	-2.46	-1.01
K-mica (KAl ₃ Si ₃ O ₁₀ (OH) ₂)	-6.19	-13.79	-11.15	-10.16	-10.17	-9.89	-8.65
Ferrihydrite Fe(OH) ₃	-7.74	-9.49	-9.48	-9.15	-9.01	-9.10	-8.58
K-feldspar (KAlSi ₃ O ₈)	-6.19	-9.68	-8.5	-8.1	-8.27	-7.99	-7.88
Melanterite (FeSO ₄ :7H ₂ O)	-3.64	-3.38	-3.91	-3.87	-3.81	-3.87	-4

From Table 3.5, K- feldspar, K-mica, and Kaolinite were undersaturated, which shows their potential dissolution (Moyo et al., 2023; Roisenberg et al., 2015). Alunite was supersaturated at the decant point S1, with a pH value 3.30. In their study, Malakooti et al. (2015) observed supersaturation of alunite after modeling AMD and impacted water in the pH range of 3.64-7 using the PHREEQC geochemical model. Candeias et al. (2014) further supported this observation by suggesting that alunite and quartz are formed at a lower pH than 3.5 in high SO_4^{2-} AMD water (eqn 3.6).



Equation 3.6

The concentrations of Mn ranged from (9- 21) mg/L, which was above the minimum permissible guideline in wastewater discharge of 0.1 mg/L (DWAF, 2004). High levels of Mn may originate from the oxidation of sulphide metals (for example, when Mn is a component of pyrite) and from chemical reactions with adjacent minerals such as carbonates and clays (Tran et al., 2020). The Mn-bearing minerals were all undersaturated in all the sampling points at pH < 3.3 (Table 3. 5). This is mainly due to Mn-bearing minerals starting to precipitate from the solution at pH ≥ 9 . Mn exists as Mn^{2+} in AMD, river, and dam water at pH 0-7 and starts precipitating or forming solids at pH>7. Dzombak and Morel (1991) reported similar findings and attributed them to Mn hydroxides $\text{P}k_1$ value of 9-9.5

3.3.2 Characterization of sediments

Figure 3.4 shows the XRD spectra of the sediments eMalahleni.

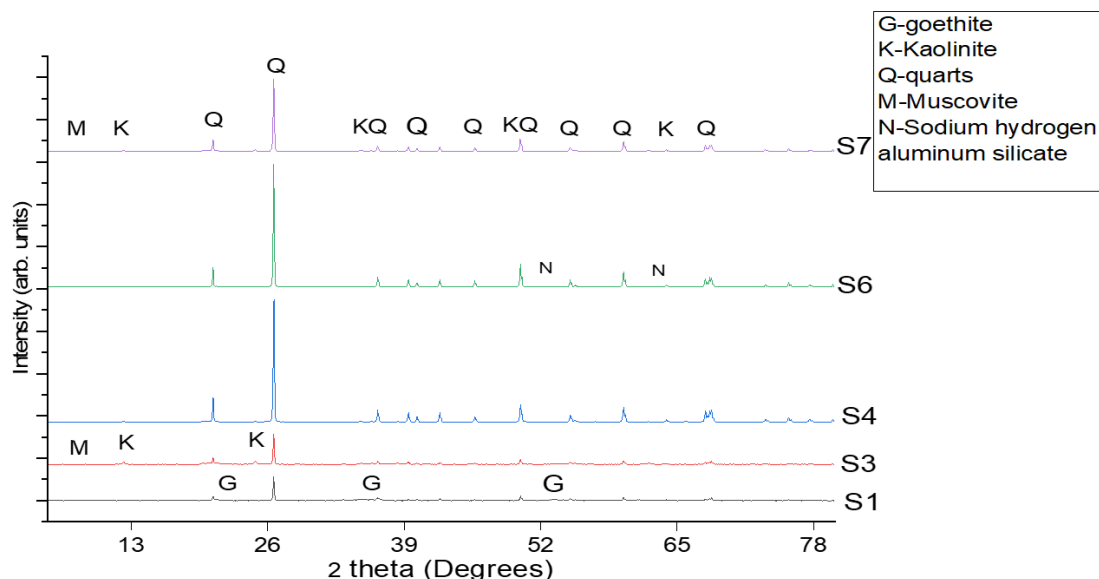


Figure 3. 4: XRD spectra of sediments collected from AMD-impacted area in eMalahleni.

Sample S1 which was collected at the decant point showed the presence of kaolinite, quartz, and goethite mineral phases. Kaolinite and quartz indicate the geological characteristics of sandstone and coal mineralogy (Roisenberg et al., 2015). The presence of goethite is attributed to the precipitation of Fe(oxy) hydroxide minerals from the oxidation of iron sulphide minerals at the decant point. Figure A in the appendices shows pictorial views where samples were collected. Sediments from S1, were yellowish red, which is characteristic of goethite (Figure A). Similar findings were reported by Espan˜a et al. (2005) and Singer et al. (2020) who suggested that goethite is more likely to precipitate at old mine sites than in freshly precipitated colloidal particulates. Sample S3 collected at the dam outlet showed the presence of quartz, kaolinite, and muscovite. The sediments from S3 were coated with a yellow precipitate (Figure A), showing precipitation of Fe-(oxy)hydroxides, which XRD did not detect due to low concentration or amorphous nature. However, in areas of low Fe, such as S4, S6, and S7, XRD identified kaolinite and quartz. The color of sediment materials shows a deficiency of Fe (oxy)hydroxides (Figure A). However, sodium hydrogen aluminium silicate and muscovite peaks were observed at S6 and S7, respectively, indicating the presence of silicate minerals. SEM micrographs of the sediments and EDS spectrum are presented in Figure 3.5.

SEM-EDS analysis was performed for semi-quantitative identification of mineral phases not identified by XRD.

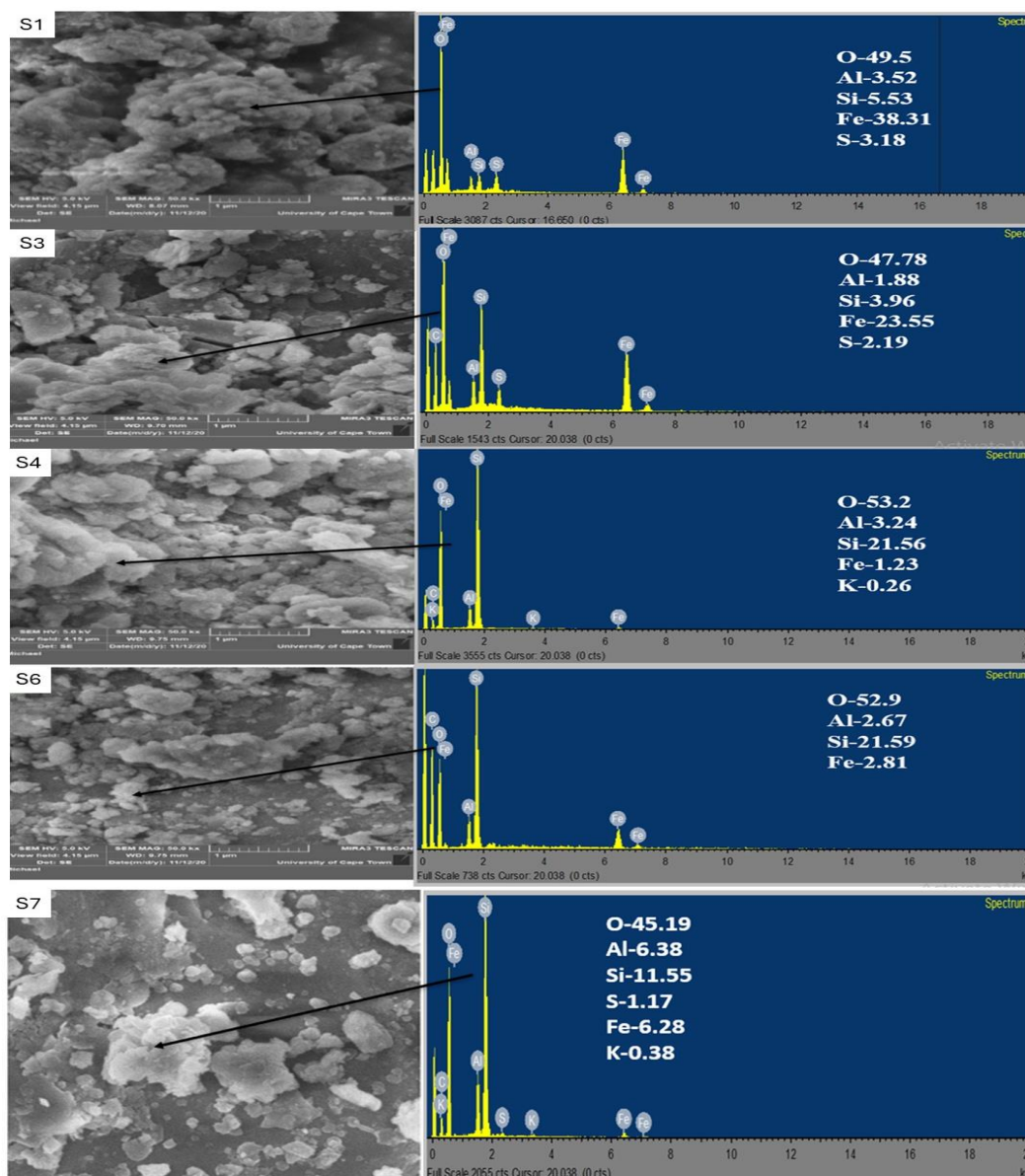


Figure 3. 5: SEM micrographs and corresponding SEM-EDS of AMD-impacted sediments.

SEM images of S1 showed large lamps surrounded by aggregates of small spherical materials enriched with Fe-O-rich mineral phases. The atomic ratio of O/Fe (1.29) was within the stoichiometric mineral goethite range as reported by Miler et al. (2009). This indicates enrichment with Fe-(hydr)oxides, which showed onsite oxidation of pyrite (Moyo et al., 2023). These findings corroborate with XRD, which detected the presence of goethite. The % w/w of 3.18 % (S) observed at S1 is ascribed to SO_4^{2-} being adsorbed on the surface of goethite at acidic pH (Gitari et al., 2010). Although XRD detected quarts of minerals in S1 sediments,

EDS showed an Al/Si ratio of 0.64, indicating a low level of quartz. SEM images of sediments from Site S3 showed sharp blade-like precipitates surrounded by lamps of irregularly shaped particles. EDS showed a O/Fe ratio of 2.02, which conforms with the stoichiometric ratio of goethite. However, XRD did not detect the mineral, mainly due to low levels or its amorphous behavior. The Al/Si ratio of 0.47 was observed by EDS, indicating a low concentration of quartz. Sediments from S4 and S6 showed a heterogeneous material enriched with Si and O. The EDS stoichiometric ratio of Al/Si from S4 and S6 was 0.15 and 0.12, respectively, indicating high levels of quartz. These findings corroborated with XRD, which detected the presence of mineral quarts from the sites. Site S7 shows a heterogeneous material with some small cubic material enriched with Fe, Al, S, and O, suggesting precipitation of Al-Fe (oxy) hydroxy sulphates minerals phases. The Fe/S molar ratio for S7 samples was 5.38, which is within the stoichiometric ratio of schwertmannite as reported by Bigham et al. (1996). The ratio was also within the chemical composition range (Fe/S 4.6-8.3) for schwertmannite, as reported by Bigham and Nordstrom (2000). This data shows hydrolysis and oxidation of iron pyrite within the sediment precipitating schwertmannite (Hammarstrom et al., 2005). The sediments also showed an Al/Si ratio of 0.55, indicating low levels of quarts. Low levels of quarts could be attributed to the dilution of the minerals in the wetland.

3.3.3 Elemental Concentration of Toxic Metals in Sediments

Table 3.6 shows the sediment characteristics of toxic metals.

Table 3. 6: Concentration of toxic metals from sediments (mg/kg).

Site	pH	Cr	Mn	Ni	Cu	Zn	As	Cd	Hg	Pb	Al	Fe
S1	3.30	3.519	3.722	0.823	2.817	51.078	0.677	0.177	0.0067	1.948	677	14330
S4	2.71	1.327	1.624	0.189	0.487	0.512	0.089	0.0014	0.0021	0.648	245	816
S7	2.95	4.635	2.576	0.585	1.955	2.814	0.215	0.020	0.0046	1.24	768	1125
Bg	8.5	4.787	15.45	1.829	1.075	1.836	0.137	0.005	0.0015	0.782	315.2	799

Background concentrations (Bg)- the amounts of selected elements in sediment unaffected by mining activities.

Sediments from S1, S4, and S7 were selected to represent the decant point, river, and downstream of the wetland. Background (Bg) samples were obtained from Mooifontein of the upper Olifants River catchment. From Table 3.6, water where background sediments were collected had pH values >7, indicating AMD had not impacted them. The concentrations of Cr, Mn and Ni ranged between (1.3-4.6) mg/kg, (1.6-3.7) mg/kg, and (0.189-0.823) mg/kg, respectively, which were less than their corresponding background values. The levels of Cu,

Zn, As, Cd, Pb and Al were (1.955 -2.817) mg/kg, (2.814-51.078) mg/kg, (0.089-0.677) mg/kg, (0.02-0.177) mg/kg, (0.648-1.948) mg/kg and 245-768 mg/kg respectively and two of these values were greater than their corresponding background values. The levels of Fe ranged from 816-14330 mg/kg, all of which were greater than the background value. It was observed that most toxic metal concentrations were above the background value, which shows AMD contributed to the leaching of surrounding geology.

3.3.4 Sediment Quality Indices

3.3.4.1 Ecological risk assessment of sediments impacted by AMD

Table 3.7 shows the classification of sediments according to the potential ecological risk index (RI). Samples from site S1 reflected a low ecological risk index for toxic metals except Cd, Hg, and As, with very high risk, high risk, and moderate risk, respectively.

Table 3. 7: E_r^I and RI of toxic metals in sediments.

Sample site	Hg E_r^I	Cd	As	Cu	Cr	Zn	Pb	Ni	R^I
S1	186.8	1587.2	49	13	1.4	27.8	12.45	2	1879.65
Risk grade	High risk	Very high risk	Moderate risk	Low risk	Low risk	Low risk	Low risk	Low risk	Very high risk
S4	56	8.4	6.5	2.25	0.5	0.25	1.45	0.52	75.89
Risk grade	Moderate risk	Low risk	Low risk	Low risk	Low risk	Low risk	Low risk	Low risk	Low risk
S7	120	120	16	9	1.92	1.5	7.951	1.55	277.92
Risk grade	Considerate risk	Considerate risk	Low risk	Low risk	Low risk	Low risk	Low risk	Low risk	Moderate risk

From Table 3.7, the R^I (1879.65) value for S1 indicated very high risk. Very high E_r^I for Cd at S1 shows that the metal is likely to impact soil and water quality due to sulphides from mining and geological activities (Wu et al., 2020). At the sample site S4, E_r^I showed a low risk for all toxic metals except Hg, which was classified as moderate. R^I value indicated low risk; thus, AMD is less likely to cause pollution to sediments at S4. Sediments from S7 show a considerable risk for Hg and Cd, while the other metals reflect a low ecological risk. The RI value was less than 300, which is in the range of moderate risk. Cd metal was observed to contribute large values in evaluating potential ecological risk due to mining activities (Affandi et al., 2018).

3.3.4.2 Geo-accumulation Indices of Selected Metals in Sediments

Table 3.8 shows the Igeo values for toxic metals. It is evident that Cu (S1, S7), Pb (S1, S4) and Al (S1, S4, S7), Fe (S4, S7) and As (S7), Cr(S7), Zn (S7), are in class 1, indicating zero pollution in sediments. The Igeo values for Hg (S1, S7), As (S1, S4) Cr (S1) and Ni (S1), Cu (S4), Cd (S7 and Pb (S7) are in the range of 1 to 2, which indicates contamination to moderate contamination. Mn (S1, S7), Cd (S4), Cr (S4) Zn (S4) and Ni (S7) (S1), Mn (S4), Ni (S4), are in the fourth Igeo class, indicating intermediate to highly polluted. Cd (S1) and Zn (S1) belong to the fifth class of the Igeo, which means the sediments were highly polluted. The extreme enrichment of Pb (S7), As (S1, S4), Cd (S1), and Zn(S1) in sediments is mainly due to long-term exposure of surrounding geology to AMD. This indicated that levels of Cd, As, Zn, and Pb were likely to cause harm to organisms that dwell in sediments.

Table 3. 8: Geo-accumulation indices of toxic metals in Blesboklaagte sediment in Mpumalanga province, South Africa.

Sample site	Hg	Cd	As	Cu	Cr	Zn	Pb	Ni	Al	Fe	Mn
S1	1.57	4.73	1.7	0.81	-1.03	4.2	-0.49	-1.7	0.52	3.76	-2.6
Sediment quality	Unpolluted-Moderately polluted	Highly polluted	Unpolluted to moderately polluted	unpolluted	Unpolluted to moderately polluted	Highly polluted	unpolluted	Unpolluted to moderately polluted	unpolluted	Moderately to highly polluted	Moderately polluted
S4	-0.1	-2.47	-1.2	-1.7	-2.47	-2.3	-0.21	-3.8	-0.95	-0.56	-3.8
Sediment quality	unpolluted	moderately polluted	Unpolluted to moderately polluted	Unpolluted to moderately polluted	Moderately polluted	Moderately polluted	unpolluted	Moderately to highly polluted	unpolluted	unpolluted	Moderately to highly polluted
S7	1.03	1.433	0.06	-0.26	-0.62	0.03	-1.15	-2.3	0.66	-0.09	-2.3
Sediment quality	Unpolluted to moderately polluted	Unpolluted to moderately polluted	unpolluted	unpolluted	unpolluted	unpolluted	Unpolluted to moderately polluted	Moderately polluted	unpolluted	unpolluted	Moderately polluted

3.4 Discussions

The discussions were based on the general chemical changes that occurred as AMD from the decant point mixes with dam and stream water. The AMD at the decant point was characterized by pH of 3.3, Eh (214 mV), EC (1863 mS/cm) with dominance of Fe, SO_4^{2-} , Al, Mn, Mg, Na, K, Si and Cl^- . However, the concentration of Fe observed at S1 was highest as compared to other sampling points, indicating oxidation and hydrolysis of Fe as AMD get in contact with atmospheric oxygen. The presence of Na and K showed dissolution of aluminosilicate minerals as depicted by XRD which showed the presence of kaolinite and muscovite. The chemical analysis of sediments from S1 showed dominance of Fe and Al which were reddish brown, suggesting precipitation of Fe-Al rich mineral phases. Significant amounts of Zn, Cu, Pb, Al and Cr were observed in sediments suggesting presence of their mineral phases or their coprecipitation or adsorption on Fe-hydroxy oxides minerals. These results were supported by SEM-EDS and XRD which suggested the precipitation of goethite at the decant point. The presence of Al minerals at the decant point agreed with SI values which showed supersaturation with respect to alunite.

As AMD mixes with water and AMD from other decant points at S2, there was a drop in pH from 3.30 to 2.76. The elements Na, Ca, Cl^- and SO_4^{2-} increases in aqueous solution, indicating dissolution of aluminosilicate minerals, sulphate and chloride bearing minerals. The dissolution of aluminosilicate minerals was supported by undersaturation of K-mica and K-feldspar. XRD detected Al bearing minerals as silicates (Kaolinite and Muscovites) and not as SO_4^{2-} . The absence of Aluminum sulphate minerals in the area could be due to its amorphous nature or conservative behavior. Waters and Webster-Brown (2013) indicated that Al has a conservative behavior in streams impacted by AMD at $\text{pH} < 3.8$ due to formation of Al-sulphate complexes such as AlSO_4^- . The levels of Fe in aqueous solution decreases, suggesting precipitation of Fe-bearing minerals. This was supported by the colour of the sediments which were orange, indicating possible precipitation of Fe^{3+} hydroxides.

The sample site S6 was a dam in which AMD from the decant points was also flowing into. As AMD was flowing from the decant point into the dam, there was a decrease in pH from 3.30 to 2.75 indicating oxidation and hydrolysis of Fe^{2+} to Fe^{3+} upon exposure to oxygen. The elements, Ca, Mg, Al, Mn, K, SO_4^{2-} and Cl^- increases in as dam water mixes with AMD indicating contamination from AMD.

There was a slight decrease in pH from 2.76 to 2.69 at site S3 which was an outlet from the dam. Decrease in pH is attributed to continuous oxidation of Fe^{2+} to Fe^{3+} or oxidation of minor sulphides present in the stream and dam. The precipitation of Fe^{3+} decreases pH due to the release of H^+ . The precipitation of Fe^{3+} bearing minerals is further evidenced by the presence of goethite in the sediments as suggested by SEM-EDS. In addition to that the precipitates were coated by reddish brown precipitates. The elements, Al, Mn, Ca, Mg, Zn, Na, K, Si and SO_4^{2-} remained almost unchanged as compared to dam water suggesting slight change in chemistry as impacted water decant from the dam.

The sample site S4 was a point where impacted water from the dam was mixing with stream water. A slight increase in pH and EC was observed from S3 to S4. Most elements remained almost unchanged except Al and K which shows slight decrease as compared to S3. However, the concentrations of these elements were much higher than the decant point. Chemical analysis of sediments showed a decrease in Al, Fe, Zn, Cr and Mn in comparison with decant point, indicating dissolution of their respective minerals at acidic pH.

The sample site S5 in the stream was a point where stream water mixes with impacted water from S4 and S2. There was a slight increase in pH and a slight decrease in EC which was ascribed to dilution of AMD with stream water. The concentration of elements remained almost the same except Fe which slightly increases indicating continued oxidation and hydrolysis of Fe^{2+} .

The highest concentration of SO_4^{2-} , Cl^- and metals such as Al, Mn, Sr, Ca, Mg and Na were higher downstream of the wetland than upstream. This agreed with high EC (3110 mS/cm) and TDS (1524 mg/L) which were observed downstream at the point, indicating water had undergone different hydrogeochemical evolution in the wetland as it mixes with AMD from decant points. Garlhard et al. (2016) showed that an increase in concentration at low pH values reflects sulphide oxidation and small amounts of aluminosilicate minerals which to some extent consumes acidity. This was further elaborated by SEM-EDS and XRD analysis of sediments from S7 which showed presence of schwertmannite and aluminosilicate minerals. The results corroborates with Chikanda et al. (2021) during the evaluation of iron colloids' behaviour at near-neutral pH. Furthermore, the saturation indices showed undersaturation of aluminosilicate minerals, K-feldspar and K-mica, indicating their potential dissolution. This corroborates with the negative correlation of pH and Si which indicates leaching of aquifer rocks at acidic pH.

3.5 Conclusion

Hydrogeochemistry of AMD-impacted water and sediments was successfully evaluated. pH was observed to slightly decrease as AMD flows from decant point and mixes with dam and stream water. The decrease in pH was due to hydrolysis and precipitation of Fe-hydroxides and other associated metal sulphides. The concentration of Fe was decreasing as AMD flows into river, dam and downstream of wetland. Elemental analysis of sediments showed high levels of Fe at decant point which tend to decrease as AMD flows into the river and slightly increase downstream of wetland. The chemical species such as SO_4^{2-} , Cl^- , Al, Mn, Sr, Ca, Mg and Na were observed to decrease as AMD from decant point and mixes with dam and river water. The highest increase of the chemical species in impacted water was observed downstream of the wetland than upstream, mainly due to sulphide oxidation and some silicate weathering. The hydrogeochemical facie revealed that the Ca-Mg- SO_4 -Cl was controlling water type. PHREEQC geochemical modelling showed oversaturation of alunite, indicating that Aluminium sulphates minerals were controlling concentration of Al at decant point. XRD and SEM-EDS detected the presence of goethite mainly at the decant point and schwertmannite downstream of the wetland. AMD was observed to contribute to toxic metal pollution in sediments, with Cd having the highest toxic levels at the decant point. Sulphide oxidation and silicate weathering were the major mechanisms controlling the hydrogeochemistry of AMD and impacted water. It was found that AMD and impacted water were highly acidic and contained high amounts of toxic metal and sulphate above South African guidelines for wastewater discharge

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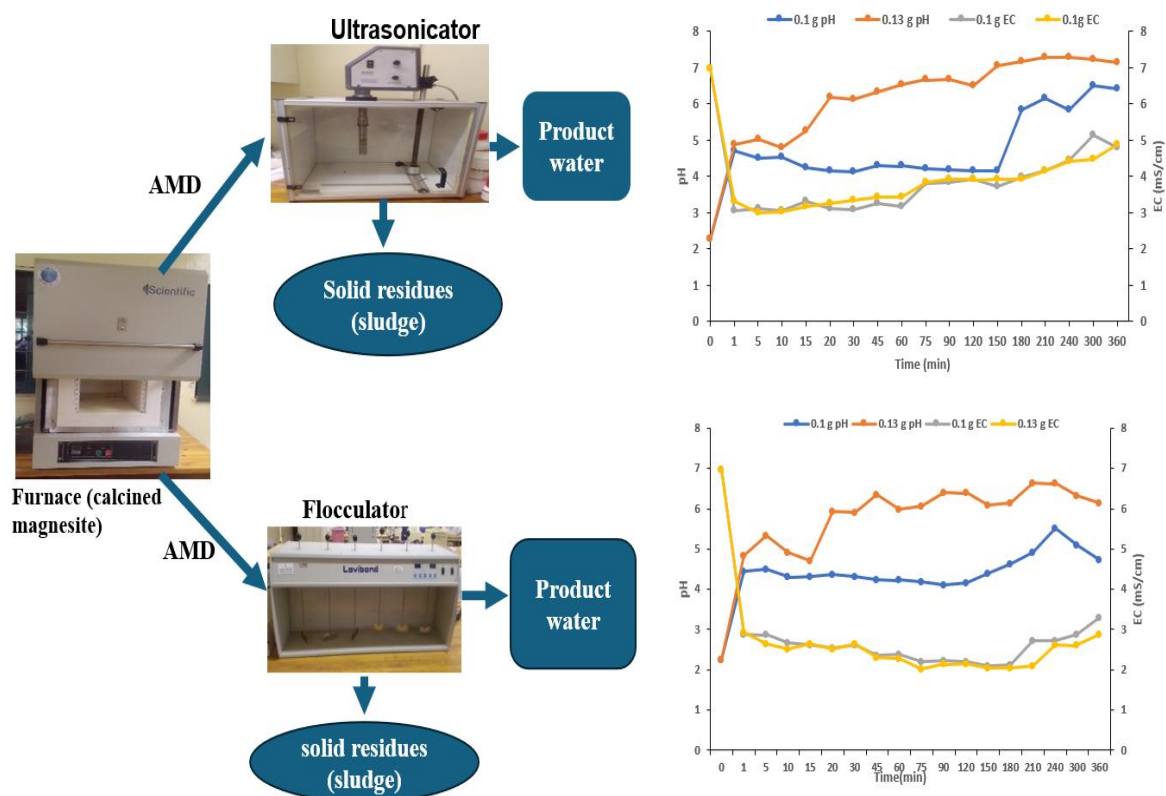
Chapter 4

Treatment of acid mine drainage using calcined magnesite: Comparison of effectiveness of sonication and flocculation of Reaction Mixtures.

Highlights

- Acid mine drainage (AMD) is of environmental concern, research is focusing on designing new methods.
- Effectiveness of sonication and flocculation in treatment of AMD with calcined magnesite was compared varying dosage and contact time.
- Sonication was more effective than flocculation because sonication raised pH faster and enhance precipitation of more minerals than flocculation.
- The chemicals species Ca, Mg and SO_4^{2-} were above the recommended guidelines in product water in both methods

Graphical Abstract



Abstract

This chapter compares the effectiveness of sonication and flocculation in the treatment of acid mine drainage (AMD) with calcined magnesite. This was accomplished by evaluating calcination temperature, contact time and dosage. The efficiency of sonication and flocculation was examined by lowering dosages to 1.0 g/100 mL and 1.3 g/100 mL and evaluate major contaminants removal over time. PHREEQC geochemical modelling with WATEQF database were used for geochemical modelling of product water at selected contact time. X ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Scanning Electron microscopy equipped with energy dispersive spectroscopy (SEM-EDS and X ray fluorescence spectroscopy (XRF) were used for characterization of solid residues, magnesite and calcined magnesite. Simulated acid mine drainage (AMD) containing Fe, Ca, Al, Mn, Mg, Zn and SO_4^{2-} at concentrations of 56.0, 199.0 89.0, 21.0 ,50, 2 and 1808 mg/L respectively was formulated using worst case sinario of species from eMalahleni. The optimum temperature for calcinating magnesite was found to be 800 °C. SEM-EDS, XRF, FTIR and XRD showed magnesite calcined at 800 °C to be mainly MgO (periclase). An optimum pH of 9.58 was achieved within 30 minutes using 0.4 g/ 100 mL S/L ratio with sonication while an optimum pH of 9.38 was achieved after 60 minutes with flocculation. At these optimum conditions for both sonication

and flocculation, removal of Fe, Al and Mn was $> 90\%$ while the removal of SO_4^{2-} was $\approx 60\%$. The dosages of 0.1 g/100 mL and 0.13 g/100 mL showed oversaturation with respect to gibbsite, goethite, ferrihydrite and amorphous iron hydroxide at specific contact times. The effectiveness of sonication over flocculation was observed at contact time 360 minutes. The two tailed p values for percentage removal of chemical species and pH were extremely significant, indicating superiority of sonication over flocculation. The concentrations of Ca, Mg and SO_4^{2-} increased significantly at contact time of 360 minutes in product water when using sonication than flocculation, indicating extensive forces produced by ultrasonication over time. The EDS elemental analysis at contact time 60 minutes and 0.1 g/100 mL showed %w/w of Al (5.83) and Fe (4.6) when using flocculation and Al (8.3) and Fe (5.48) when using sonication. Thus, sonication is more effective in enhancing precipitation of minerals than flocculation. Sonication was observed to raise pH faster and precipitate more minerals compared to flocculation. However, the levels of Fe and Al meet the guidelines for irrigation water at $\text{pH} < 4$ and $\text{pH} < 7$ respectively, while the levels of Mn, Ca, Mg and SO_4^{2-} were above the guidelines when using both methods. Based on these findings, sonication was observed to be more effective in the neutralization of AMD with calcined magnesite than flocculation.

Keywords: Acid mine drainage; Calcined magnesite; flocculation; neutralization; sonication.

4.1 Introduction

The economy of South Africa depends on the mining of gold and coal. However, it leaves behind tailings and voids, which expose sulphide minerals to oxygen and water, causing the formation of acid mine drainage (AMD) (Kefeni and Mamba, 2020; Skousen et al., 2016). Acid mine drainage can dissolve the surrounding geology, increasing the concentration of toxic metals like Cu, Hg, Co, Zn, Pb, Ni, Co, and As in uncontaminated water resources (Menzel et al., 2021). High toxic metal and sulphate content in AMD can render water sources unfit for domestic, irrigation, and livestock uses (Gitari et al., 2008). Impacts of AMD were reported in the Witwatersrand basin in Gauteng and Middleburg Mpumalanga, where gold and coal have been mined. In the Witwatersrand Western basin, AMD was found to have high SO_4^{2-} concentration of ≈ 3500 mg/L, $\text{pH} < 3$, high levels of toxic metals (McCarthy, 2011). In the Witbank area, a high SO_4^{2-} concentration above 200 mg/L was reported in Witbank Dam due to AMD from coal mines (McCarthy, 2011).

Due to the environmental impacts of AMD, the government has encouraged the remediation of river systems, receptor dams, and wetlands, which are impacted by AMD (DWA, 2013). The remediation technology should be situational-based, economical, clean, and sustainable (DWA, 2013). The treatment methods are classified into passive and active (Chen et al., 2021). Active treatment methods are precipitation, biological sulphate removal, ferrite processes, flocculation, membrane technology, filtration, and ion exchange (Taylor et al., 2005; Wang et al., 2021). Passive techniques include limestone, artificial wetlands, and bioremediation (Skousen et al., 2019; Taylor et al., 2005). Passive methods have been used because they are cheap, require less labor once constructed, require less material loading, and are easy to maintain. In contrast, active methods are mostly used because they can treat large amounts of AMD, need a shorter time to achieve the required target, and occupy a small land area (Akciil and Koldas, 2006; Hallberg and Johnson, 2005). Furthermore, different mechanisms such as adsorption, chelation, oxidation-reduction, and neutralization/precipitation are processes behind these methods (Taylor et al., 2005).

Precipitation is the most used active method in neutralizing AMD (Mogashane et al., 2023). However, precipitation/neutralization requires chemicals to raise the pH of AMD and form metals, and some of these chemicals are limited by the generation of excessive sludge rich in metals (Wei et al., 2005). For this reason, AMD can be considered a source of valuable

resources (Naidu et al., 2019). Research is moving from conventional treatment, which involves treating and discharging waste, to sustainability, which deals with recovering valuable products from AMD. Thus, there is a need to look for alternative ways to address the sustainability treatment of AMD to eliminate excessive sludge produced by recovering beneficial products. Recently, cavitation has gained attention for application in AMD treatment due to its ability to increase the rate of chemical reaction by increasing the kinetic energy of reacting particles compared to normal agitation (Kalombe et al., 2020). Cavitation causes solid particles' fragmentation, resulting in solid particles' dissolution into liquid particles during solid-liquid reactions (Hagenson and Doraiswamy, 1998; Leong et al., 2011).

Madzivire et al. (2013) applied the cavitation technique to remediate mine water with coal fly ash. They used a jet loop reactor to generate hydrodynamic cavities during their study. They observed that the pH increased from 8 to 11 within 15 minutes because of rapid mixing inside the reactor due to cavitation. They further indicated that cavitation facilitated the precipitation of metals and the removal of SO_4^{2-} from the solution. A preliminary work done by Novela et al. (2019) applied ultrasound to generate cavities during neutralization of AMD with magnesite and compared the efficiency with the agitation method. Their results showed that the reaction of 1g of magnesite with 100 mL of AMD for 60 minutes with agitation increased pH from 2-9.4 and achieved >50 % removal efficiency for SO_4^{2-} while the use of cavitation on the same AMD magnesite mixtures for the same time interval increased pH from 2-8.6 and achieved ≥ 90 % SO_4^{2-} removal.

Masindi et al. (2016) used locally available magnesite as an AMD neutralizing agent. Their results showed that magnesite has the potential to raise pH from 2 up to 10 after agitating for 60 minutes using 1 g/100 mL dosage. They further showed a decrease in the amount of Fe, Mn, Zn, Al, Ca and SO_4^{2-} in treated water indicating the formation of new mineral phases. Magnesite, being a form of carbonate, is less soluble during AMD treatment, magnesite armoring can occur due to reaction of MgCO_3 with Fe^{3+} forming a layer of $\text{Fe}_2(\text{CO}_3)_3$ on the surface of magnesite preventing further dissolution (Letjiane et al., 2019). Calcinating magnesite may disrupt armoring, leading to increased alkalinity due to the formation of MgO. Magnesium oxide (MgO) can be used as an alkaline material to neutralize AMD by raising pH and precipitating metals as hydroxides (Johnson and Hallberg, 2005). The rise in pH is attributed to the dissolution of MgO, releasing OH^- ions (Eqn. 4.1). A study by Sulaiman et al.

(2018) showed that pH was rising from 2.48 to 7 using chemical grade MgO as a neutralizing agent with a contact time of 10 minutes.



This study is aiming to generating cavitations using ultrasonication in treatment of AMD with calcined magnesite while comparing the effectiveness of this technology with flocculation. The null hypothesis of comparing the two methods suggest that sonication is more effective than flocculation in AMD treatment. To the best of our knowledge, no work has been done in treatment of AMD with calcined magnesite and sonication. The objectives of the study were: 1) Determination of the optimum temperature of calcination of magnesite, 2) evaluation of physicochemical parameters of calcined magnesite, 3) to compare the effectiveness of cavitation and flocculation in the treatment of AMD using calcined magnesite 4) to evaluate the pollutant removal capacity of calcined magnesite.

4.2 Materials and Methods

4.2.1 Materials

The analytical grade chemicals for preparing synthetic AMD were purchased from Rochelle Chemicals. These chemicals include $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, and $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ and concentrated H_2SO_4 . The mineral magnesite was obtained from the Folovhodwe magnesite mine in the province of Limpopo in South Africa. The collected magnesite was milled with a Ball milling machine (Retsch RS 200 vibratory Mill) to a particle size of 32 μm and kept in Zip-Lock plastic bags.

4.2.2 Preparation of Synthetic AMD

During preparation of synthetic AMD, 0.220 g $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, 1.097 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 0.0645 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 0.495 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.7312 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, and 0.00883 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$ were dissolved in 1L of Milli-Q water (18.2 $\text{M}\Omega$ resistance) containing 0.5 mL of concentrated H_2SO_4 . The resulting solution contained Fe^{3+} (56 mg/L), Ca^{2+} (199 mg/L), Al^{3+} (89 mg/L), Mn^{2+} (21 mg/L), Mg^{2+} (50 mg/L), Zn^{2+} (2 mg/L), and SO_4^{2-} (1808 mg/L). The synthetic AMD was prepared using worst case scenario of concentrations of AMD recorded in samples collected from Mpumalanga province in the Blesboklaagte, Transvaal, and Delagoa abandoned coal mines.

4.2.3 Optimization of Calcination Temperature

The temperature of calcined magnesite was optimized by placing 10 g of magnesite in 5 crucibles and then calcined at temperatures of 200, 400, 600, 800, and 1000 $^{\circ}\text{C}$ in a muffle furnace (United Scientific, model 930 DESC 30 LITER, South Africa). The optimum temperature was evaluated by mixing 1 g of calcined magnesite with 100 mL of AMD for 30 minutes to observe the temperature with higher AMD treatment during neutralization and inorganic contaminant removal. An ultrasound processor (Hielscher UP 400 S, Germany) was used for cavitation/sonication, and Lovibond flocculation (Floc Tester, Dortmund, Germany) was used for flocculation. Sonication was performed at 0.5 cycle frequency and 60 % amplitude, while flocculation was carried out at 250 rpm. After the experiment, the final pH, Electrical Conductivity (EC), and Total Dissolved Solids (TDS) were determined with a pH/Mv/Cond/Temp multi-meter probe (Accsen, PRC). The 0.45 μm pore size nitrate cellulose membrane filter was used to filter the mixture. Product water was divided into two parts for cation and anions analysis. Three (3) drops of HNO_3 were used to preserve product water for

cation analysis to prevent the aging of metals. Both product water samples were then refrigerated below 4 °C before analysis.

4.2.4 Characterization of Calcined Magnesite and Other Solid Samples

All samples of calcined magnesite prepared at different temperatures were characterized for crystallinity using X-ray Diffraction (XRD D2 Phaser Brucker, Germany), Surface morphology using the Scanning Electron Microscopy equipped with energy dispersive spectrometry (SEM-EDS Thermo Fisher Nova NanoSEM, Holland), elemental composition using handheld X-ray Fluorescence (XRF Brucker S1 Titan, Germany) and functional groups were determined using Fourier Transform Infrared Spectrometer equipped with Platinum Attenuated Total Reflection Spectrometry (FTIR-ATR Brucker, Germany).

4.2.5 AMD Treatment Using Sonication and Flocculation

The experiments were conducted at varying contact times and dosages to compare the efficiency of sonication and flocculation in the AMD treatment using calcined magnesite. Magnesite calcined at 800°C was used during batch reactions.

4.2.5.1 Variation of Contact Time

To compare the treatment of AMD and removal of inorganic pollutants as a function of contact time, 100 mL of AMD was pipetted into 500 mL High density polyethylene beakers (HDPE) beakers. This was followed by adding 1 g of calcined magnesite to make up an S/L ratio of 1 g/ 100 mL. After that, mixtures were processed for 1, 5, 10, 15, 30, 60, 90, 120, and 180 minutes using an ultrasound sonicator and flocculator. The final pH, Electrical Conductivity (EC), and Total Dissolved Solids (TDS) were determined, and the solution was filtered and preserved for cation and anion analysis. The sludge was dried overnight and analysed for mineralogy, elemental and morphology.

4.2.5.2 Variation of Calcined Magnesite Dosage

To compare the treatment of AMD and removal of inorganic contaminants by ultrasonication and flocculation, as a function of dosage, the masses of 0.1, 0.2, 0.4, 0.6, 0.8, 1.0, and 1.2 g of calcined magnesite, were added into 100 mL solution of AMD in 500 mL HDPE plastic beakers. For sonication, mixtures were treated for 30 minutes, and flocculation mixtures were

treated for 60 minutes. After the experiment, a pH/Mv/Cond/Temp multi-meter probe (Accsen, PRC) was used to measure the final TDS, EC, and pH. The mixture was then filtered and stored for cation and anion analysis. The sludge was dried in an oven for 24 hours and analysed for elemental, morphology and mineralogy.

4.2.6 Variation of Dosage and Contact Time

Batch experiments were conducted by varying dosage and time to determine buffering regions. Solutions containing calcined magnesite: AMD ratios of 0.1 g:100 mL and 0.13 g:100 mL were sonicated and flocculated at varying contact times of 1-360 minutes. The product water's pH, EC, and TDS were determined, and the mixture was filtered and preserved for anion and cation analysis. The resultant sludge was dried at 60°C for 8 hours in an oven and then analysed for mineralogical, morphological, and elemental composition changes.

4.2.7 Analysis of Metals and Sulphate

The removal of metals and sulphates from AMD was evaluated by comparing the efficiency of ultrasonication/cavitation and flocculation. Inductively Coupled Plasma Mass Spectroscopy (ICP-MS Agilent 7900, USA) and Ion Chromatography (IC) (Metrohm 850 professional, Switzerland) were used for analysis cations and Sulphates, respectively.

4.2.8 Percentage (%) removal

The % removal of cations and SO_4^{2-} from AMD was calculated using eqn 4.2.

$$(\%) \text{removal} = \left(\frac{C_n - C_i}{C_n} \right) \times 100 \quad \text{Equation 4.2}$$

Where C_n = initial concentration, C_i = equilibrium ion concentration.

4.2.9 Geochemical Model and Statistical Analysis

To predict the mineral phases and species that can be precipitated during the reaction, the PHREEQC geochemical model with the WATEQ4F database was used in determining saturation indices (SI) and speciation of mineral phases that were likely to precipitate (Parkhurst and Appelo, 2013). If $\text{SI}=0$, it shows equilibrium between solution and minerals; if $\text{SI} < 0$, there is sub-saturation; if $\text{SI} > 0$, there is supersaturation. To further evaluate the method

which performed better, the mean of the pH values of both flocculation and sonication was compared with GraphPad statistical software.

4.3 Results and Discussions

4.3.1 Characterization of Raw and Calcined Magnesite

4.3.1.1 Elemental Composition of raw and calcined magnesite

The elemental composition of raw and calcined magnesite is shown in Table 4.1 as determined by XRF. Table 4.1 shows that raw magnesite mainly consisted of MgO (61.7 %) as the major oxide with traces of SiO₂ (1.81 %). Calcination of magnesite at 200 °C and 400 °C increased the MgO content to 62.98 % and 63.94 %, respectively. There is a steep increase in MgO content from 63.541 % to 78.748 % with calcination temperatures of 400 °C to 600 °C, respectively. The MgO content increased with increasing calcination temperature up to 85.67 % at 800 °C. This indicates the total decomposition of MgCO₃ to MgO with the complete release of CO₂ (Magagane et al., 2019). Minor and trace elements were present in calcined magnesite.

Table 4. 1: Elemental compositions of raw (RM) and calcined magnesite (Temperature units are in °C).

Element	Raw magnesite	200	400	600	800	1000
MgO	61.76	62.98	63.54	78.75	85.67	80.97
Al₂O₃	0.16	0.16	0.15	0.11	0.15	0.11
SiO₂	1.81	1.95	1.94	2.10	2.25	2.01
CaO	0.81	0.80	0.80	0.87	0.99	0.91
Fe	0.07	0.07	0.07	0.06	0.12	0.08
Ti	0.03	0.03	0.03	0.01	0.02	0.02
Cr	0.04	0.04	0.04	0.04	0.02	0.035
Sr	0.003	0.003	0.004	0.004	0.005	0.004
Ni	0.004	0.006	0.006	0.01	0.02	0.006
Mn	0.008	0.006	0.007	0.008	0.013	0.01

4.3.1.2 XRD Analysis of Magnesite

Figure 4.1 shows XRD patterns of raw and calcined magnesite. XRD patterns for RM, magnesite calcined at 400 and 600 °C show phases of mainly magnesite (MgCO₃) at 32.5, 43- and 53.9-degrees theta. There was a complete change in mineralogy with magnesite calcined at 800 °C, showing the absence of MgCO₃ peaks and the formation of periclase (MgO) peaks at 42.912 and 62.1- degree theta. The increase in MgO observed with increased calcination temperature is due to the decomposition of MgCO₃. (Huang et al., 2020) reported similar results, which showed an increase in MgO content with an increase in calcination temperature of magnesite indicating complete removal of CO₂.

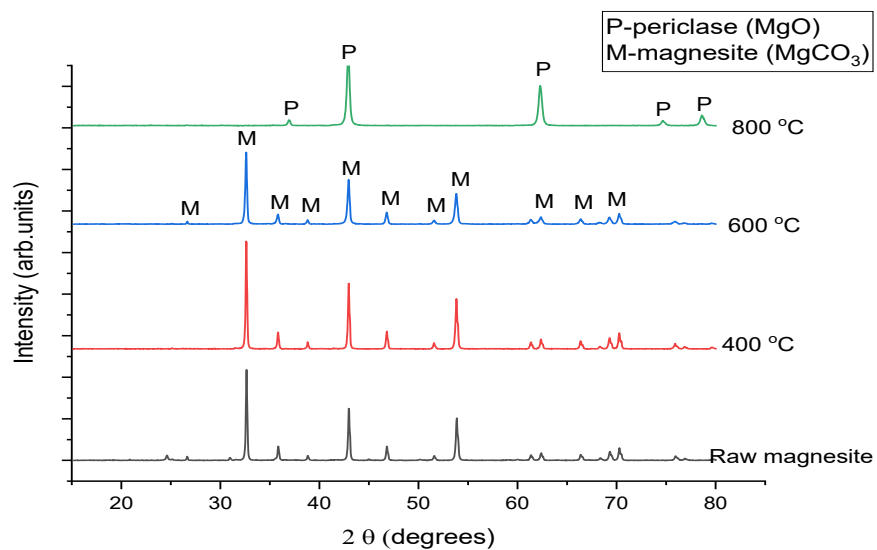


Figure 4. 1: XRD patterns of calcined and raw magnesite.

4.3.1.3 SEM image and EDS analysis of calcined and raw magnesite

Figure 4.2 shows SEM-EDS of raw and calcined magnesite.

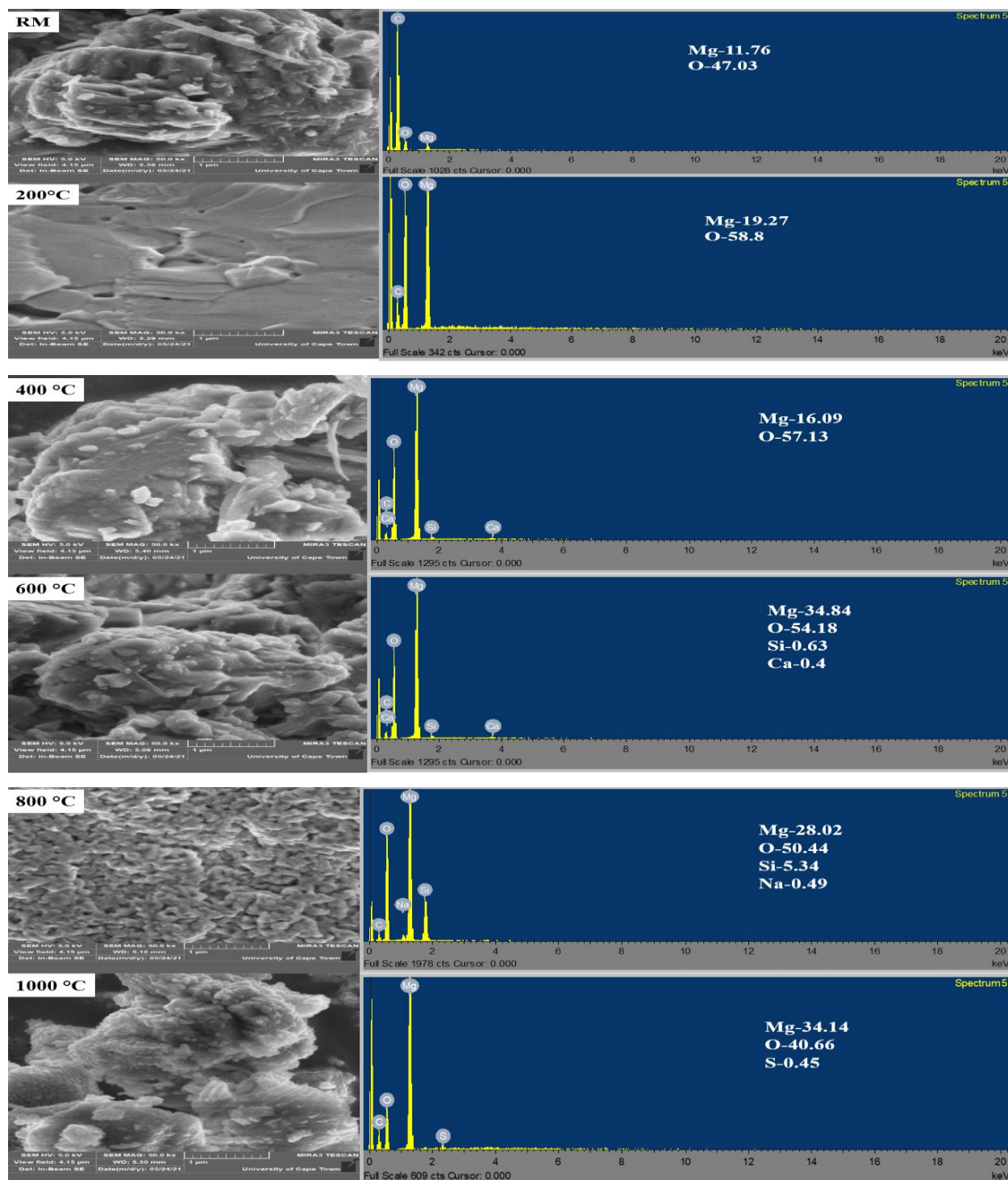


Figure 4. 2: SEM-EDS of raw and calcined magnesite

The SEM images in figure 4.2 shows that raw magnesite (RM) is a heterogeneous material enriched with Mg (11.76 %) and O (47.03 %). As temperature increases to 200 °C, the morphology changes to a smooth-like structure with some small holes. At 400 °C and 600 °C,

the morphology changes to irregular sheets like those observed in RM. Magnesite calcined at 800 °C shows homogeneous material with a cloud-like material with small holes; however, as temperature increased to 1000 °C, particles were clustered into larger agglomerates. (Magagane et al., 2019) reported similar results after calcining non-reactive magnesite at different temperatures and times. The change in morphology observed with increasing temperature is justified by the increase in MgO content as indicated by EDS. The change in morphology observed with increasing temperature is justified by the increase in MgO content as indicated by EDS (figure 4.2). These findings corroborate with XRF results, which showed increased MgO content from 400 °C to 600 °C.

4.3.1.4 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR analysis of raw and calcined magnesite is shown in Figure 4.3.

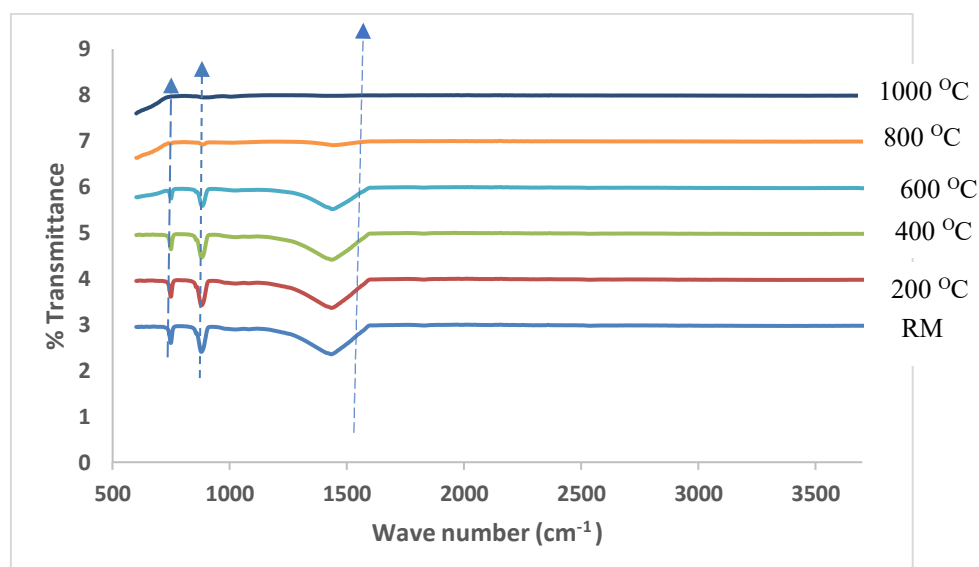


Figure 4. 3: FTIR analysis of calcined and raw magnesite.

FTIR analysis revealed carbonate peaks (CO_3^{2-}) at approximately 1450, 883, and 746 cm⁻¹ decreased or disappeared with increasing temperature. This could be due to the decomposition of MgCO_3 forming MgO , releasing CO_2 as the calcination temperature increases. (Yu et al., 2017) reported similar results after magnesite calcination for producing magnesium ions in precipitation struvite. The FTIR results corroborate with XRD results, which indicated the presence of MgCO_3 and MgO at (400 °C and 600 °C) and 800 °C respectively.

4.3.2 Optimization of Calcination Temperature

Figure 4.4 (a) and (b) show pH, Electrical Conductivity (EC), and Total Dissolved Solids (TDS) variations with calcination temperature following sonication and flocculation, respectively. Both graphs show gradual increase in pH from 400 °C to 600 °C. After that, pH increases slightly from 600 °C to 800 °C and reaches a plateau as calcination temperature rises to 1000 °C. The increase in pH is due dissolution of MgO in calcined magnesite as calcination temperature increases. Table 4.1 shows increase in MgO content with increase in calcination temperature. The dissolution of MgO releases alkalinity, increasing the solution's pH (Magagane et al., 2019). Figure 4.4a shows that the EC and TDS profile for sonication gradually decreases after reaction with raw magnesite and stabilizes afterward. The decrease in EC and TDS could be an indication of the removal of metals and sulphates from the solution following their precipitation as the pH increases (Gitari et al., 2006)

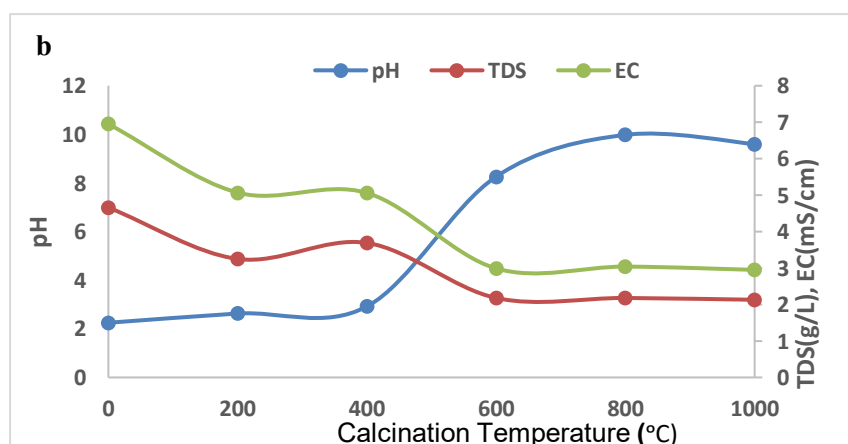
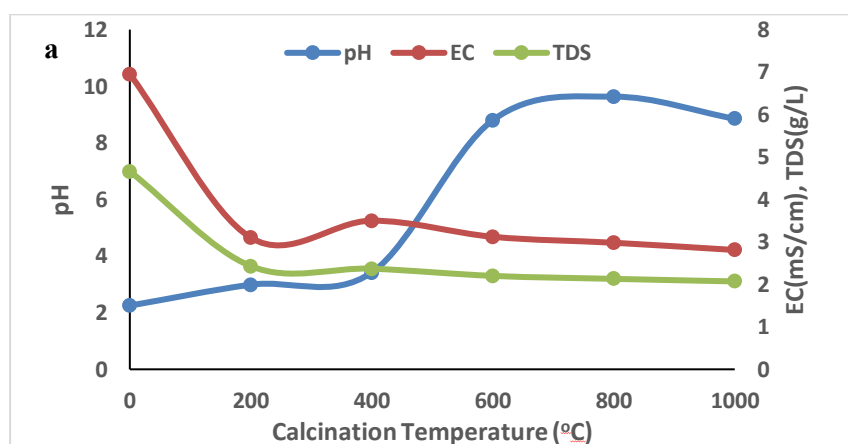


Figure 4. 4: (a) Variation of pH, EC, and TDS with calcination temperature using Sonicator (b) Variation of pH, EC, and TDS with increasing calcination temperature using flocculation. RM = 0, Calcined magnesite dosage = 1 g/100mL. Initial pH $\approx$ 2.25, EC (6.95 mS/cm), TDS 4.66 g/L). P-value = 0.1274 considered non-significant for optimum calcination temperature pH.

Figure 4.4b showed that EC and TDS in product water remained almost constant after treatment with magnesite calcined at 200 °C and 400 °C. The drastic decrease in EC and TDS observed when using sonication than flocculation is due to ultrasound applied in calcined magnesite: AMD mixtures leading to the formation of microbubbles. Figure 2.9a in chapter 2 shows a summary of bubble growth during sonication. The bubbles are formed during the rarefaction and grow to maximum size during the compression (Leong et al., 2011; Majid et al., 2015). The expansion and compression continue until the bubble collapses during the compression, forming shock waves that increase the pressure and temperature of the reaction mixture (Hagenson and Doraiswamy, 1998). Thus, the kinetic energy of calcined magnesite powders in solution increases, causing rapid collision and decreasing their particle size, increasing their reaction rate with AMD.

A temperature of 800 °C was considered optimum for the calcination of magnesite for both methods as it gave the highest pH during batch reactions. XRF, XRD, and FTIR corroborate with batch reaction because they indicated the formation of MgO at 800 °C. Sonication and Flocculation were compared by performing a two tailed test for the means of pH at an optimum temperature of 800 °C. A p value of 0.1274 was obtained and was considered non-significant. This indicates that there was no difference in the effectiveness of sonication and flocculation at 800°C. As suggested by Greenland et al. (2016), p value > 0.05 shows no difference between 2 suggested groups.

Figure 4.5 shows removal percentages of chemical species from AMD with increasing calcination temperature.

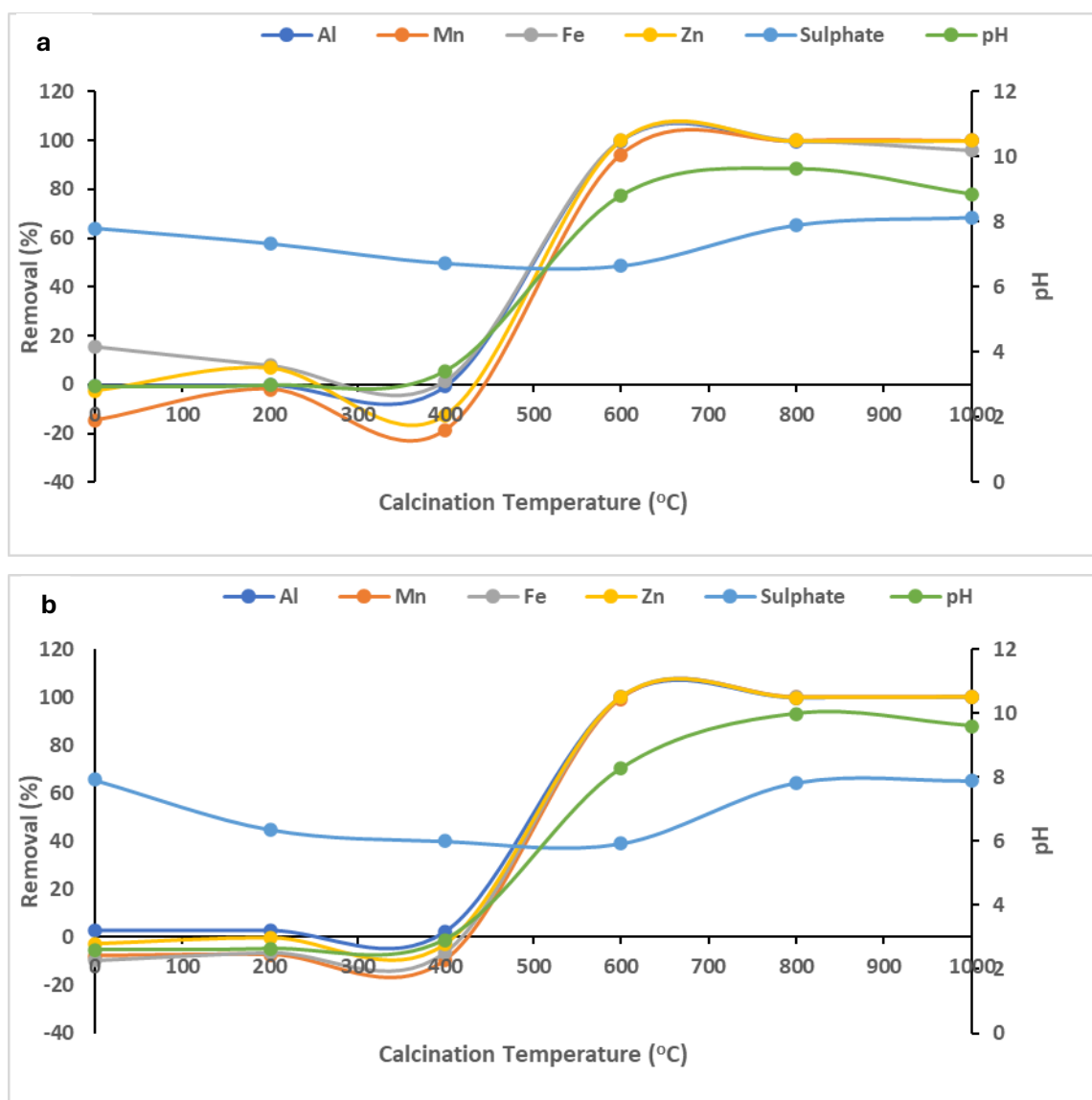


Figure 4.5: (a) The variation of calcination temperature with removal percentage of chemical species with sonication (b) The variation of calcination temperature with removal percentage of chemical species with flocculation.

The removal percentage of Fe, Mn, Al, and Zn gradually increased from $\approx 1.37\%$ at 400°C ($\text{pH} \approx 2.92$) to $\approx 99\%$ at temperatures $> 600^\circ\text{C}$ ($\text{pH} > 8.26$) in both sonication and flocculation (figure 4.5). The removal of metals could be due to their precipitation into respective metal hydroxides. From Figure 4.5a, the lowest and highest removal percentages of SO_4^{2-} were 48.5% (600°C , $\text{pH} \approx 8.8$) and 68.3% (1000°C , $\text{pH} \approx 8.5$), while in Figure 4.5b, it was 39% (600°C , $\text{pH} \approx 8.25$) and 65.6% (RM, $\text{pH} \approx 2.6$), respectively. Slightly higher SO_4^{2-} removal efficiencies observed with RM and calcined magnesite at 200°C in both sonication (RM, $\text{pH} \approx 2.95$; 200°C , $\text{pH} \approx 2.99$) and flocculation (RM, $\text{pH} \approx 2.6$; 200°C , $\text{pH} \approx 2.63$) respectively, could be due to the adsorption of SO_4^{2-} on $\text{Fe}(\text{OH})_3$ at $\text{pH} \approx 3$ and the formation of Fe-hydroxyl sulphate minerals (Gitari et al., 2010). Both methods also observed increased SO_4^{2-} removal at 800°C and 1000°C .

°C. This could be due to the dissolution of more MgO present, resulting in the precipitation of Fe-(oxy) hydroxides, which are known to adsorb SO_4^{2-} at $\text{pH} > 7$ (Gitari et al., 2010).

4.3.3 Effect of Sonication and Flocculation Time

Magnesite calcined at 800 °C was regarded as optimum and was used in other optimization experiments. Figures 4.6 a and b shows the variation of pH, EC, and TDS with contact time in treating AMD using magnesite calcined at 800 °C (CM) with sonication and flocculation, respectively.

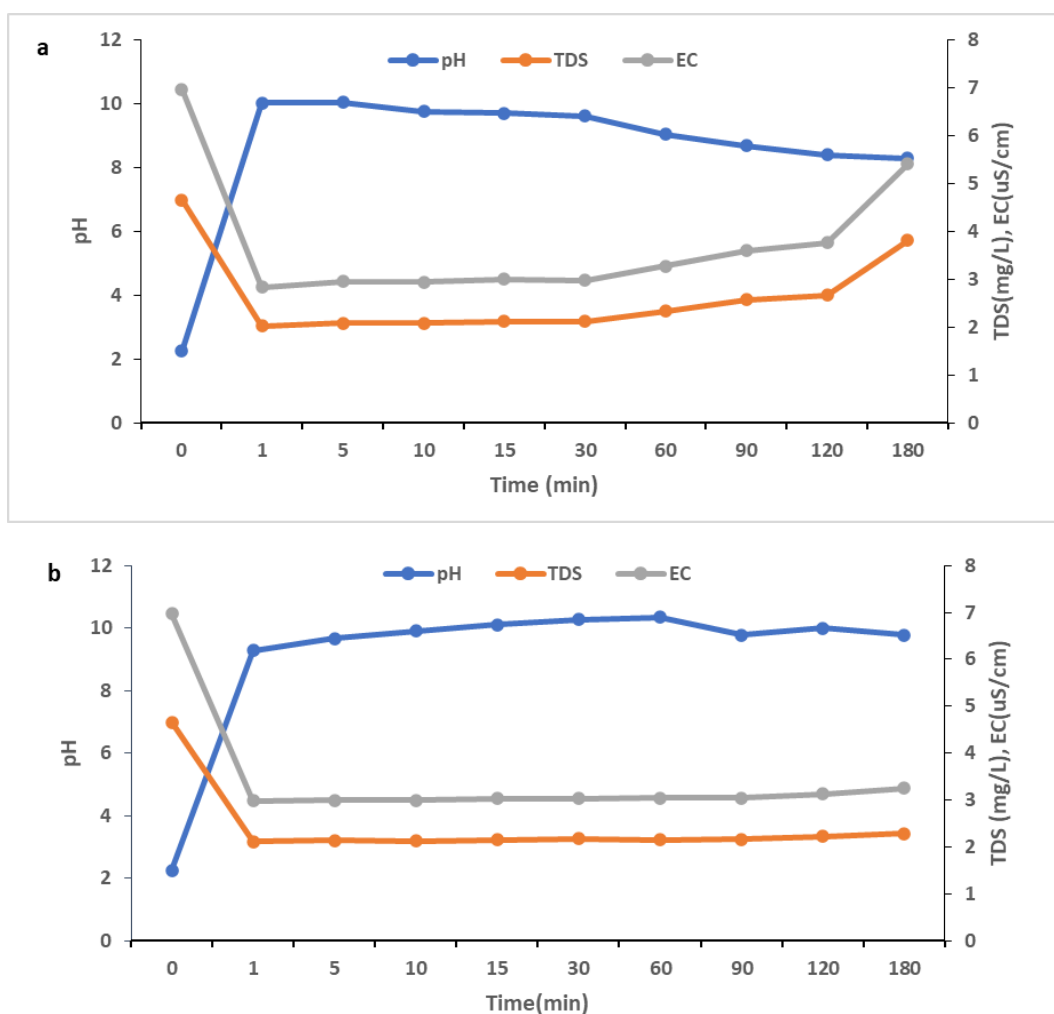
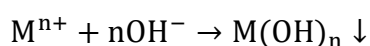


Figure 4. 6: (a) variation of pH, EC, and TDS with contact time with sonication, dosage =1g/100mL, (b) and variation of pH, EC, and TDS with contact time with flocculation, dosage= 1g/100mL CM 800 °C. P value of 0.0001 comparing means of pH values for 30 minutes contact time for sonication and flocculation respectively was considered extremely significant.

From figure 4.6, a sudden increase in pH to > 9 in 1 minute of contact time in both sonication and flocculation was observed. The rise in pH is due to the dissolution of MgO. The values of EC and TDS shows a steep decrease within 1 minute of flocculation and sonication due to precipitation of metals from the solution forming possibly metal hydroxylsulphates. Sonication increases pH from 2.25 to 10.01 within 1 minute and remained steady to about 30 minutes and thereafter start to decrease to $\text{pH} \approx 8.3$ in 180 minutes (figure 4.6 a). Flocculation increases pH from 2.25 to 9.28 within 1 minute and approaches steady state at 60 minutes with a pH value of 10.34 (figure 4.6 b). The rapid increase in pH when using sonication is attributed to cavitation induced by ultrasound which causes shock waves and microjets to fast track the dissolution of MgO by pitting its surfaces (Leong et al., 2011). Figure 4.6 a indicates a gradual decrease in EC and TDS from initial values of $6.97 \mu\text{S/cm}$ and 4.66 g/L to $2.84 \mu\text{S/cm}$ and 2.02 g/L within 1 minute respectively. Total Dissolved Solids (TDS) and Electrical Conductivity (EC) remained steady thereafter up to 30 minutes and a steady increase was observed from 60 minutes up to 180 minutes. The increase EC is ascribed to the dissolution of unreacted MgO, contributing to increase in levels of unreacted hydroxyl ions. At $\text{pH} > 8$, competition of hydroxyl ions and SO_4^{2-} ions for adsorption sites on Fe mineral phases is observed resulting in desorption of SO_4^{2-} (Gitari et al., 2010). Figure 4.6 b indicated that, EC and TDS values decreased from initial values to $2.98 \mu\text{S/cm}$ and 2.12 g/L within 1 minute respectively and remained constant as flocculation time increases. The optimum time established for sonication was 30 minutes while with flocculation was 60 minutes. The concentrations of Fe, Mn, Al, Zn and SO_4^{2-} in the treatment of AMD with calcined magnesite using sonication and flocculation respectively after 30, 60 and 180 minutes are shown in Table 3A (appendix). From the table 3A. It is observed that the removal percentage of metals (Fe, Mn, Al, and Zn) was greater than 97 %. This could indicate that at these reaction times, adding calcined magnesite to AMD raises pH until it reaches minimum solubility of metals, leading to precipitation of their respective metal hydroxides eqn 4.3 (Madzivire et al., 2011).



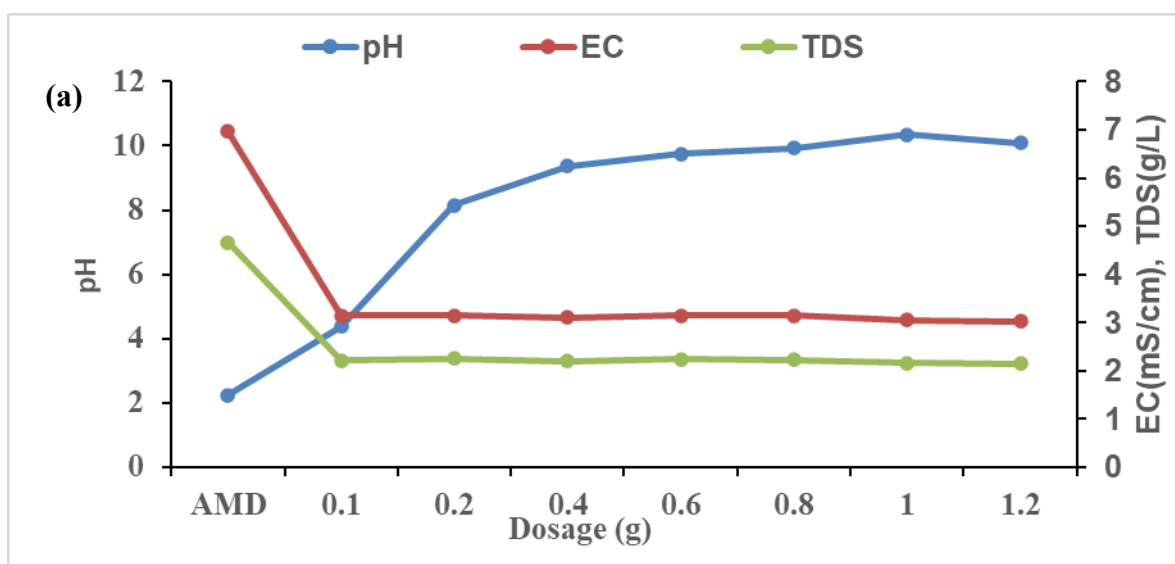
Equation 4.3

The removal percentage of SO_4^{2-} ranged from 55.1 % to 65.2 % in flocculation and sonication. Most of SO_4^{2-} remained in solution, possibly as MgSO_4^{2-} due to its high solubility product. The two methods were compared based on the p values of removal percentages of Fe, Al, Mn and SO_4^{2-} . Table 5A shows % removal and p values of Fe, Al, Mn and SO_4^{2-} for contact time of 30

minutes. A two tailed test of the means of pH for both flocculation and sonication at 30 minutes gave a p-value > 0.0001 which was considered extremely significant, indicating effectiveness of flocculation in raising pH. From the table 5A, it is observed that the mean of % removal of Fe, Mn and SO_4^{2-} had p values of 0.241, 0.999 and 0.7665 respectively which were considered not significant. This showed that both methods were effective in removing Fe, Mn and SO_4^{2-} from solution. However, % removal of Al showed a p value of 0.0021, which was considered extremely significant. This showed that sonication was effective in removing Al from AMD.

4.3.4 Effect of Calcined Magnesite Dosage

Figure 4.7 (a) and (b) show the variations of pH, TDS, and EC with a dosage of calcined magnesite with sonication and flocculation, respectively. A rise in pH with dosage was observed, indicating dissolution of more calcined magnesite and subsequently increasing alkalinity and precipitation of metal hydroxides. Figure 4.7(a) shows that the pH increase from 2.25 to 9.58 at a dosage of 0.4 g/100 mL and remained steady up to 1.2 g/100 mL. A similar trend was observed in figure 4.7 (b), where pH increased to 9.38 at a dosage of 0.4 g/100mL and remained constant with an increase in dosage.



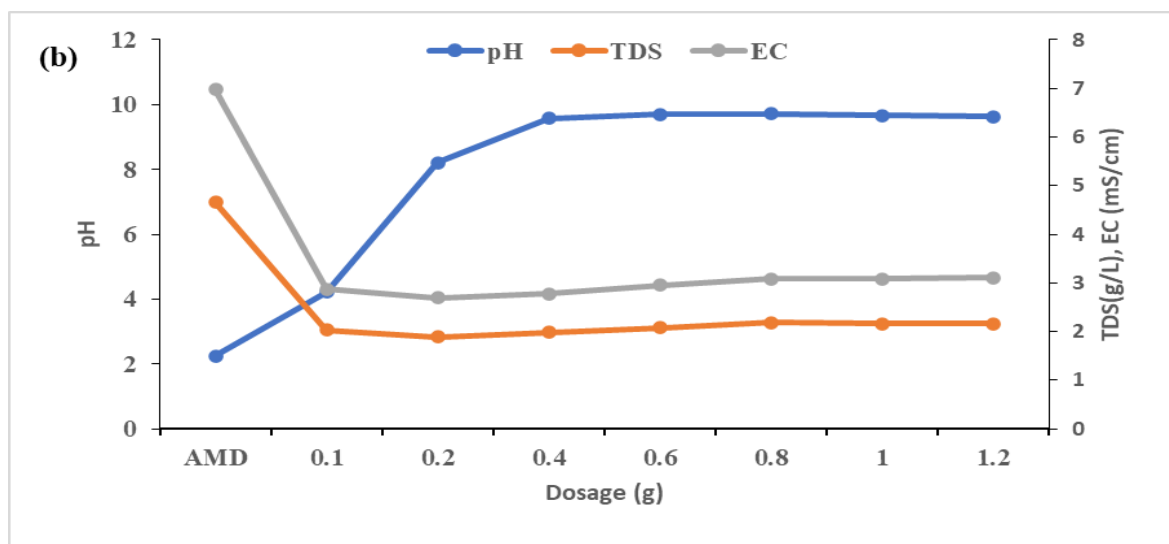


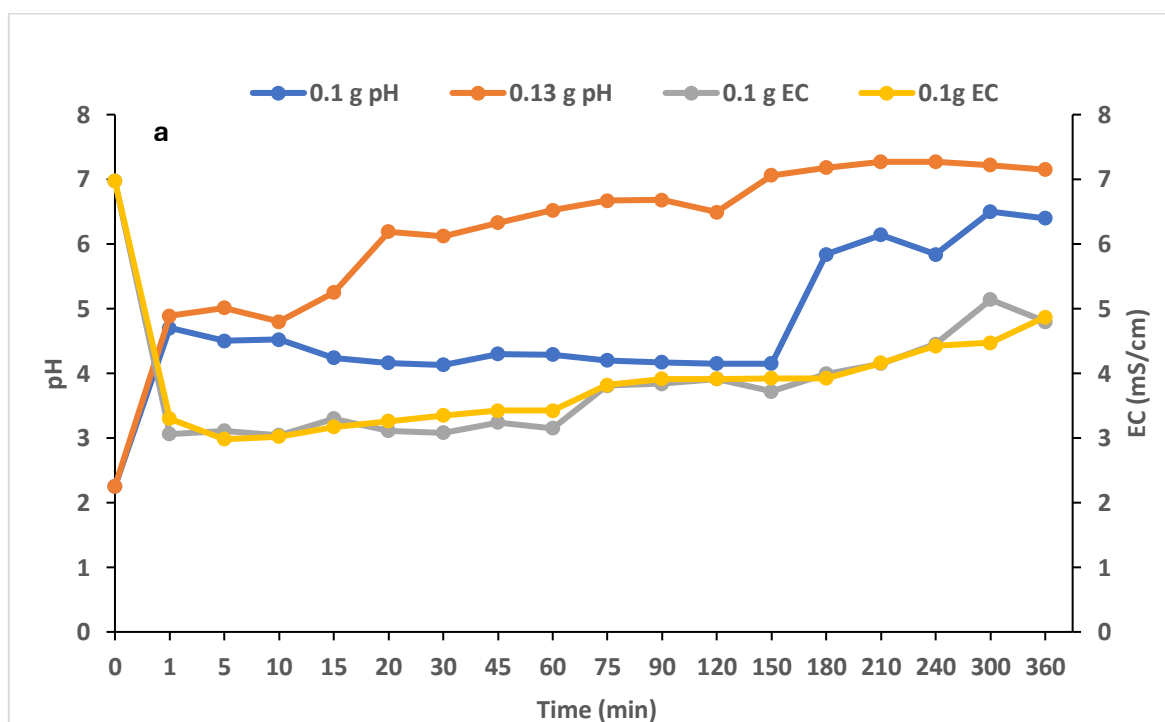
Figure 4. 7: (a) variation of pH, EC, and TDS profiles with dosage using sonication, time = 30 minutes, (b) variation of pH, EC, and TDS profiles with dosage during using flocculation, time = 60 minutes. P-value= 0.0476 comparing means of pH for 0.4 g was considered significant.

TDS and EC values showed the same trend when using sonication and flocculation. EC decreased from an initial value of 6.97 mS/cm to ≈ 3.14 mS/cm at a dosage of 0.1 g/100 mL when both sonication and flocculation were used and remained constant with an increase in dosage. TDS decreased from 4.66 g/L to ≈ 2 g/L with 0.1 g/100 mL of calcined magnesite in both flocculation and sonication and remained constant after that. The optimum dosage for both flocculation and sonication was 0.4 g/100 mL. From Table 3A, the % removal of Fe and Al was > 96 % with a dosage of 0.2 g and > 99 % with dosages of 0.6 g and 1.2 g with both flocculation and sonication. This indicates the precipitation of hydroxides of the respective metals with an increase in dosage. The removal percentage of Mn with 0.2 g of calcined magnesite was 53.7 % (pH $\approx$ 8.21) and 73.5 % (pH $\approx$ 8.15) with sonication and flocculation, respectively. Removal of > 99 % Mn was observed in both dosages of 0.6 g/ 100 mL and 1.2 g/ 100 mL at pH > 9 with both methods. This can be explained by thermodynamic calculations showing that Mn^{2+} precipitates at pH ≈ 9 . These results indicate that at a dosage of 0.6 g/100 mL, there is a higher % removal of Mn from AMD due to precipitation of Mn hydroxides. The removal of SO_4^{2-} was ≈ 60 % in both flocculation and sonication. A two tailed t-test comparing the means of pH values at a dosage of 0.4 g/ 100 mL was used to compare both methods. A p-value of 0.0476 which was considered significant was obtained (Figure 4.7), indicating effectiveness of sonication at low dosages. This is ascribed to increase in kinetic energy of particles at low dosages due to rapid mixing of ultrasonication. Both methods were also compared by evaluating the p values of percentage removals of Fe, Al, Mn and SO_4^{2-} . Table

6A shows % removal and p values of Fe, Al, Mn and SO_4^{2-} for contact time of 30 minutes and a dosage of 0.6 g/ 100 mL. A two tailed test was also performed for a dosage of 0.6 g/ 100 mL, comparing the mean of pH values. A p value of 0.0412 which was considered significant was observed. (Table 6A) This further supported the effectiveness of sonication at lower dosages. This suggestion corroborates with p values for the % removal of Fe and SO_4^{2-} at 0.6 g/ 100 mL of 0.0373 and 0.0012 respectively, which were considered significant. However, the removal % of Al and Mn were considered non-significant, suggesting no difference between the two methods at contact time of 0.6 g /100 mL.

4.3.5 The Variation of EC and pH with Dosage and Contact Time

To evaluate the Fe, Mn, and Al buffering regions, the dosage was reduced from 0.4 g to 0.1 g and 0.13 g /100 mL, and reactions were carried out varying contact time. Figures 4.8 (a) and (b) shows trends in pH and EC of neutralization reactions at calcined magnesite to AMD dosages of 0.1 g and 0.13 g / 100 mL with sonication and flocculation, respectively.



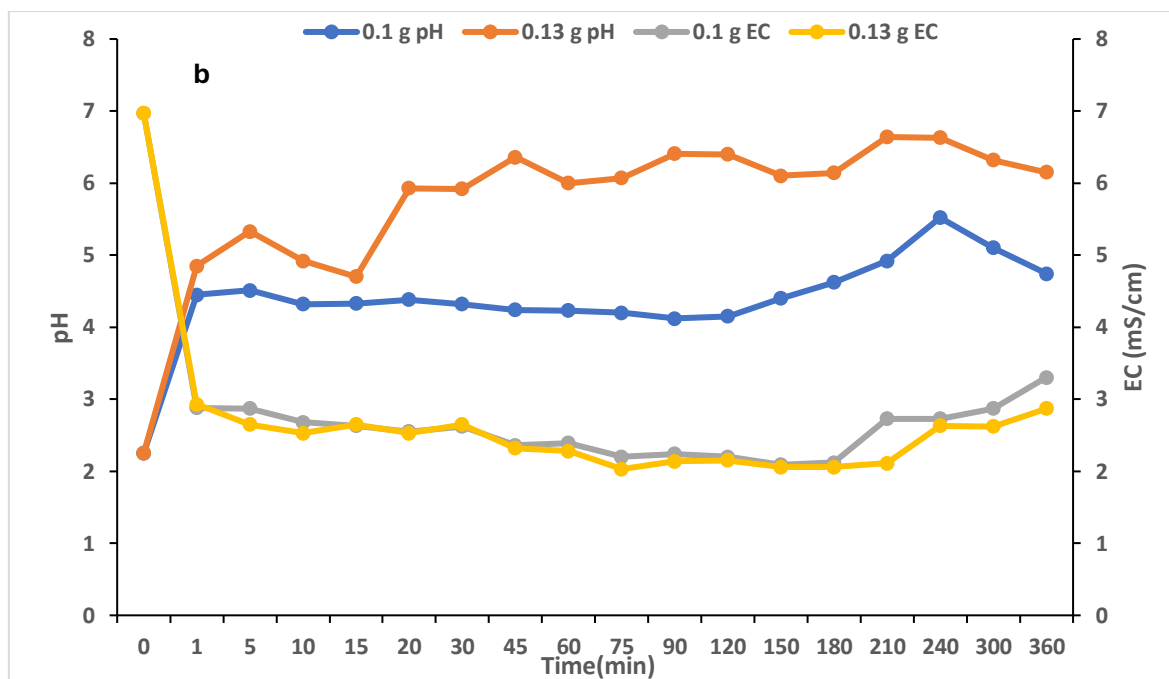


Figure 4. 8: (a) Variation in pH and EC profiles with time and dosage with sonication (b) Variation of pH and EC profiles with time and dosage with flocculation. P-value < 0.001 comparing means of pH at 360 minutes contact time and 0.1 g/ 100 mL for both methods was considered extremely significant.

An immediate rise in pH is observed after mixing AMD with calcined magnesite, followed by a plateau and buffering with an increase in time. Figure 4.8 (a) shows that a dosage of 0.1g/ 100 mL has two buffering regions at pH $\approx$ 4 from 1 minute to 150 minutes and at pH $\approx$ 6 from 180 minutes to 360 minutes. The buffer region at pH $\approx$ 4 can be ascribed to the hydrolysis of Fe^{3+} , while at pH $\approx$ 6 may be due to hydrolysis of Al^{3+} (Gitari et al., 2006). Hydrolysis occurs when Fe^{3+} , Al^{3+} , and Mn^{2+} consume OH^- and release protons (H^+) which counteracts the pH increase from the dissolution of MgO (eqns. 4.4-4.6) (Vadapalli et al., 2008). The trend for a dosage of 0.13 g shows three buffering regions with sonication (Figure 4.8a). The first was at pH $\approx$ 4.8 from 1 to 10 minutes, the second at pH $\approx$ 6.10 from 20 to 60 minutes, and the third at pH $\approx$ 6.67-7.22 from 75 to 360 minutes. The buffering region at pH $\approx$ 4.8 may ascribed to the hydrolysis of Fe^{3+} . The buffering at pH $\approx$ 6-7.22 is due to hydrolysis of Al^{3+} .



A rise in pH with increasing dosage and reaction time showed that these factors control the chemistry of product water in neutralization reactions. From Figure 4.8 a, there was a decrease in EC from 6.96 mS/cm to 3 mS/cm and remained constant for about 20 minutes. From 30 minutes up to 360 minutes, EC gradually increased from about 3.23 mS/cm to 4.87 mS/cm respectively. The factor that leads to high EC after long sonication reaction times is the dissolution of unreacted MgO, which results in high concentrations of unreacted OH⁻. High EC can also be attributed to the re-solubilization of sulphate minerals, which causes an increase in sulphate concentration with time. From Figure 4.8 b, a dosage of 0.1 g/ 100 mL showed a buffering region from 1 minute to 120 minutes at pH $\approx$ 4. After that, pH increases to $\approx$ 5.52 and decreases gradually to 4.74 as flocculation time increases to 240 and 360 minutes, respectively. From figure 4.8 (a), sonication showed two distinct buffering regions as compared to flocculation in which only one buffering region was visible. Both methods were also compared by evaluating the p values at contact time of 360 minutes for both dosages. A two tailed test comparing the means of pH at 360 minutes contact time showed a p-value < 0.001 , which indicates that sonication performed much better at lower dosages.

Unlike sonication, the flocculation plot at 0.13 g/ 100 mL shows two clear buffering regions from 1 to 15 minutes with pH $\approx$ 4.9 and 20 minutes to 210 minutes with pH $\approx$ 6.4 (Figure 4.8 b). Figure 4.8 b shows a decrease in EC from 6.97 to 3 mS/cm in 1 min of flocculation and, after that, decreases steadily to about 2 mS/cm after 210 minutes. This could be explained by the precipitation of Al-Fe-hydroxides, which adsorb SO₄²⁻ or incorporate it into its structures (Madzivire et al., 2011). From 210 to 360 minutes, EC slightly increased from 2.08 to 2.87 mS/cm, respectively. The slight increase in EC is due to unreacted OH⁻ from the dissolution of MgO.

4.3.6 Thermodynamic Modelling with PHREEQC Geochemical Modelling

Calculated Saturation indices for 0.1 g/ 100 mL and 0.13 g/ 100 mL Calcined magnesite: AMD ratios are shown in Tables 4.2 and 4.3.

Table 4. 2: Saturation indices values of minerals at a selected time with sonication.

Dosage	0.1g			0.13g		
Time	10	60	360	10	60	360
pH	4.15	4.29	6.51	5.25	6.09	6.40
Al(OH) _{3(a)}	-2.80	-2.34	-0.35	-0.36	0.50	-1.11
Anhydrite	-0.62	-0.63	-0.64	-0.80	-0.73	-0.64
Fe(OH) _{3(a)}	-6.52	-6.52	-1.69	-3.42	-2	1.62
Ferrihydrite	-6.46	-6.46	-1.40	-3.36	-1.94	1.68
Gibbsite	-0.11	0.24	2.34	2.33	3.19	2.34
Goethite	-0.15	-0.63	4.20	2.47	3.90	4.20
Gypsum	-0.40	-0.35	-0.42	-0.58	-0.51	-0.42
Hausmannite	-32.08	-30.59	-13.89	-22.93	-17.53	-13.89
Hematite	0.76	0.76	10.40	6.94	9.80	10.4
Manganite	-12.97	-12.43	-6.16	-9.56	-7.48	-6.16

Table 4. 3: Saturation indices of minerals at selected times with flocculation.

Dosage	0.1g			0.13g		
Time	10	60	360	10	60	360
pH	4.35	4.23	4.74	4.7	5.56	6.15
Al(OH) _{3(a)}	-1.78	-2.43	-3.98	-1.25	-1.65	-0.39
Anhydrite	-0.81	-0.77	-0.76	-0.8	-0.79	-1.84
Fe(OH) _{3(a)}	-5.71	-6.21	-5.10	-4.82	-4.24	-2.17
Ferrihydrite	-5.65	-6.15	-5.01	-4.76	-4.18	-2.11
Gibbsite	0.91	0.26	-1.29	1.44	1.04	2.30
Goethite	0.19	-0.32	0.79	1.07	1.65	3.72
Gypsum	-0.59	-0.55	-0.54	-0.58	-0.57	-1.62
Hausmannite	-30.1	-31.08	-27.07	-27.34	-20.72	-16.06
Hematite	2.38	1.37	3.59	4.15	5.32	9.46
Manganite	-12.25	-12.61	-11.11	-11.21	-8.72	-6.92

The Saturation indices values indicate that Al(OH)_{3a} and gibbsite were controlling the levels of Al³⁺ in the product water of both sonication and flocculation. Fe(OH)_{3a}, ferrihydrite, goethite, and hematite controlled the amount of Fe³⁺ in product water in both flocculation and sonication. The saturation indices were discussed to elaborate further on the chemistry of product water and solid residues.

4.3.7 Metal and Sulphate Removal Mechanisms in Neutralization Reactions

Compositional analysis of AMD, product water, and sludge generated during the treatment of AMD with calcined magnesite with sonication and flocculation paved the way for the prediction of mechanisms for the removal of SO_4^{2-} and toxic metals. Results from mineralogical, elemental analysis of sludge and chemicals species analysis of product water indicated that precipitation and adsorption of metal hydroxides and hydroxyl sulphates are major mechanisms responsible for removal from AMD. Tables 4.4 and 4.5 show the chemical compositions of product water during neutralization and treatment of AMD with calcined magnesite with sonication and flocculation, respectively.

Table 4. 4: Composition of product water in treating and neutralizing AMD with 0.1 g and 0.13 g of calcined magnesite with sonication (concentration is in mg/L except pH) at contact time of 10, 60 and 360 minutes.

Parameter	AMD	0.1g Treated water			0.13g Treated water			TWQR (DWAf, 1996)	TWQR (DWAf, 1996)
		10	60	360	10	60	360		
pH	2.25	4.52	4.29	6.4	4.79	6.08	7.15	6.5-8.4	6-9
Element									
SO₄²⁻	3820	3039	2713	3817	1582	1796	3329		0-200
Mn	17.524	17.5	17.075	17.186	16.846	6.375	11.79	0-0.02	0-0.05
Al	70.83	47.714	35.148	0.0925	4.090	0.809	0.209	0-5	0-0.15
Fe	43.854	1.856	0.593	0.02	0.862	0.073	0.065	0-5	0-0.1
Mg	51.88	336.1	414.8	422	371	458	867.8		0-30
Ca	186.70	188.2	221.8	199	181	205.5	440		0-32
Zn	2.146	1.82	2.04	1.08	1.3	0.04	0.0075	0-1	0-3
Cr		0.014	0.013	0.001	0.002	0.002	0.003	0-0.1	0-0.05
Ni		0.11	0.12	0.078	0.102	0.001	0.003	0-0.2	
Cu		0.03	0.07	0.002	0.013	0.019	0.004	0-0.2	0-1
Sr		0.05	0.07	0.06	0.054	0.065	0.15		

Table 4. 5: Composition of product water during treatment and neutralization of AMD with 0.1 g and 0.13g of calcined magnesite with flocculation (Concentration is in mg/L except pH) at contact time of 10, 60 and 360 minutes.

Parameter	AMD	0.1g Treated water			0.13g Treated water			TWQR irrigation (DWAf, 1996)	TWQR portable (DWAf 1996)
		10	60	360	10	60	360		
pH	2.25	4.35	4.25	4.74	4.94	5.55	6.15	6.5-8.4	6-9
Element									
SO ₄ ²⁻	3820	1619	1685	1757	1596	1686	1984	N/L	0-200
Mn	17.52	16.855	17.33	16.41	16.64	14.63	14.21	0-0.02	0-0.05
Al	70.83	59.086	32.99	0.030	18.68	0.038	0.096	0-5	0-0.15
Fe	43.85	2.221	1.651	0.641	1.54	0.0169	0.034	0-5	0-0.1
Mg	51.88	319.3	368.1	402.9	365.3	403.8	487	N/L	0-30
Ca	186.7	184.5	189.6	187	183.6	183.5	228.2	N/L	0-32
Zn	2.146	1.82	2.04	0.18	1.3	0.004	0.0075	0-1	0-3
Cr		0.019	0.004	0.009	0.002	0.0009	0.002	0-0.1	0-0.05
Ni		0.103	0.103	0.077	0.105	0.061	0.022	0-0.2	N/A
Cu		0.032	0.02	0.002	0.026	0.001	0.002	0-0.2	0-1
Sr		0.05	0.052	0.059	0.058	0.059	0.082	N/L	N/A

4.3.7.1 Toxic metal removal mechanisms at 0.1 g/ 100 mL dosage

From Table 4.4 and 4.5, the removal of Fe was > 95 % with 0.1 g for contact time 10, 60 and 360 minutes. The decrease in levels of Fe³⁺ at pH≈ 4 is ascribed to precipitation of Fe(OH)₃ which precipitate out of AMD solution at pH of 3 (Letjiane et al., 2019). The results corroborate with SEM-EDS and XRF which showed increase in % w/w of Fe (Table 4.1A & 4.1B). The main difference between the two methods was observed with a contact time of 360 minutes in which the final pH was 4.74 and 6.4 with flocculation and sonication respectively. Table 9A shows the % removal of major chemical constituents and p values of mean pH and % removal for a dosage of 0.1 g/ 100 mL. A two tailed t test of the mean values of pH values of the two methods (flocculation and sonication) was < 0.0001 and was considered extremely significant. This indicates that sonication was more effective in raising pH than flocculation. A pH of 4.74 obtained with flocculation enhanced the precipitation of Fe while a pH of 6.4 obtained with sonication enhanced precipitation of Al. EDS analysis showed a %w/w (Fe, 8.53) when using flocculation and % w/w (Fe, 3.69) when using sonication (Table 1 A) indicating precipitation of Fe(OH)₃ at low pH values. A p value for the % removal of Fe for both methods was < 0.0001 which was considered, extremely significant, indicating the difference between two methods in Fe removal. EDS % w/w of Al in which 7.32 was observed with sonication while 6.95 with flocculation. However, a p value of 0.750 which was considered not significant was calculated, EDS showed Al was being removed at pH 6.4. Most Al was observed to precipitate at pH value of 4.74, which is the first hydrolysis of Al as supported by Nordstrom and Ball (1986)

who found the chemistry of acidified SO_4^{2-} waters to be controlled by gibbsite at pH 4.5-5. EDS elemental analysis showed that sonication was more effective in the removal of Al from AMD. Table 4.3, calculation of SI values indicates oversaturation with respect to gibbsite at 360 minutes with sonication. Gitari et al. (2006) observed minimum solubility of Al^{3+} at pH 6-6.5. The Mn removal was < 5 % for both methods. Mn is known to precipitate from solution at pH $\approx$ 9 which is near its first hydrolysis of 9.

4.3.7.2 Toxic metal removal mechanisms at 0.13 g/100 mL dosage

Removal of Fe was > 98 % and > 96 % with 0.13 g for with sonication and flocculation respectively for contact time 10, 60 and 360 minutes (Table 4.4 & 4.5), suggesting complete precipitation of Fe(oxy)hydroxyoxides from solution. From Table 4.2 & 4.3, Goethite and haematite were found to be oversaturated for whole entire region. XRF and SEM EDS showed increase in composition of Fe in the sludge for contact time, 30, 60 and 360 minutes. The superiority of sonication over flocculation was observed at a contact time of 360 minutes, at which sonication raised pH to 7.15 while flocculation to a value of 6.15. The p value of the mean of pH comparing the two methods at 360 minutes was < 0.0001 which was considered extremely significant. The % removal of Al from AMD water treated with 0.13 g/ 100 g was > 52 % for contact time 10 minutes, and > 98 % for contact time 60 and 360 minutes for both methods (Table 4.4 & 4.5). This indicates an increase in precipitation of Al bearing minerals with increase in contact time. Calculation of SI indices show oversaturation of $\text{Al}(\text{OH})_{3(a)}$ at 60 minutes contact time and gibbsite for the entire contact time region for both methods. SEM-EDS detected Al rich mineral phase encapsulated with Fe, S and Mn (Table 4.1A). This indicates formation of Al-Fe hydroxysulphate mineral at pH 5-5.6. The main difference between the two methods is observed at contact time 360 minutes. Table 10A shows the % removal of major chemical constituents and p values of mean pH and % removal for a dosage of 0.13 g/ 100 mL. The p value of mean of % removal of Al was 0.0369 and was considered significant. Effectiveness of sonication over flocculation is also observed with contact time 60 minutes in which the final pH was 6.52 and 6.0 respectively. A two tailed test was performed comparing sonication and flocculation at a contact time of 60 minutes. The removal efficiency and pH were evaluated, and p values used to compare both methods. The p value of pH was < 0.0001 which was considered extremely significant, however the p value of 0.6239 for removal of Al was considered not significant. The removal of Mn^{2+} at contact time 60 minute was 63.6 with sonication and 16.5 with flocculation. The p value for removal of Mn was < 0.0001 and

was considered extremely significant, indicating superiority of sonication in Mn removal. This is ascribed to adsorption on of Mn on $\text{Al}(\text{OH})_3$ due to superior mixing with sonication. EDS elemental analysis showed % w/w of Mn of 2.19 with sonication while BDL with flocculation. XRF results corroborates with EDS, showing presence of 1.024 % of MnO (Table 4.1B). sonication enhanced the precipitation of Mn at 60 minutes contact time than flocculation.

4.3.7.3 Removal mechanisms of Ca, Mg and SO_4^{2-}

The levels of Ca were observed to remain almost constant in product water for entire contact time region with 0.1 g with sonication (Table 4.4). A dosage of 0.13 g, Ca concentration remained almost constate for 10- and 60-minutes contact time but gives higher concentration at 360 minutes. The concentration of Mg was increasing with increase in contact time. This is ascribed to dissolution of calcined magnesite, releasing Mg^{2+} into solution. XRF and EDS elemental analysis showed a decrease in the amount of MgO and Mg in solid residues compared with calcined magnesite (Table 4.1A and 4.1B). XRD observed (Fig 4.E) absence of MgO peaks in solid residues obtained after neutralizing AMD with calcined magnesite dosages. The main difference between two methods was observed with a dosage of 0.13 g/ 100 mL at a contact time of 360 minutes. At this contact time Mg, Ca and SO_4^{2-} had concentrations of 867.8, 440 and 3329 mg/L respectively with sonication while flocculation Mg, Ca and SO_4^{2-} concentrations of 487, 228 and 1984 mg/L respectively. This indicates that at 360 minutes, rapid mixing in sonication causes resolubilization of Ca, Mg and SO_4^{2-} from the sludge back into the solution. The same process is not observed with flocculation. The concentration of SO_4^{2-} shows removal of 26 %, 34% and 7 % with a dosage of 0.1 g. A dosage of 0.13 g shows removal of 61.6 %, 56 % and 9 % of SO_4^{2-} . These percentages indicate less removal of SO_4^{2-} due to high solubility of MgSO_4 . In their study, Bologo et al. (2012) reported low SO_4^{2-} after neutralization and treatment of AMD with lime and $\text{Mg}(\text{OH})_2$. Low removal efficiencies observed at a contact time of 360 minutes for both dosages shows solubilization of SO_4^{2-} . These results corroborate with EC values for same contact time, as SO_4^{2-} is a major component responsible for high EC.

4.3.8 Comparing with South African Water Quality Standards

The chemical composition of product water obtained during sonication is compared with South African Water quality standards (Table 4.4) (DWAF, 1996). The product water quality obtained at $\text{pH} > 4$ was within the range of the water quality guidelines for irrigation water for Fe. The product water obtained at a contact time of 360 minutes ($\text{pH} > 6$ and $\text{pH} > 7$ for 0.1

and 0.13 g, respectively meets TWQR for irrigation of Al. SO_4^{2-} , Mg, Ca, and Mn remained in solution at concentrations above the irrigation and domestic water regulations. Cr, Ni, Cu, Sr, and Mo were present in product water with domestic and irrigation water quality regulations. These elements are from the dissolution of calcined magnesite. The alkali earth metals, SO_4^{2-} and Mn, might require further treatment options to polish the product water. Mn requires increased calcined magnesite dosage to raise pH near its first hydrolysis constant. Several authors have reported using downstream treatment methods such as reverse osmosis in removing Ca, Mg and SO_4^{2-} from product water (Letjiane et al., 2019). The results are presented for 0.1 g and 0.13 g calcined magnesite: AMD ratio with flocculation (Table 4.5). Water quality at $\text{pH} > 4$ was within the recommended Fe irrigation guidelines. The product water obtained at a contact time of 360 minutes ($\text{pH} > 6$ and $\text{pH} > 7$ for 0.1 and 0.13 g) meets TWQR for irrigation and potable water of Al. SO_4^{2-} , Mg, Ca, and Mn remained in solution at concentrations above the irrigation and domestic water regulations. Cr, Ni, Cu, Sr, and Mo were present in product water with domestic and irrigation water quality regulations.

4.3.9 Comparison of Treatment Options

This section summarizes the effectiveness of each method in AMD treatment. During the optimization of calcination temperature, a dosage of 1 g/ 100 mL of calcined magnesite (800 °C) showed a 99.9 % removal of Fe, Al, Mn and Zn when using both methods. The p value for comparing both pH and removal % was not significant, which showed no difference between two methods. When optimization contact time, flocculation was more effective in raising pH than sonication. The p value, comparing means of pH was extremely significant indicating superiority of flocculation, however the p value of % removal was not significant showing no difference between two methods in terms of metal removal. During optimization of dosages, lower dosages showed effectiveness of sonication. The p values for pH of 0.4 g and 0.6 g were extremely significant and considered significant indicating superiority of sonication at lower dosages. The two methods were both effective in removal of Mn and Al, however sonication was effective in Fe removal as shown by p value of Fe removal % which was considered significant. Effective of sonication at low dosages is ascribed to increase in kinetic energy at low dosages, increasing rate of reaction. The pH and concentration of chemical constituents of product water after treatment of AMD with calcined magnesite with sonication and flocculation are in table 4.5 & 4.6 respectively. From these tables, it was observed that sonication raised pH higher than flocculation at dosage of 0.1g/100mL and 0.13 g/100 mL for 360 minutes. The

mean pH p values for both dosages were < 0.0001 , indicating superiority of sonication at lower dosages. The removal of Al and Fe were $> 96\%$ for both dosages, indicating effective removal of these metals. A dosage of $0.13\text{ g}/100\text{ mL}$ showed higher % removal of Mn with sonication than flocculation. This is because sonication raised pH to 7.15 which is near the first hydrolysis of $\text{Mn}(\text{OH})_2$ (pH 9) at which Mn starts to precipitate from solution. In the literature, Mn^{2+} has been reported to precipitate from solutions at $\text{pH} \approx 9$ (Seo et al., 2017). A dosage of $0.13\text{ g}/100\text{ mL}$ showed significant amounts of Ca, Mg and SO_4^{2-} to increase in product water when using sonication than flocculation for contact time of 360 minutes. This indicates extensive forces which builds and breaks the surface of the sludge when sonication for 360 minutes. The superiority of this technology of increasing concentration of Mg, Ca and SO_4^{2-} can be applied in industry to recover Mg and Ca sulphates bearing minerals from calcined magnesite.

4.4. Conclusion

This work focused on the remediation of AMD with calcined magnesite, comparing the effectiveness of sonication and flocculation. The MgO content increased with increasing calcination temperature, with the highest content observed at 800°C . Magnesite calcined at 800°C gave the highest pH during neutralization of AMD compared to RM, which was at 200, 400, 600, and 1000°C . XRD, SEM-EDS, XRF and FTIR showed the dominance of MgO at 800°C . The variation of contact time showed that sonication attained optimum time of 30 minutes while flocculation attained an optimum of 60 minutes, however the p values for pH was not significant. The graph for variation of dosage was optimum at $0.4\text{ g}/100\text{ mL}$ for both methods, however p values for percentage removal and pH showed significance difference, indicating superiority of sonication over flocculation. At dosages of $0.1\text{ g}/100\text{ mL}$ and $0.13\text{ g}/100\text{ mL}$, sonication was more superior in raising pH and removal of metals than flocculation at 360 minutes. Two tailed P value for pH and metal removal percentage was extremely significant, showing effectiveness of sonication over flocculation. PHREEQC geochemical modelling showed oversaturation with respect to goethite, gibbsite, ferrihydrite and amorphous iron hydroxide when using both methods. However, SEM EDS showed that sonication enhanced the precipitation of more minerals than flocculation at contact time of 60 and 360 minutes at dosages of 0.1 g and 0.13 g . Sonicating for 360 minutes increased significant amounts of Mg, Ca and SO_4^{2-} in product water than flocculation. Ultrasonication can be applied in AMD treatment at pilot scale for the recovery of Mg, Ca and SO_4^{2-} salts

AMD. The study found that sonication raised the pH faster and precipitated more minerals than flocculation, resulting in better neutralization of AMD with calcined magnesite.

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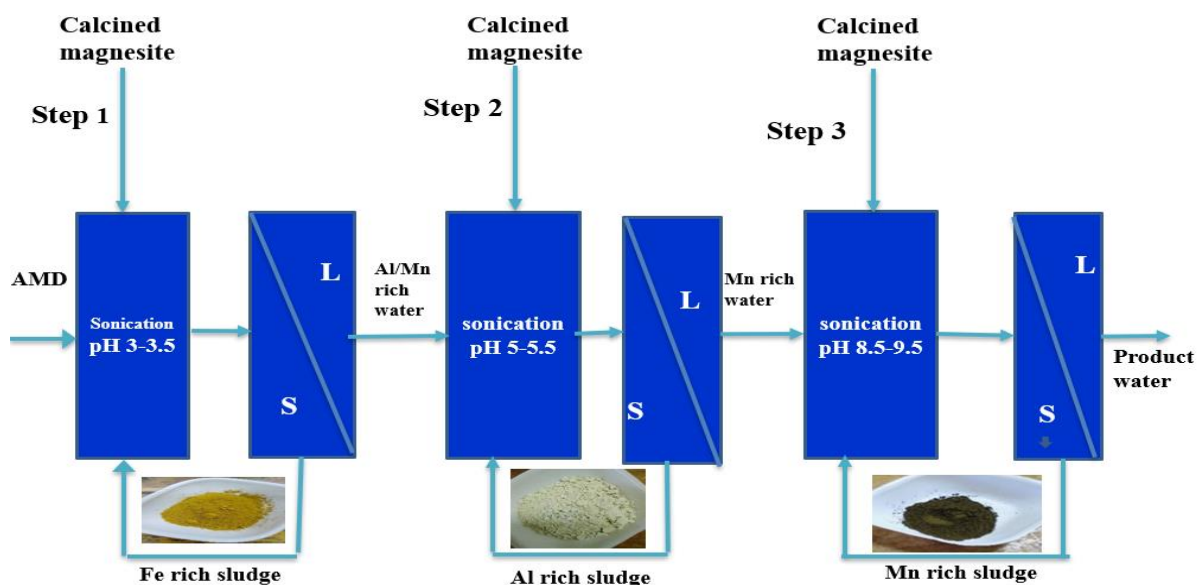
Chapter 5

Sequential recovery of Fe, Al, and Mn metal oxides in Acid mine drainage using calcined magnesite ultrasonic treatment

Highlights

- Sequential precipitation and sludge enrichment were investigated during AMD treatment with calcined magnesite with sonication.
- Fe^{3+} showed enrichment up to cycle 3 and was recovered as goethite, ferrihydrite and schwertmannite.
- Al^{3+} was recovered as gibbsite and basalumite and showed enrichment up to cycle 3
- Mn^{2+} showed enrichment up to cycle 2 and was recovered as ramsdellite and desautelsite minerals
- Quantities of metals recovered were within the range, which can be further processed into valuable minerals for industrial applications.

Graphical Abstract



Abstract

A three-step process was implemented for the ultrasound-assisted recovery of Fe, Al, and Mn-rich minerals from acid mine drainage (AMD) using calcined magnesite for treatment. Simulated acid mine drainage (AMD) containing Fe, Ca, Al, Mn, Mg, Zn, and SO_4^{2-} with

concentrations of 56.0, 199.0, 89.0, 21.0, 50, 2.0, and 1808 mg/L, respectively, was prepared. A known mass of calcined magnesite was added to AMD to precipitate Fe^{3+} , the filtrate was used to recover Al^{3+} , and lastly the filtrate from this step was used for precipitation of Mn^{2+} . In each step, the metal rich sludge was enriched with more minerals through recycling for treatment of more AMD. The resultant sludge, after treatment, was enriched with metals by treating AMD and product water over five cycles. The mineralogical and elemental compositions of the recovered metal-rich sludge at the end of each cycle were characterized using X-ray diffraction (XRD), scanning electron microscopy equipped with energy dispersive (SEM-EDS), and X-ray fluorescence spectroscopy (XRF). Product water was analyzed using inductively coupled plasma mass spectrometry (ICP-MS) and ion chromatography (IC) for metals and SO_4^{2-} , respectively. The optimum pH levels for the recovery of Fe were 3-3.5, with recovery of > 93.7 . Product water from Fe recovery was used as feed for Al recovery. Al precipitated well at pH 5-5.5 with a recovery of > 90.4 %. The water from Al recovery was used for the recovery of Mn. Mn precipitated at a pH of 8.5-9.5 with recovery of > 74.5 %. Sludge obtained from step 1 showed dominance of ferrihydrite- $\text{Fe}(\text{OH})_3$, goethite- FeOOH , and schwertmannite- $\text{Fe}_8\text{O}_8(\text{OH})_6(\text{SO}_4)\cdot n\text{H}_2\text{O}$. Sludge obtained from step 2 showed the dominance of gibbsite- $\text{Al}(\text{OH})_3$ and basaluminite- $\text{Al}_4(\text{SO}_4)(\text{OH})_{10}$, while sludge from step 3 showed precipitation of an Mn-rich mineral ramsdellite- MnO_2 and Mn. The Mn-bearing minerals were coprecipitated with Mg as indicated by the presence of Desautelsite- $\text{Mg}_6\text{Mn}_2(\text{CO}_3)(\text{OH})_{10}$ and brucite- $\text{Mg}(\text{OH})_2$ mineral phases. The metals Fe, Al, Mn, Ni, and Cu in product water recovered after step 3 were below the recommended guidelines for irrigation, while Ca, Mg, and SO_4^{2-} remained at higher levels. Calcined magnesite ultrasonic treatment has the potential to be applied in the remediation and recovery of metals from AMD. However, downstream treatment methods are required to polish the product water further and improve the enriched sludge's purity.

Keywords: recovery, metals, calcined magnesite, acid mine drainage, sonication.

5.1 Introduction

Acid mine drainage (AMD) is one of the major environmental problems in South Africa, particularly in the Gauteng and Mpumalanga Provinces, where the mining of coal and gold is a significant economic activity (Munyengabe et al., 2020). AMD is formed when sulphide rich minerals react with water in the presence of oxygen and microorganisms (*Thiobacillus ferrooxidans* and *Thiobacillus thiooxidans*), resulting in low pH water containing high concentrations of potentially toxic metals and SO_4^{2-} which are difficult to control and requires high treatment costs (Abiye and Ali, 2022; Chen et al., 2021). If AMD is not managed properly, it can significantly harm the environment, including dams, rivers, municipal infrastructure, agricultural, industrial, portable water supplies, animals, and aquatic plants (Galhardi and Bonotto, 2016). To prevent further contamination, AMD must be treated to meet environmental regulations before being discharged into the environment.

Conventional treatment options for AMD often lead to generation of toxic sludge enriched with toxic metals, which may find their way into the environment through leaching (Kefeni et al., 2017). This led to a paradigm shift towards reducing sludge and improving operating costs and sustainability (Naidu et al., 2019). The shifts are driven towards recovering precipitated metal hydroxide/oxides from the sludge, aiming to obtain valuable resources while meeting effluent discharge limits. The most common approach for recovering metals from AMD is selective precipitation due to its high efficiency and low operational costs (Vo et al., 2020). Selective precipitation entails the recovery of metal hydroxides or sulfides based on the solubility products of each dissolved metal (Seo et al., 2017). Several researchers have adopted selective precipitation as a method for the recovery of metals such as Fe, Al, Mn, Cu, Zn, and Ni from AMD (de Almeida Silva et al., 2019; Hu et al., 2022; Le et al. 2020; Seo et al., 2017; Wei et al., 2005).

Le et al. (2020) successfully recovered 99.7 % of $\text{Fe}(\text{OH})_3$ and 99.3 % of $\text{Al}(\text{OH})_3$ using selective precipitation with pilot-scale Fluidized Bed Homogenization Crystallization (FBHC). (Seo et al., 2017) compared the neutralizing agents NaOH, Na_2CO_3 , and $\text{Ca}(\text{OH})_2$ in the recovery of Fe, Al, and Mn from AMD discharging from the Samma-Taejeong coal mine in South Korea. They observed that the $\text{Fe} > \text{Al} > \text{Mn}$ recovery sequence was 99.2–99.3 %, 70.4 %–82.2 %, and 37.8–87.5% at pH values of 4.5, 5.5, and 8.5, respectively. In another study, Hu et al. (2022) evaluated the feasibility of recovering highly concentrated Fe from AMD by

oxidizing Fe^{2+} to Fe^{3+} using H_2O_2 followed by pH adjustment with NaOH and the coagulant polyacrylamide (PAM) to precipitate and remove Fe^{3+} at a pilot scale. Their study showed that the precipitation rate of Fe^{3+} at pH 3.8 was 99.04%, and Fe^{3+} decreased from 505.71 mg/L to 4.87 mg/L. Ryan et al. (2017) and de Almeida Silva et al. (2019) recovered Fe as iron oxides at pH 3.6 after adjusting pH with NaOH and observed precipitation of $\text{Fe}(\text{OH})_3$ mixed with $\text{Al}(\text{OH})_3$ at pH of 3.5-5.5. This limitation was resolved by oxidation of Fe^{2+} to Fe^{3+} either by aeration or H_2O_2 to selectively precipitate $\text{Fe}(\text{OH})_3$ at pH $\approx$ 3.5, followed by $\text{Al}(\text{OH})_3$ recovery at pH $\approx$ 5.5. In another study, 33.5% of Fe was separately recovered at pH 4 from 391.2 mg/L Fe AMD, followed by 7.8 % Cu at pH 7 from a 75.11 mg/L Cu AMD using hydrated lime as a neutralizer (Masuda et al., 2019). Few researchers have recovered metal oxides/hydroxides/hydroxy sulphates for industrial applications (Mogashane et al., 2023). Metal oxides have several industrial applications, such as catalysis, water treatment, and battery manufacturing. However, there is a need to consider the market value, quality, and quantity of the recovered minerals. Thus, there is a need for further research into other precipitation parameters and their impact on sludge characteristics to improve sludge value further (Ryan et al., 2017). Recycling sludge may improve metal oxide value by increasing the amount and quality of the metal-rich minerals generated.

Furthermore, using ultrasound to enhance the neutralization of AMD with calcined magnesite may improve sludge characteristics. Our previous work compared the effectiveness of sonication and flocculation in neutralizing and treating AMD with calcined magnesite. The results indicated that sonication raised pH faster, gave more distinct buffering regions, and favored precipitation of minerals over flocculation. These advantages necessitated ultrasonication in treating AMD and recovering selected metals using calcined magnesite. This work aimed at using ultrasound for stepwise recovery of metals through their enrichment in the sludge, activation of the sludge, and reuse for treatment of AMD over several cycles. The specific objectives of this work were 1) To optimize the selective precipitation of Fe, Al, and Mn in AMD by using calcined magnesite for pH adjustment and ultrasonic treatment, 2) To enrich sludge with metals through treatment of AMD over several cycles, and 3) To characterize the resultant sludge and product water.

5.2 Materials and Methods

5.2.1 Chemicals and Reagents

Analytical grade reagents such $(\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O})$, $(\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O})$, $(\text{MnSO}_4 \cdot \text{H}_2\text{O})$, $(\text{MgSO}_4 \cdot 7\text{H}_2\text{O})$, $(\text{CaCl}_2 \cdot 2\text{H}_2\text{O})$, $(\text{ZnSO}_4 \cdot 7\text{H}_2\text{O})$ and concentrated H_2SO_4 which used to prepare synthetic AMD were purchased from Rochelle chemicals. Magnesite was collected from the Folovhodwe magnesite mine in Limpopo Province, South Africa. The collected magnesite was milled using a Ball milling machine (Retsch RS 200 vibratory Mill) to pass through a $32 \mu\text{m}$ particle size sieve and then calcined at 800°C in a furnace. The elemental composition of raw and calcined magnesite is shown in Table 5.1.

Table 5. 1: Elemental compositions of raw magnesite and calcined magnesite.

Element (%)	Raw magnesite	Calcined magnesite
MgO	61.76	85.67
Al₂O₃	0.164	0.146
SiO₂	1.81	2.25
CaO	0.809	0.994
Fe₂O₃	0.074	0.123
K₂O		0.052
Ti	0.027	0.022
Cr	0.041	0.022
Sr	0.003	0.005
Cu	0.001	0.001
Ni	0.004	0.016
Mn	0.008	0.013

5.2.2 Preparation of Synthetic AMD

Synthetic AMD containing Fe (56 mg/L), Ca (199 mg/L), Al (89 mg/L), Mn (21 mg/L), Mg (50 mg/L), Zn (2mg/L) and SO_4^{2-} (1808 mg/L) was prepared by dissolving 0.220 g $\text{Fe}_2(\text{SO}_4)_3 \cdot \text{H}_2\text{O}$, 1.097 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$, 0.0645 g $\text{MnSO}_4 \cdot \text{H}_2\text{O}$, 0.495 g $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$, 0.7312 g $\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$, 0.009 g $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, respectively in Milli-Q water ($18.2 \text{ M}\Omega$) with 0.5 mL of concentrated H_2SO_4 in a 1000 mL volumetric flask. The synthetic AMD was prepared to simulate concentrations of AMD recorded in samples collected from Mpumalanga province in the eMalahleni abandoned coal mines.

5.2.3 Sequential Recovery of Metals from AMD

A three-step process was designed following (Ryan et al., 2017; Wei et al., 2005) for sequential precipitation of Fe-, Al- and Mn-oxides/hydroxides/hydroxy sulphates from AMD. Figure 5.1 shows a sequential process for recovering Fe-, Al-, and Mn-oxides/hydroxides from AMD using calcined magnesite and sonication. The steps are detailed in sections 2.3.1 to 2.3.2.

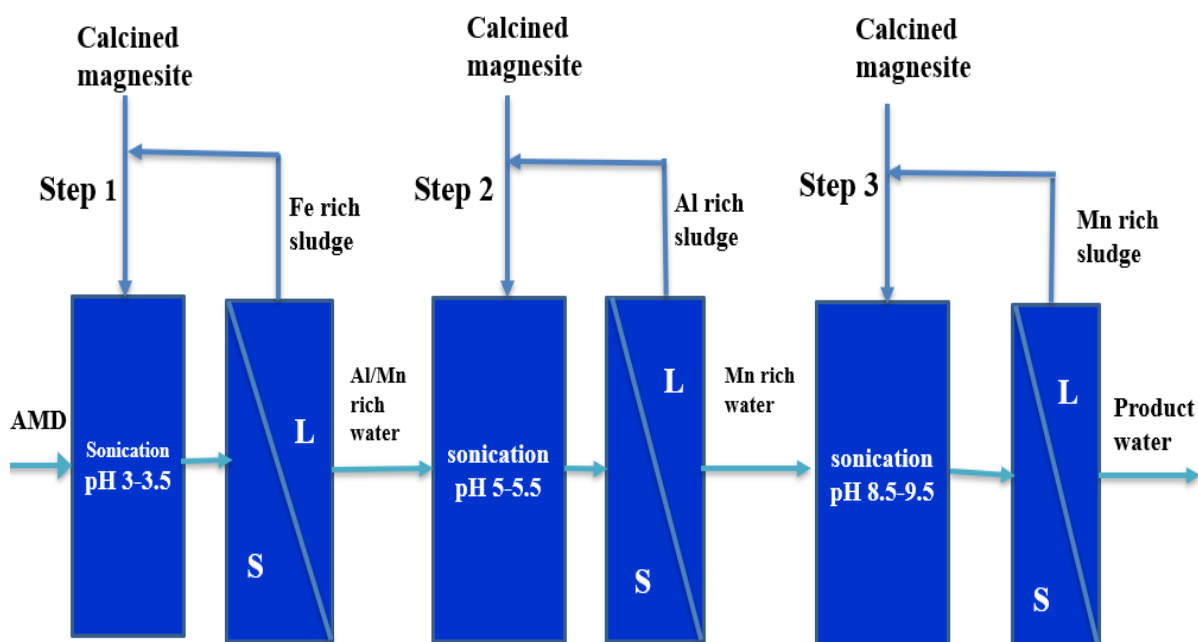


Figure 5. 1: Flow diagram showing recovery of Fe, Al, and Mn metal oxides from AMD. S- metal rich sludge, L-liquid filtrate.

5.2.3.1 Recovery of Fe-rich Sludge

Step 1 - Five cycles were performed to recover Fe metal oxide from AMD and enrich the sludge with Fe oxides. In cycle 1, a mass of 0.05 g calcined magnesite was added to 100 mL of AMD to raise pH to 3-3.5 under continuous sonication for 90 minutes to maximize Fe precipitation. The solution pH, Electrical Conductivity (EC) and Total Dissolved Solids (TDS) were measured using a Pc 8 pH/Mv/Cond/Temp multi-meter probe (Accsen, PRC). The Fe-rich sludge was filtered out using a 0.45 μm pore nitrate cellulose filter membrane, leaving a filtrate with non-ferric metals, such as Al and Mn, which was used in step 2. The Fe-rich sludge was reactivated by air drying and milled with a mortar and pestle. In cycle 2, reactivated Fe-rich sludge from cycle 1 was mixed with 0.04 g of fresh calcined magnesite and used to neutralize and treat 100 mL of AMD. The addition of 0.04 g fresh calcined magnesite was done to maintain pH at 3-3.5 since Fe-rich sludge alkalinity was saturated. The Fe-rich sludge was filtered out and reactivated. The Al-rich product water was kept and used as feed for the recovery of Al. The process was repeated in cycles 3, 4, and 5, adding 0.04 g of calcined magnesite at the end.

5.2.3.2 Recovery of Al-rich Sludge

Step 2 - A mass of 0.04 g calcined magnesite was added to 100 mL of product water from step 1 to raise the pH to 5-5.5 under continuous sonication. Sonication was allowed to continue for

90 minutes to maximize Al precipitation. After that, mixtures were filtered using a 0.45 μm pore nitrate cellulose filter membrane, and the filtrate was transferred to step 3 for recovery of Mn oxides. The sludge was air-dried and re-activated by milling using a mortar and pestle. In Cycle 2, a mass of 0.04 g dried reactivated Al-rich sludge was mixed with 0.03 g of calcined magnesite and sonicated with 100 mL of Al-rich water from Step 1. The addition of fresh calcined magnesite was to sustain the final pH of the reaction mixture at levels of 5-5.5 since Al-rich sludge alkalinity was exhausted. During cycles 3, 4, and 5, the same process was repeated, adding 0.03 g of fresh calcined magnesite at the end.

5.2.3.3 Recovery of Mn-rich Sludge

Step 3 - Five cycles were carried out during the recovery of Mn-rich sludge. In cycle 1, a mass of 0.01 g of calcined magnesite was mixed with 100 mL of product water from step 2 to raise pH to 8.5-9.5 under continuous sonication. Sonication was allowed to continue for 90 minutes to maximize Mn precipitation. The Mn-rich sludge was filtered using a 0.45 μm pore nitrate cellulose filter membrane. The sludge was reactivated by air drying and milling with a mortar and pestle. During cycle 2, a mass of 0.01 g of the reactivated Mn-rich sludge was mixed with 0.01 g of fresh calcined magnesite and used to treat and raise pH to 8.5-9.5 of 100 mL successive product water from step 2 under continuous sonication for 90 minutes. The Mn-rich sludge was filtered and reactivated. The same process was repeated in cycles 3, 4, and 5, adding 0.01 g fresh at the end.

5.2.4 Characterization of Calcined Magnesite and Metal-rich Sludge

Calcined magnesite and sludge were characterized for elemental composition using handheld X-ray Fluorescence (XRF Brucker S1 Titan, Germany). The sludge was characterized for crystallinity using X-ray Diffraction (XRD D2 Phaser Brucker AXS, Germany), Surface morphology using the Scanning Electron Microscopy equipped with energy dispersive spectrometry (SEM-EDS Thermo Fisher Nova NanoSEM, Holland). A representative and pulverized portion of the sample was measured using a Bruker D2 Phaser diffractometer, with a step size of 0.02° , two theta (Θ) angle, and a counting time of 2 seconds per step, applied over a range of 20 to $90^\circ 2\Theta$. The same method was used for Al-rich sludge after changing the range from 5 to $100^\circ 2\Theta$. This was done because the chromatograms were difficult to identify due to the amorphous nature of the material. XRD analysis of Mn-rich sludge was done with a counting time of one second per step over a range of 5 - $90^\circ 2\Theta$.

5.2.5 Analysis of Metal Species and Sulphate in the Product Water

Product water was analyzed to evaluate the residual metal species and sulphate concentration at each cycle during the treatment of AMD with calcined magnesite and the reuse of sludge. Metal species analysis was determined using Inductively Coupled Plasma Mass Spectroscopy (ICP-MS Agilent 7900, USA), while sulphates were analyzed using ion chromatography (IC Metrohm 850, Switzerland).

5.2.6 Percentage Recovery

The following reaction calculated the percentage removal of metal species and SO_4^{2-} from AMD and product water (eqn 5.1).

$$\text{Percentage recovery (\%)} = \left(\frac{C_{\text{in}} - C_{\text{out}}}{C_o} \right) \times 100 \quad \text{Equation 5.1}$$

Where C_{in} = concentration of metal species in aqueous phase before pH adjustment (mg/L), C_{out} = concentration of metal in aqueous phase after pH adjustment (mg/L), and C_o concentration of specific metal in raw AMD (mg/L).

5.3 Results and Discussions

5.3.1 Metal and Sulphate Removal

Table 5.2 shows the AMD and product water concentrations for steps 1, 2, and 3. In Step 1, the Fe (III) concentration decreases from 45.76 mg/L to ≤ 2.9 mg/L for all cycles. The corresponding % removal for cycles 1-5 were 98.5, 96.9, 93.7, 98.7, and 98.9 %, respectively. Consequently, this indicated that most of Fe (III) was removed from AMD in step 1, suggesting precipitation of Fe-(oxy) hydroxides-rich mineral phases. The highest SO_4^{2-} removal of 64 % achieved in step 1 could be ascribed to the precipitation of schwertmannite or adsorption and substitution of SO_4^{2-} for hydroxide ions on ferrihydrite (Gitari et al., 2010). Al and Mn concentrations remained almost constant, indicating they did not precipitate from AMD. This enhanced the precipitation of pure $\text{Fe}(\text{OH})_3$ from the solution. Wei et al. (2005) reported the decrease Fe^{3+} at $\text{pH} \approx 3.5$ during treatment of AMD with ammonia. Sulphate and Ca remained relatively higher, while Mg levels increased from 52 mg/L (AMD) to 420 mg/L in solution during step 1 (Table 5.2). The increase in Mg levels is ascribed to the dissolution of MgO from calcined magnesite. High levels of Mg, Ca, and SO_4^{2-} could be ascribed to the association of Mg and SO_4^{2-} and partly CaSO_4 that remain in solution due to high solubility products $\{\text{MgSO}_4 (5.9 \times 10^{-5}) \text{ and } \text{CaSO}_4 (4.93 \times 10^{-5})\}$ (Vhahangwele and Gitari, 2019). The trace metals Cu and Ni were observed to be present in treated water, indicating their dissolution from surfaces of calcined magnesite.

In step 2, the pH of product water from step 1 was raised from 3.5 to 5.5 using calcined magnesite (Table 5.2). The concentration of Al^{3+} decreased from 89.5 mg/L to ≤ 0.9 mg/L for all cycles, indicating ≥ 97.9 % removal from the solution. A noticeable decrease in SO_4^{2-} concentration from step 1 to step 2 indicates possible removal of Al with SO_4^{2-} . This indicated the adsorption of SO_4^{2-} on the surface of Al-oxyhydroxides and incorporation into the precipitating Al-oxy hydroxy sulphates. From Table 5.2, the concentration of Ca and Mg remained relatively constant at $\text{pH} \leq 5$ -5.5. The removal % of Zn was ≥ 93.4 % at pH 5-5.5. Cu also showed a decrease in concentration from a maximum of 29 $\mu\text{g/L}$ in step 1 to 1 $\mu\text{g/L}$ in step 2. These results showed that Cu and Zn were precipitating from solution at a pH of 5-5.5. According to Park et al. (2015), Zn hydroxide precipitates from solution at $\text{pH} \approx 7$, while Cu hydroxide precipitates from solution at $\text{pH} \approx 5.3$.

Step 3 shows a decrease in Mn concentration from 20.2 mg/L to ≤ 1.107 mg/L, indicating ≥ 95 % removal (Table 5.2).

Table 5. 2: Chemical composition of product water showing alkali earth, trace elements, and minor elements after treatment of AMD.

Treatment	Cycle	pH	EC (mS/cm)	TDS (g/L)	Fe (mg/L)	Al (mg/L)	Mn (mg/L)	SO ₄ ²⁻ (mg/L)	Mg (mg/L)	Ca (mg/L)	Zn (mg/L)	Cu (µg/L)	Ni (µg/L)
AMD	-	2.3±0.0	7.0±0.05	4.65±0.0	45.8±0.01	90.7±0.71	22.3±1.0	3514±156	52.1±0.89	187±1.1	2.3±0/16	-	-
Step 1	1	3.2±0.1	3.5±0.04	2.5±0.01	0.7±0.057	88.2±8.96	21.8±0.59	1645±4	412.1±9.1	204±14.4	2.04±0.024	19.6±1.6	146.7±3
	2	3.5±0.03	3.1±0.1	2.2±0.06	1.4±0.51	89.7±2.95	22.1±0.1	1558.5±4	416.7±8	203±15.5	1.9±0.07	25.0±6.2	133.8±3.4
	3	3.1±0.1	3.4±0.02	2.3±0.04	2.9±0.44	89.9±3.18	21.6±0.12	1830±12	402.3±13	183±10.8	1.9±0.03	20.4±4.1	130.4±1.7
	4	3.1±0.03	2.8±0.02	2.0±0.02	0.6±0.02	90±0.8	20.8±1.65	2022.8±41	410.3±10.5	196.3±5	1.9±0.03	26.9±1.4	173.4±5.8
Step 2	5	3.2±0.12	2.9±0.006	2.1±0.1	0.5±0.04	89.5±1.4	22.2±0.09	1861±33	420.4±4.9	202±16.8	1.9±0.026	29.5±1.9	149.4±2.1
	1	5.4±0.06	2.2±0.01	1.6±0.01	0.05±0.02	0.09±0.07	21.0±0.17	1080.7±12	428.3±16.3	209.4±11.3	0.1±0.09	6.3±4.4	79.8±7.8
	2	5.1±0.16	3.2±0.07	2.3±0.006	0.04±0.043	0.9±0.89	22.1±0.52	1070±10	420.7±12	198.7±21.8	0.1±0.01	14.3±4	181.6±1.4
	3	5.3±0.2	2.4±0.05	1.7±0.021	0.05±0.005	0.07±0.078	21.4±0.3	1075±5	387.7±19.9	196.3±6.4	0.13±0.03	2.4±0.6	89.2±7
Step 3	4	5.3±0.2	3.2±0.17	2.3±0.04	0.03±0.02	0.02±0.01	20.8±1.1	1031±12	431.3±2	199.7±5.8	0.15±0.04	1.8±0.37	105.7±4.9
	5	5.2±0.05	3.2±0.01	2.4±0.01	0.05±0.02	0.1±0.04	20.2±0.88	1009±8.9	402±12.3	206.7±12.3	0.13±0.03	1.4±0.35	92.4±4.35
	1	9.0±0.08	2.6±0.02	1.8±0.01	0.03±0.025	0.04±0.015	0.08±0.01	901.8±2.8	299.3±18	190±10.5	0.003±0.002	1.2±0.0	4.2±1.08
	2	9.2±0.3	2.8±0.03	2.0±0.02	0.05±0.054	0.04±0.015	1.0±0.09	1030±27	300.7±9.5	171±8.7	0.0039±0.005	2.0±0.56	7.0±1.79
	3	9.5±0.08	2.1±0.03	1.5±0.03	0.04±0.03	0.04±0.017	0.008±0.001	1014±36.9	292±8.9	170.7±4.1	0.004±0.004	1.6±0.44	9.2±0.018
TWQR For irrigation	4	9.4±0.1	3.6±0.01	2.6±0.01	0.02±0.01	0.05±0.03	0.01±0.01	1010±28	284.7±8.3	181±10.5	0.007±0.00	0.5±0.04	3.8±0.32
	5	9.1±0.1	3.9±0.08	2.8±0.06	0.04±0.03	0.004±0.4	0.01±0.02	997.1±9.	309.3±17	173.3±4.0	0.003±0.00	0.03±0.0	1.3±0.52
TWQR For irrigation		6.5-8.4	0-0.4	0-0.26	0-5	0-5	0-0.02	N/L	N/L	N/L	0-1	0-200	0-200
TWQR For Portable		6-9	0-0.7	0-0.45	0-0.1	0-0.15	0-0.05	0-200	0-30	0-32	0-3	0-1000	N/L

The decrease in concentration is due to precipitation of various phases of (MnO_x) with different molar ratios between O and Mn (Seo et al., 2017). The concentrations of Mg and Ca decrease from (ave 413 mg/L; 201 mg/L) to (Mg 296 mg/L; Ca 177 mg/L), respectively, indicating precipitation of Mg and Ca minerals. Similar findings were reported by Vadapalli et al. (2008) during the treatment of AMD with coal fly ash. Sulphate concentration remained relatively high in product water from step 3. This may be explained by the absence of gypsum in sludge due to its high K_{sp} of 2.4×10^{-5} . Gypsum formation is the main mechanism responsible for sulphate removal; however, it tends to occur rapidly on existing gypsum crystals and at pH values of 11-12.5 (Aubé and Lee, 2015). Chatla et al. (2023) also suggested that gypsum precipitation with lime lowers SO_4^{2-} concentrations to a minimum of 1500 mg/L at room temperature. Nickel level decreased from 181.6 $\mu\text{g/L}$ in step 3 to 1.25 $\mu\text{g/L}$ in step 3, indicating precipitation at pH 8.5-9.5.

5.3.2 Comparison to South Africa Water Quality Guidelines

The chemical composition of product water (step 3, cycle 5) was compared with South African water guidelines for irrigation water (Table 5.2). The product water meets the South African guidelines for irrigation water except for alkaline earth metals and SO_4^{2-} which remained high in solution. Mg and Ca species form relatively high solubility salts and remain in solution, possibly as MgSO_4 and CaSO_4 ; thus, other treatment methods are needed to polish the product water. This corroborates with EC and TDS, which exceeded the TWQR for irrigation and potable water guidelines. Product water needs further polishing to recover MgSO_4 and water that meets drinking water guidelines.

5.3.3 Elemental Composition of Metal-rich Sludge

This section presents the elemental characterization of metal-rich sludge from step 1 to step 3. Table 5.3 shows the elemental composition of Fe-rich sludge obtained from step 1, showing the concentration of elements from all five cycles.

Table 5. 3: Elemental composition of Fe-rich Sludge.

Element (%)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Fe₂O₃	33.12	39.55	43.17	42.63	42.23
Al₂O₃	2.26	2.01	3.05	4.37	3.48
MnO	0.12	0.12	0.7	0.12	0.12
MgO	8.5	8.32	9.71	8.32	7.64

From Table 5.3, the Fe rich sludge showed constant increase in % w/w of Fe_2O_3 with continuous recirculation of sludge from cycle 1 (33.12 %) to cycle 5 (42.23 %). The concentration of Fe_2O_3 remained almost constant between cycle 4 (42.63 %) and cycle 5 (42.23 %) indicating an optimum saturation and metal attenuation condition was reached during the reaction. There was a decrease in % w/w of MgO from 85.67 (CM) to a minimum of 7.64, indicating dissolution of MgO in calcined magnesite releasing alkalinity. Minor and traces of Al_2O_3 and MnO were also observed in the Fe rich sludge indicating successful recovery of Fe-rich sludge.

Table 5.4 shows the chemical characteristics of Al-rich sludge obtained after treatment of product water from step 1 with calcined magnesite and re-cycled sludge.

Table 5. 4: Elemental composition of Al-rich sludge.

Element (%)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Fe_2O_3	0.96	0.94	1.11	0.72	0.41
Al_2O_3	32.78	35.39	35.93	35.91	35.93
MnO	0.42	0.27	0.27	0.63	0.67
MgO	10.92	8.20	7.41	9.91	12.11

From Table 5.4, it is observed that Al-enriched sludge increased in % w/w of Al_2O_3 with continuous reuse from cycle 1 (32.78 %) to cycle 3 (35.93 %) and remained almost constant after that, indicating an optimum saturation and metal attenuation condition was reached during the reaction. A decrease in MgO to an average of 9.714 % was observed, indicating its dissolution. The amount of Mg decreases slightly from cycles 1 to 3, indicating that an optimum neutralization condition was reached during the recirculation of Al-rich sludge. However, an increased MgO observed in cycles 4 to 5 could be explained by Le Chatelier's principle in which the addition of fresh calcined magnesite causes an increase in the concentration of unreacted MgO in sludge. Traces of MnO and Fe_2O_3 were also present, indicating the successful removal of Al from Al-rich product water.

Table 5. 5: shows the chemical characteristics of Mn-rich sludge obtained after product water treatment from step 2 with calcined magnesite and reused sludge.

Table 5. 5: Elemental composition of Mn-rich sludge.

Element (%)	Cycle 1	Cycle 2	Cycle 3	Cycle 4	Cycle 5
Fe_2O_3	0.09	0.10	0.11	0.07	BDL
Al_2O_3	0.27	2.08	0.64	0.59	0.09
MnO	16.66	19.50	13.17	13.64	11.64
MgO	43.02	34.93	41.95	41.74	43.21

The Mn rich sludge have showed % weight of MnO (max. 19.55) and MgO (max 43.03). The MnO increases from cycle 1 (16.66 %) to cycle 2 (19.55 %) and decreases from cycle 3 (13.17 %)-5 (11.64 %), implying that more calcined magnesite is needed for enrichment of sludge with MnO rich sludge. The decrease in MnO content from cycle 2 to cycle 5 is due to the solubility of metal hydroxides (Log K_s for Mn 12.7, Mg 11.3) which shows they both precipitates at approximately the same pH (Genik-Sas-Berezowsky and Stiksmas, 2003). This reduces the alkalinity required to treat and neutralise Mn rich water from step 2 resulting in the decrease in concentration of Mn oxides in sludge during re-use of Mn rich sludge. Consequentially, precipitation of MnO mixed with MgO was observed. These results corroborate with Bologo et al. (2012) who observed precipitation of MnO_2 and $Mg(OH)_2$ at pH 9-11.5 during treatment of AMD with magnesium hydroxide. Recovery of Mn bearing minerals mixed with $Mg(OH)_2$ would probably be the shortcoming of treatment of AMD with calcined magnesite with sonication, however the Mn rich sludge can be reused up to cycle 2 or 3 for enrichment with more metals.

5.3.4 Characterization of Magnesite and Sludge by XRD

The XRD Spectra of raw and calcined magnesite are shown in Figure 5.2. Raw magnesite shows mainly $MgCO_3$ at 32.5, 43- and 53.9-degree theta, while calcined magnesite shows peaks of periclase (MgO) peaks at 42.912 and 62.1-degree theta. The increase in MgO observed with increased calcination temperature is due to the decomposition of $MgCO_3$.

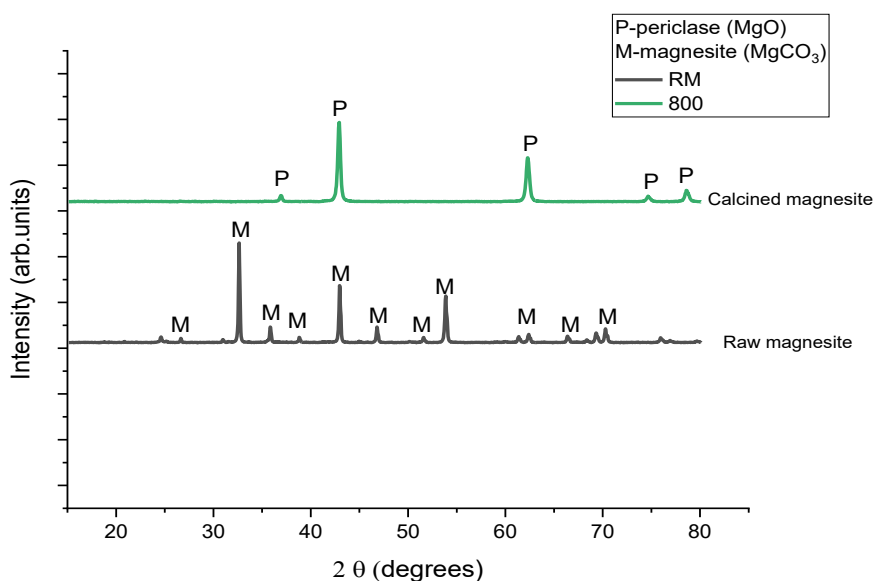


Figure 5. 2: XRD spectra of raw and calcined magnesite.

Figure 5.3 shows XRD spectra of Fe-rich sludge for 5 cycles obtained from step 1. From Figure 5.3, the XRD peaks were highly amorphous from cycles 1-5, evidenced by the diffractograms, which become noisy for confident XRD phase analysis with diffract, Eva.

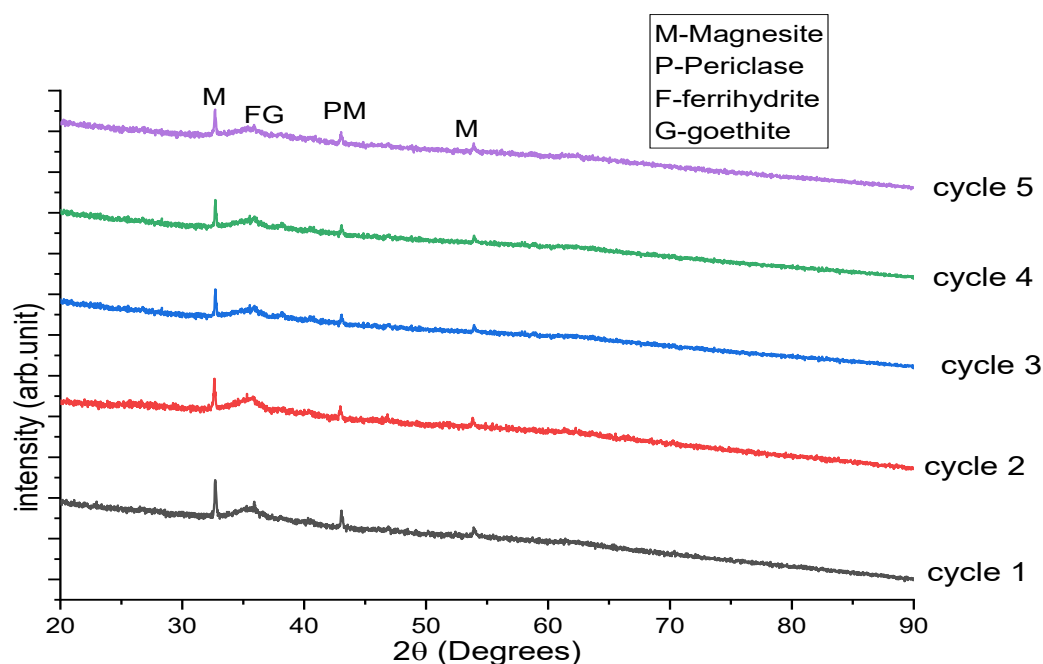
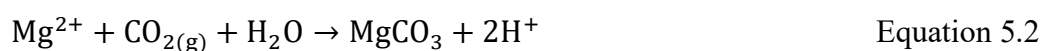


Figure 5.3: XRD spectra of Fe-rich sludge for cycles 1-5.

The XRD Peaks show the presence of magnesite, periclase, goethite, and ferrihydrite from cycles 1-5. All the XRD peaks showed a broad peak at around 35 degrees theta, resembling a 2-line ferrihydrite mineral (Ryan et al., 2017). The presence of ferrihydrite and goethite minerals phases is apparent from the reddish-brown coloration of the sludge. These results are consistent with Ryan et al. (2017) and Seo et al. (2017), who obtained a mixture of amorphous Fe-phases, ferrihydrite, schwertmannite, and, to a lesser extent, goethite after raising the pH of mine water to 3 using NaOH. The results also agree with XRF, which detected high levels of Fe_2O_3 in Fe-rich sludge (Table 5.3). The presence of magnesite could be due to the ingress of CO_2 (eq. 5.2) because the reactions were carried out in an open space. Future studies may recommend inert conditions to prevent reaction with atmospheric CO_2 . The presence of periclase showed the presence of unreacted MgO. XRF detected the presence of MgO (9.71 % .max) in Fe-rich sludge.



The XRD spectra of Al-rich sludge for cycles 1-5. It is shown in Figure 5.4.

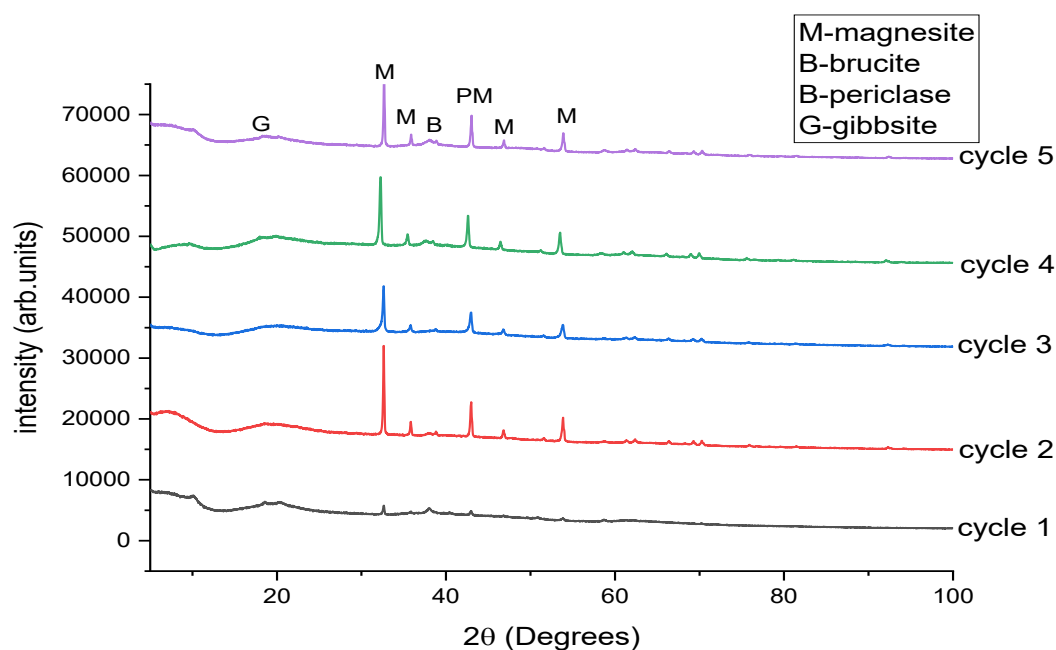


Figure 5. 4: XRD spectra of Al-rich sludge for cycles 1-5.

The XRD spectra showed the presence of magnesite (MgCO_3), brucite [$\text{Mg}(\text{OH})_2$], periclase (MgO), and gibbsite ($\text{Al}(\text{OH})_3$]. The presence of brucite is ascribed to the hydration of periclase (MgO) during neutralization and treatment of AMD. The presence of gibbsite is apparent from the white color of Al-rich sludge. Two broad peaks were observed near 7° and 20° , suggesting the presence of Aluminium hydroxyl sulphates composition with an intermediate between hydrobasaluminite and basaluminite (Sánchez-España, 2008). The broad peaks show that the material is amorphous or close to amorphous.

Figure 5.5 shows the XRD spectra of Mn-bearing minerals obtained after treatment and neutralization of Mn-rich water from step 2 (cycles 1-5). The XRD spectra of cycles 2 and 3 slightly differed from cycles 1, 4 and 5. The peaks in cycles 2 and 3 were not visible due to low intensity; however, when they were plotted alone, they showed distinct peaks of mineral phases. The visible XRD spectra showed peaks of Desautelsite – $\text{Mg}_6\text{Mn}_2(\text{CO}_3)(\text{OH})_{16} \cdot 4\text{H}_2\text{O}$, brucite, Ramsdellite (MnO_2) magnesite and periclase. The mineral phase desautelsite showed co-precipitation of Mg and Mn-oxides because they become insoluble at relatively same pH (Genik-Sas-Berezowsky and Stiksmá, 2003). The mineral desautelsite was also detected by Sánchez-España and Yusta (2015) during the establishment of the precise pH ranges at which the toxic metals were removed from the acidic solutions in the absence of standard ferric and aluminous adsorbent.

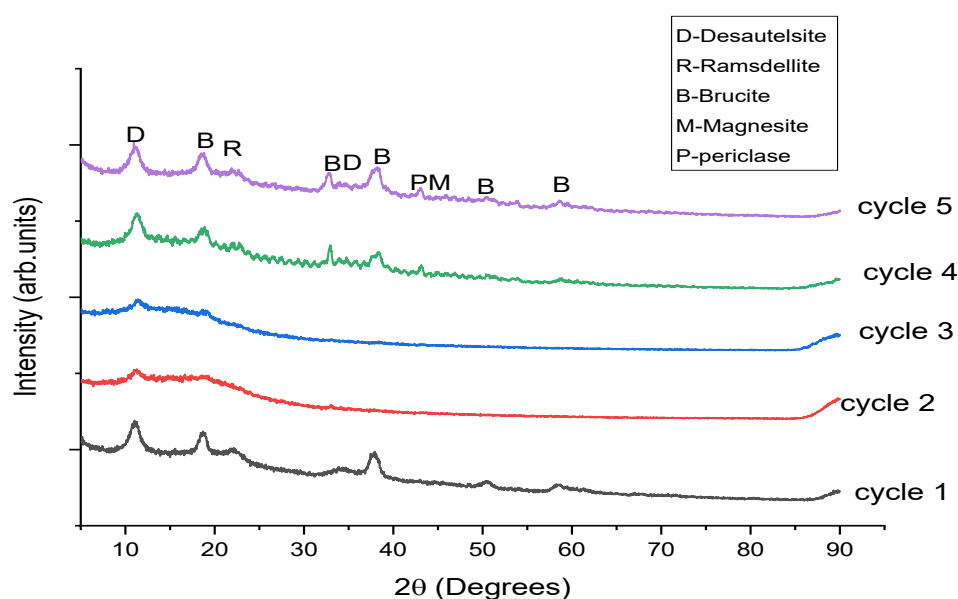


Figure 5. 5: XRD spectra of Mn-rich sludge.

The presence of brucite is observed in Mn-rich sludge from all cycles, indicating precipitation of Mg at the same pH range as Mn. Significant levels of MgO and MnO₂ were detected in Mn-rich sludge in cycles 1-5 by XRF, indicating mixed precipitation of the oxides (Table 5.5). The identification of Ramsdellite (MnO₂), which indicates Mn-oxides' presence, is also depicted in the greyish-black colour of Mn-rich sludge. In their study Hassas et al. (2022) detected the presence of Ramsdellite mineral phase after adjusting pH to pH 9.5 using ammonium hydroxide during the evaluation of recovery of critical elements from AMD obtained from 3 AMD treatment sites in lower Kittanning (USA).

5.3.5 Characterization of Sludge by SEM-EDS

This section covers the SEM and SEM-EDS analysis of Fe-, Al- and Mn-rich sludge. SEM was utilized to better understand the mode of interaction of AMD with calcined magnesite and the formation of mineral phases. This was achieved by assessing the change in morphology of the resulting solid residues and compared with unreacted calcined magnesite. SEM-EDS was utilized to identify the mineral phases of the neutralization reactions semi-quantitatively. SEM-EDS of calcined magnesite and Fe-rich sludge are shown in Figure 5.6.

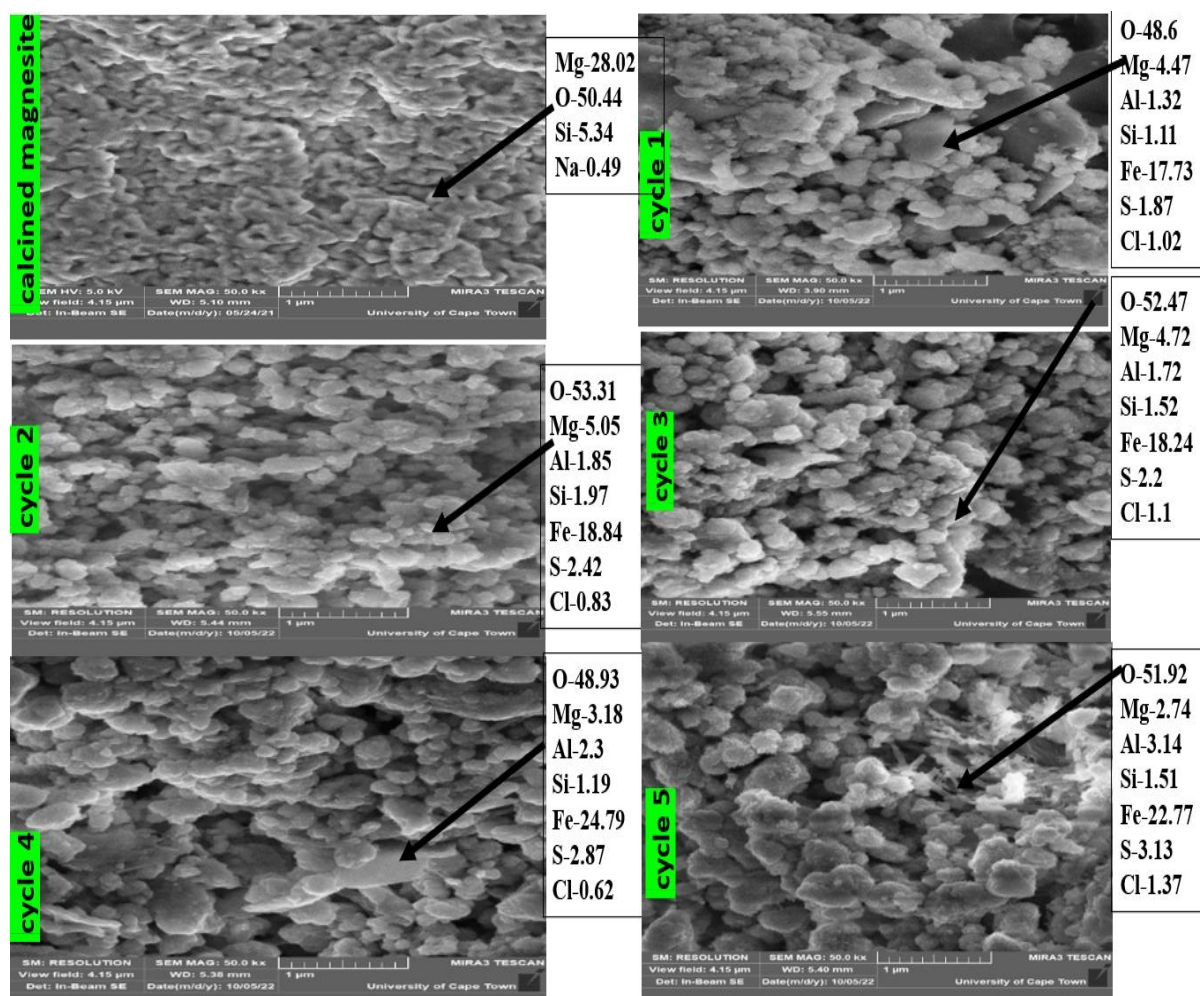


Figure 5. 6: SEM micrographs of Fe-rich sludge with accompanying EDS analysis.

SEM image of Calcined magnesite showed homogeneous material with a cloud-like material with small pores. The SEM images of Fe-rich sludge from cycle 1 show bladeliike material mixed with uneven, rough platelets and spherical structures, providing evidence of precipitates/mineral phases coating the surface of calcined magnesite. The difference with calcined magnesite is the detection of Fe, Al, and S. Fe and O were the major components indicating the precipitation of Fe-(oxy) hydroxides such as goethite and ferrihydrite as detected by XRD (figure 5.3). EDS confirmed this with an O/Fe of 2.74, which conforms with the stoichiometric ratio of goethite. This corroborates with XRF which showed high % w/w of Fe_2O_3 and traces of Al and Mn (Table 5.3). This was further confirmed by the recovery of Fe, which reached 98.5 % (Table 5.2).

The micrographs of Fe-rich sludge from cycles 2 and 3 show some spherical particles that are heavily aggregating together and filling spaces between large spheres, forming a dense mass, which indicates that re-using of Fe-rich sludge could be responsible for enrichment with

mineral phases that are deposited on the surface of calcined magnesite. This was supported by EDS which showed an increase in % w/w Fe from 17.73 in cycle 1 to 18.84 and 18.24 in cycles 2 and 3, respectively. This conforms to high % recoveries of Fe for cycles 2 and 3, reaching 96.9 and 93.7 %, indicating successful selective precipitation of Fe-bearing minerals (Table 5.2). XRD detected the presence of goethite while XRF showed the increase in Fe_2O_3 as sludge is recirculated from cycle 1 to 2 and 3. There was also a noticeable increase in S from cycles 1 to 2 and 3, indicating precipitation of Fe-hydroxy sulfates. This was showed by EDS which indicated Fe/S stoichiometric ratios of 7.79 and 8.2 for cycles 2 and 3, which conforms with schwertmannite. The results corroborate with Vecino et al. (2021) who proposed integration of selective precipitation and ion exchange processes for the separation and recovery of valuable metals from AMD. The slight increase in S could also be ascribed to the adsorption or substitution of SO_4^{2-} for hydroxide ions on ferrihydrite. Vadapalli et al. (2008) suggested that at $\text{pH} \approx 3$, Fe^{3+} precipitates to form amorphous oxyhydroxides and ferric hydroxides, which have large surface areas and are known to adsorb some of the SO_4^{2-} .

The Micrographs from cycle 4 show large spheres aggregating, filling spaces between particles of different shapes. This could be evidence for the enrichment of re-used sludge with minerals phases. Some needlelike particles were observed, indicating the precipitation of goethite mineral with continued sludge recycling. The corresponding EDS showed an increase in % w/w Fe to 24.78 compared to cycle 3, indicating enrichment with minerals. The precipitation of goethite was supported by the O/Fe value 1.9, which was within its stoichiometric ratio. Recirculation of metal-enriched sludge also showed a slight increase in % recovery to 98.7. The images of sludge from cycle 5 showed large spherical particles aggregating together. Some rod-like features which were more clearly visible than those in cycle 4 were observed, indicating precipitation of more goethite with the continued recycling of sludge. The results were in agreement with Aeppli et al. (2019) who reported the transformation of metastable ferrihydrite to needle-like goethite. EDS showed Fe of 22.77 % w/w, which supported enrichment of sludge with minerals as recycling continues. The recovery of Fe reached 98.5% indicating a slight increase with the recirculation of sludge. The O/Fe value 2.28 was observed, which also conforms with the stoichiometric ratio of the mineral goethite. XRD spectra of sludge from cycle 4 and 5 also detected the presence of mineral goethite. The trend of Si observed from EDS of Fe-rich sludge decreased from % w/w of 5.34 in Calcined Magnesite to an average of 1.46 (cycle 1-5). This could be ascribed dilution effect, as the concentration of Fe increases in the sludge, a corresponding decrease in Si is observed.

Figure 5.7 shows the SEM images of Al-rich sludge after treatment of AMD with calcined magnesite and recirculated sludge.

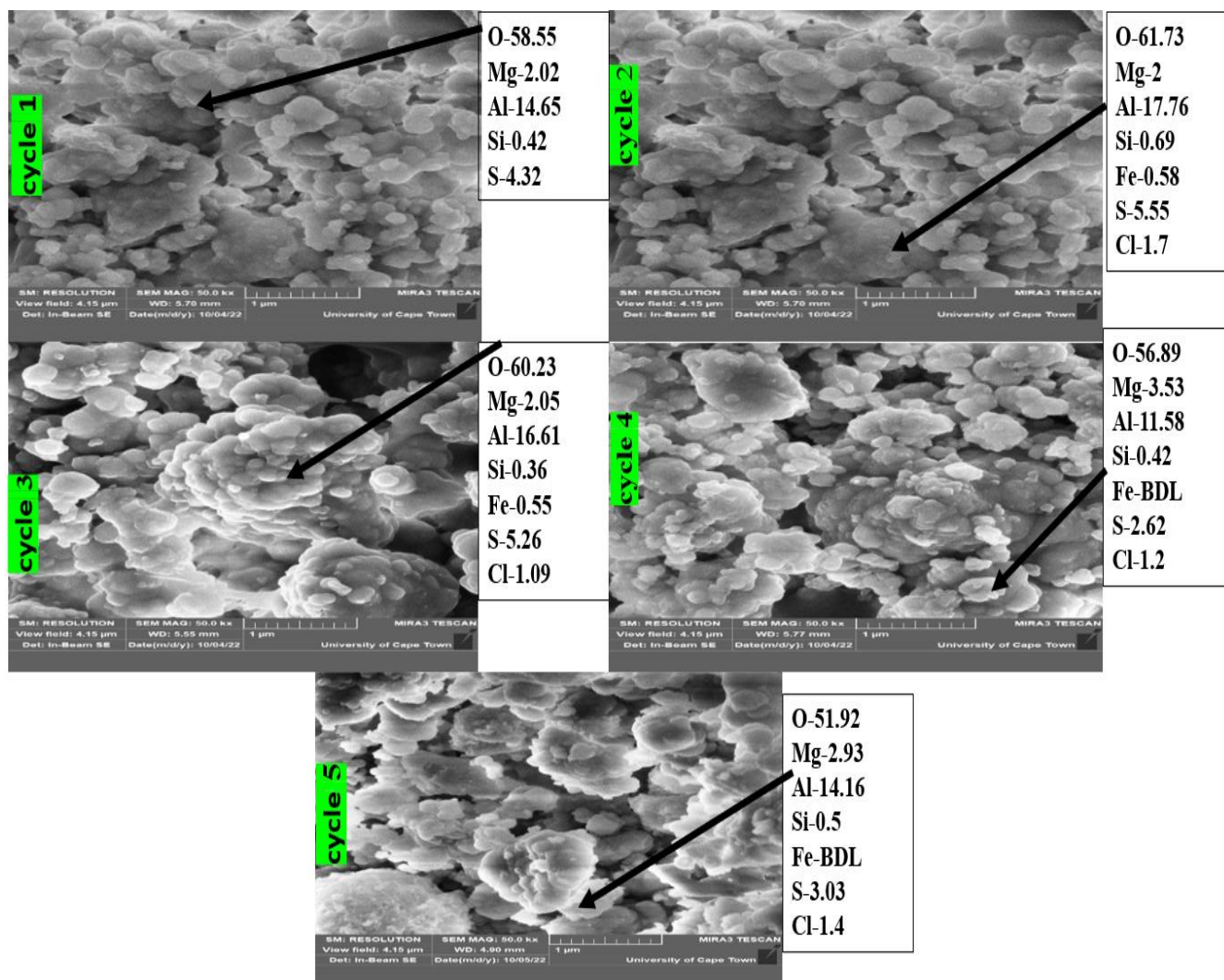


Figure 5.7: SEM micrographs of Al-rich sludge with accompanying EDS analysis.

The morphology of samples from cycle 1 appears to be composed of spheres aggregating together, filling spaces between large spheres. Some large irregular aggregates with small spheres between them are observed. This provides evidence for the formation of precipitates/mineral phases coating the magnesite surface. The difference with calcined magnesite is the detection of Al, O, and S. The detection of Al and O indicated the precipitation of Al-(oxy)hydroxides. This was further confirmed by the recovery of Al, which reached 97.1 %. This was also supported by XRF and XRD, which detected Al_2O_3 and gibbsite, respectively (Table 5.4, Figure 5.7). The detection of S suggested the precipitation of Al-hydroxylsulphates.

The morphology of sludge from cycle 2 shows similarity with precipitates from cycle 1. However, the EDS showed an increase in %w/w of Al to 17.76, indicating enrichment with minerals by reusing sludge. EDS results also corroborate with XRF, which showed an increase in % w/w of Al_2O_3 from cycle 1 to 2. High removal percentage of 97.9 % was also observed in cycle 2. The morphology of Al-rich sludge from cycle 3 shows small spherical particles aggregating, forming platelet-shaped lumps and some large irregularly shaped particles. The corresponding EDS show slight decrease in Al to 16.61 compared to cycle 2. This indicates that the calcined magnesite was approaching its constant neutralization efficiency. This agreed with XRF which showed that the % w/w of Al_2O_3 remained almost constant from cycle 2 to 3. The sludge from cycle 4 showed large spheres aggregating, forming dense masses and platelet-shaped particles. The corresponding EDS decreased in %w/w to 11.58, indicating that the calcined magnesite has reached its optimum neutralization efficiency. Despite the decrease in % w/w of Al, the elements Al and S remained major components of the sludge, showing an Al/S ratio of 4.42 which is near the molar stoichiometric ratio of basaluminite and hydrobasaluminite. This indicated precipitation of Al-hydroxysulphates bearing minerals with recirculation of Al enriched sludge. The results corroborates with Caraballo et al. (2019) who reported the geochemical and mineralogical processes for metalloids and metal movement and attenuation from sulphate-rich AMD controlled by aluminium sulphate precipitation. The % recovery of Al remained at 99% compared to cycle 3. The Al-rich sludge from cycle 5 showed a heterogeneous material characterized by leaf-like, flower-shaped material aggregating to form large platelet lumps, confirming the deposition of new mineral phases. EDS supported this, which showed enrichment with Al, S, and O, suggesting precipitation of Al-hydroxyoxides and hydroxysulphates. The Al/S molar ratio of 4.67 was observed, suggesting the presence of basaluminite and hydrobasaluminite. This also conforms with high % Al recovery 98.5 %. (Table 5.2). A noticeable decrease in S observed in cycles 4-5 could be ascribed to the solubilization of SO_4^{2-} from the surface of Al-oxy(hydr)oxides.

The SEM images of Mn-rich sludge for cycles 1-5 are shown in Figure 5.8.

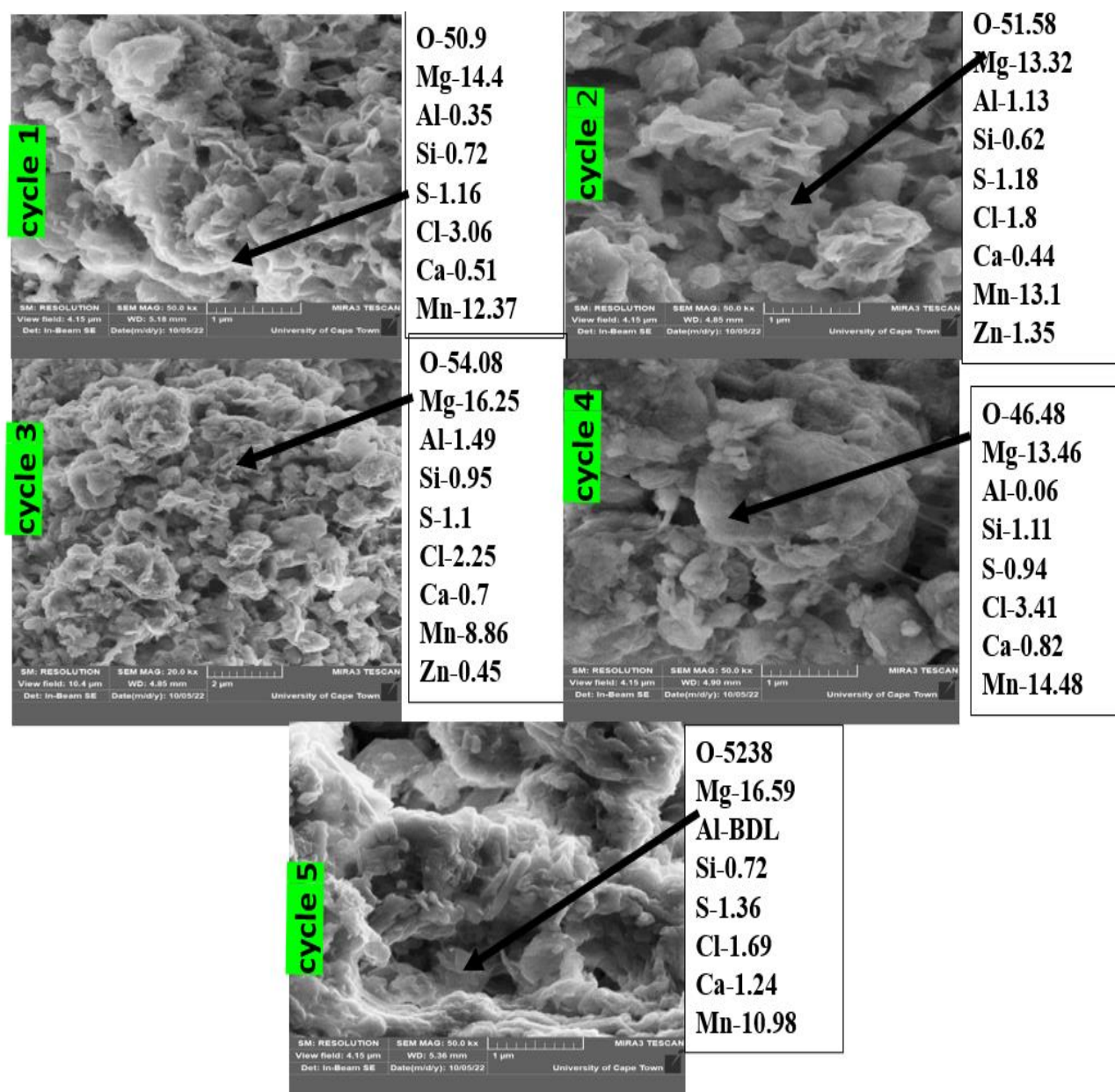


Figure 5.8: SEM micrographs of Mn-rich sludge with accompanying EDS analysis.

Mn-rich sludge from cycle 1 showed irregular material characterized by leaf-like, spongy-shaped particles enriched with Mn, Mg, O, and minor elements of S, Ca, Cl, and Si. This indicates the precipitation of Mg-Mn-(oxy) hydroxides-rich mineral phases. The removal percentage of Mn was 93.8 % and a corresponding decrease in concentration of Mg from 402 to 299 mg/L was observed (Table 5.2), suggesting coprecipitation of these metals. The results corroborate with XRD analysis, which detected the precipitation of mineral phase, desautelsite ($\text{Mg}_6\text{Mn}_2(\text{CO}_3)(\text{OH})_{16}\cdot 4\text{H}_2\text{O}$), brucite ($\text{Mg}(\text{OH})_2$) and Ramsdellite (MnO_2). The results also agree with XRF, which detected high levels of Mg and Mn (Table 5.5). In their study Macingova et al. (2016) reported EDS results which confirmed coprecipitation of Mg and Mn

during the oxidative precipitation of AMD with NaOH and KMnO_4 . The Mn-rich sludge from cycle 2 showed a leaf-like material with some spherical particles. The removal % increase to 94.6 % cycle 1 (Table 5.2), indicating enrichment of sludge with metals due to recirculation of metal rich sludge. This is supported by EDS showed an increase in % w/w compared to cycle 1. Similar results were observed with XRF which showed an increase in % w/w of MnO from cycle 1 to 2. XRD spectra also showed precipitation of Ramsdellite, a Mn bearing mineral phase (Figure 5.5). Cycle 3 showed spongy-like platelet material aggregating, forming irregular lumps. Small spherical particles are observed to be filling spaces between irregularly shaped material, suggesting evidence for the deposition of mineral phases. The recovery % of Mn was 95.9, however, the EDS showed a decrease in % w/w of Mn to 8.8 compared to cycle 2. This is attributed to a reduction in alkalinity due to the precipitation of Mg at the same pH range as Mn. This observation was also supported by XRF which showed a decrease in % w/w of Mn as metal rich sludge is recycled from cycle 2 to 3. Cycle 4 shows irregularly shaped material aggregating together, forming large lumps. EDS and XRF shows a slight increase in MnO content, however a decrease in % removal of Mn to 93.2 % showed coprecipitation with Mg. Cycle 5 showed blade-like material surrounded by spongy and rod-like material with corresponding EDS, indicating a further decrease in the content of Mn. There was a decrease in % removal of Mn to 90.5 % which supports the low levels of Mn in recycled sludge (Table 5.2). The reduction in levels of MnO was also detected by XRF (Table 5.5). However XRF and EDS showed that Mn rich sludge had low purity due to coprecipitation of Mn with Mg.

5.3.6 Comparison with Other Treatment Methods

Table 5.6 compares recovery efficiencies from this study and other selective precipitation processes. The selective precipitation methods used neutralization agents such as NaOH, CaO, Na_2CO_3 , and $\text{Ca}(\text{OH})_2$. The methods showed recovery efficiencies for Al and Fe, similar to the current study. However, recovery efficiencies for Mn from other methods were lower than in this study. The current study evaluated the metal enrichment using the sludge from cycles 1-5. High recovery percentages for cycles 2-5 were observed, indicating metal enrichment in the sludge. However, this was not the case with other methods, which only performed one cycle.

Table 5.6: Recovery efficiencies were compared with other selective precipitation methods.

Table 5. 6: Comparison of recovery efficiencies with other selective precipitation methods.

Technique employed	Experimental conditions	% recovery of elements	Publication Details
Step 1, Cycle 5	Adjusting pH with Sonication and calcined magnesite	98.9 % Fe recovery at pH 3-3.5	Current study
Step 2, Cycle 5	Adjusting pH with Sonication and calcined magnesite	98.5 % Al recovery at pH 98.5	Current study
Step 3, Cycle 5	Adjusting pH with Sonication and calcined magnesite	90.4 % Mn recovery at pH 8.5-9.5	Current study
Sequential selective precipitation	Metals were selectively precipitated from AMD using NaOH, Ca(OH) ₂ , and Na ₂ CO ₃ using stirring.	-greater than 99.2 % of Fe was recovered at pH 3.3 - 70.4-82.2% of Al was recovered at pH-5.5. - 37.8-87.5 of Mn was recovered at pH 8.5	(Seo et al., 2017)
Selective precipitation and Fluidized Bed Homogenization Crystallization (FBHC)	-Fe and Al were recovered via selective precipitation and FBHC, respectively, using stirring as agitation and NaOH as a neutralizing agent.	-99.8 % recovered of Fe at pH 3.8 -98.9 % recovered at pH 5.5.	(Le et al., 2020)
Sequential selective precipitation	Fe and Al were recovered using selective precipitation adjusting pH with NaOH, CaO, Na ₂ CO ₃ , Ca(OH) ₂ and NH ₄ OH.	-98.6 % of Fe was retrieved at a pH of 3.5-7 -97.2 % of Al was recovered at a pH of 6-7	(Wei et al., 2005)
Selective precipitation	Selective precipitation by raising pH with 4M NaOH	More than 98 % of Fe was recovered at pH 3.6	(de Almeida Silva et al., 2017)

5.3.7 Beneficiation potential of study findings

The % w/w of Fe observed in cycle 4 & 5 of metal enriched sludge corroborates with XRF, which detected high levels of Fe_2O_3 (Table 5.3). The values of Fe reported in cycles 4 and 5 were within the range reported by Wang et al. (2021) of 35.2 % after the process of biotechnology to recover iron ore. The results show that the recirculation of Fe-rich sludge results in the enrichment and recovery of Fe sludge, which can be further processed in Fe-making plants to obtain Fe resources, which can be sold to offset treatment costs. The Fe rich sludge can be beneficiated to Fe-oxides for water treatment, catalysts, pigments for painting and steel (Wei et al., 2005). The highest Al value of 17.76 % was observed in cycle 2. These results were within the range reported by Hassas et al. (2022), who recovered 24% Al at pH 5-5.5 while evaluating the recovery of critical elements from AMD. The results showed that the Al-rich sludge can be purified to remove contaminants using methods such as the Bayer process and can be processed further for the synthesis of valuable Al resources, which can be used as catalysts and in water treatment (Hassas et al., 2022). The level of Mn recovered was in range with Hassas et al. (2022), who recovered Mn from AMD. The purity of Mn can be enhanced by oxidative precipitation, and the recovered mineral is applied industrially as catalysts and in the manufacture of batteries (Hassas et al., 2022).

5.4 Conclusions

The experiment aimed to investigate the sequential precipitation of Al, Mn, and Fe from AMD, evaluating the metal enrichment of the sludge during reuse and the product water chemistry. The three metals Fe, Al, and Mn were successfully recovered with high purity through sequential precipitation at pH values of 3-3.5, 5-5.5, and 9-9.5, respectively. The re-use of Fe and Al-rich sludge showed metal enrichment in all cycles, while the re-use of Mn-rich sludge showed enrichment in cycles 1 and 2 due to co-precipitation with Mg. Fe, Al, and Mn were removed to below the guidelines for irrigation water, while Ca, Mg, and SO_4^{2-} remained at higher levels. Future studies recommend the treatment of product water to recover potable water and salts. The high purity of recovered metals suggests their potential use for industrial applications such as catalysts, batteries, fertilizer, and pigment manufacturing.

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Chapter 6

Conclusions and Recommendations

6.1 Conclusions and Recommendations

This work was outlined with the main objective of recovering beneficial products from acid mine drainage through the development of an acid mine drainage integrated management technology.

The specific objectives were:

- To determine hydrogeochemical characteristics of surface waters and sediments impacted by acid mine drainage in eMalahleni, Mpumalanga Province, South Africa
- To compare the effectiveness of sonication and flocculation in the treatment of acid mine drainage using calcined magnesite
- To evaluate the sequential recovery of Fe, Al, and Mn minerals in Acid mine drainage using calcined magnesite ultrasonic treatment.

The above objectives were well accomplished, and the next conclusions for each objective were drawn. Acid mine drainage (AMD) decanting from abandoned coal mines in eMalahleni affects the quality of surface water and sediments. The study found that, AMD was characterized by low pH and high concentrations of SO_4^{2-} and toxic metals, such as Fe, Al, and Mn, which exceeded South African guidelines for wastewater discharge. The hydrogeochemical facies revealed the dominance of the Ca-Mg- SO_4 -Cl water type, which is typical of AMD and rock-water interaction. The geo-accumulation index (I_{geo}) indicated extreme metal pollution in sediments at specific sites. The potential ecological risk index showed low to very high ecological risk due to toxic metals in sediments. The study concluded that AMD impacts surface water and contributes to poisonous metal pollution in sediments. The second section of the work compared the effectiveness of sonication and flocculation in treating and neutralizing AMD with calcined magnesite. Both methods were effective in raising pH to about 10 with a dosage of 1 g/ 100 mL at contact time of 30, 60 and 180 minutes. The p value for pH and % removal was not significant, showing no difference between the two methods. However, at low dosages of 0.1 g/ 100 mL and 0.13 g/ 100 mL, sonication was more effective in raising pH and removal of metals than flocculation at 360 minutes. The P value for pH and metal removal percentage was extremely significant,

indicating superiority of sonication over flocculation. Furthermore, ultrasonication for 360 minutes released significant amounts of Mg, Ca and SO_4^{2-} than flocculation. Sonication can be further applied in AMD treatment at pilot scale for the recovery of Mg, Ca and SO_4^{2-} from AMD. The study found that ultrasonication raised the pH faster and precipitated more minerals than flocculation, resulting in better neutralization of AMD with calcined magnesite.

The third section evaluated ultrasonication in the sequential precipitation of Al, Mn, and Fe from AMD and metal enrichment through sludge reuse for treatment of more AMD and comparing the product water with South African guidelines for irrigation and domestic use. The study found that the Al-enriched sludge increased in the percentage of Al_2O_3 with continuous reuse from cycle 1 to cycle 3. Recycling Fe-rich sludge resulted in the enrichment and recovery of high-purity Fe sludge from cycle 1 to cycle 3. Additionally, the recycling of Mn-rich sludge showed enrichment in cycles 1 and 2 due to co-precipitation with Mg. The %w/w of the recovered metals in enriched sludge have potential use for industrial applications such as catalysts, batteries, fertilizer, and pigment manufacturing. The product water meets the South African guidelines for irrigation and domestic except for Mg, Ca and SO_4^{2-} which remained at higher levels.

The following recommendations were made in line with the findings from this study.

- Remediation of AMD from decant points before discharge into surface water.
- More studies on treating and neutralizing AMD using calcined magnesite with sonication for contact times of 4 hrs, 6 hrs, 10 hrs, 15 hrs, and 24 hrs.
- Further treatment of product water using downstream treatment methods to recover portable water.
- Recovery of Mg and SO_4^{2-} from AMD
- Treatment and recovery of metal oxides from filed AMD using calcined magnesite with sonication.
- Establish a pilot plant whereby Al and Fe sludge is reused for 3 cycles while the Mn rich sludge is recycled for 2 times.

Appendices

Figure 1A below shows the pictures where samples were collected from eMalahleni, Mpumalanga, South Africa

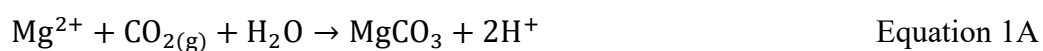


Figure 1A: Pictorial of sites where AMD decant, and AMD impacted water were collected. (S1) decant point where AMD was flowing from an abandoned coal mine (S2) collection of decant points (S3) decant point from the dams, (S4) a point in the river where AMD from dam mixes with river water (S5) Dam (S6) a point downstream of the wetland.

Mineralogical Characterization of solid residues

XRD analysis of solid residues

XRD did not detect Al, Mn, or Fe-minerals (Figure 2A), mainly due to their low concentration or amorphous nature. XRD analysis of solid residues revealed the presence of magnesite (MgCO_3) and brucite $\text{Mg}(\text{OH})_2$. The formation of brucite from AMD is due to the dissolution of MgO . Magnesite formation could be due to the ingress of carbon dioxide during neutralization (equation. 1A).



The peak of MgO was absent in the residues, indicating its dissolution. Masindi et al. (2016) observed similar results during the neutralization of AMD with magnesite.

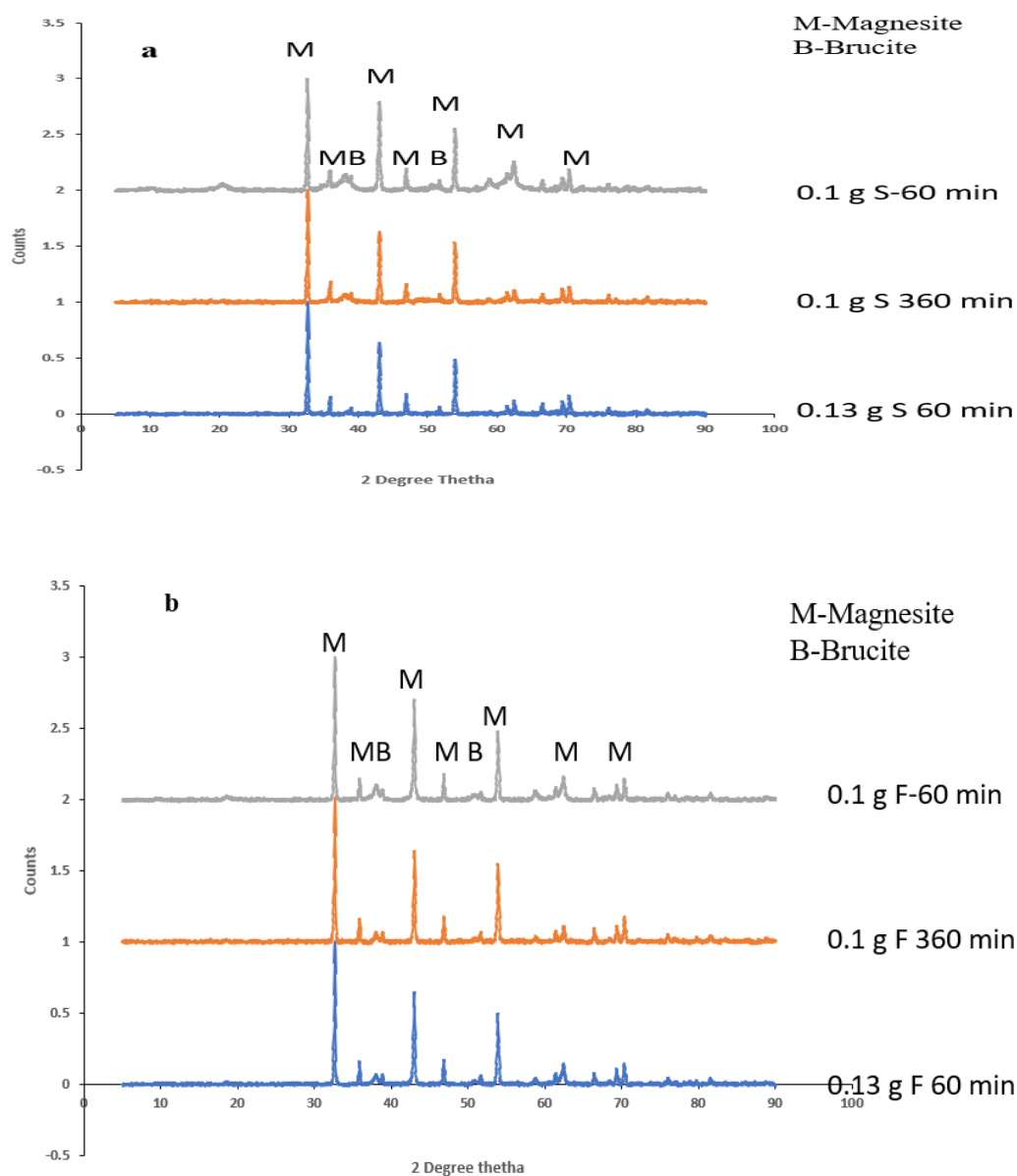


Figure 2A: (a) XRD Spectra of solid residues obtained after treatment of AMD using calcined magnesite with sonication (b) XRD Spectra of solid residues obtained after treatment of AMD using calcined magnesite with flocculation.

SEM-EDS Analysis of Sludge

During experiments, the PHREEQC geochemical model predicted the precipitation of Al, Fe, and Mn-hydroxyoxides; however, XRD detected the minerals. SEM-EDS was used to semi-quantitatively identify these minerals. Figure 2A shows the SEM and corresponding SEM-EDX profiles for samples from the solid residues obtained with flocculation and sonication,

respectively. SEM and SEM-EDX profiles of magnesite calcined at 800 °C are shown in Figure 2 for comparison. Figure 2 shows that the morphology of calcined magnesite is a nano-homogeneous material with small circular particles. Calcined magnesite was observed to be enriched with Mg and O, which indicates that it is MgO. From Figure 2A, 0.1F-60 (flocculation of 0.1 g/100 mL for 60 minutes) solid residues are homogeneous and consist of small circular particles coated with cemented precipitates. The difference with calcined magnesite is the detection of Al, Fe, and S. The detection of Al, Fe, and S would probably show some Al, Fe-hydroxy sulphates mineral-rich phases. There is a decrease in Mg and Si, which shows their dissolution from the calcined magnesite. From Figure 2A, the morphology 0.1F-360 (flocculation of 0.1 g/ 100 mL for 360 minutes) did not differ much from 0.1F-60. Al, Fe, and S were detected, indicating the presence of Al-Fe (oxy)hydroxides and hydroxy sulphates. The morphology of 0.13F-60 (Flocculation of 0.13 g/ 100 mL for 60 minutes) resembles that of 0.1F-60. However, it also shows that some didn't react with AMD. EDX shows Al, Fe, and S enrichment, indicating Al-Fe hydroxy sulphates mineral phases (Table 1A). From EDX results, it is observed that % of Fe is decreasing in solid residues. The decrease in the % of Fe is attributed to the removal of $\text{Fe}(\text{OH})_3$ at $\text{pH} \approx 3-3.5$ (Letjiane et al., 2019)

From Figure 3A, 0.1S-60 (sonication of 0.1 g/ 100 mL for 60 minutes) solid residues are homogeneous, and the surface is smooth with precipitates cementing together. It was observed to be enriched with Fe, Al, and S, and a small % of Ca was detected. This shows the presence of Al, Fe-hydroxyoxides, and hydroxysulphates mineral phases. However, the % of Fe and Al was higher in 0.1S-60 than in 0.1F-60, which indicates sonication was more effective at this dosage and time. From Figure 3A, 0.13S-60 (sonication of 0.13 g/ 100 mL for 60 minutes) solid residues appear to be homogeneous material with precipitates cementing together. Its difference with calcined magnesite is the presence of Al, Fe, S. This shows the presence of Al-Fe hydroxy sulphates. There is also a corresponding increase in Mn, possibly due to adsorption on Al-hydroxyoxides. The morphology of 0.1S-360 (sonication of 0.1 g/ 100 mL for 360 minutes) shows larger agglomerates of particles coated with precipitates. EDX analysis of the residues shows enrichment with Al, Fe, and some smaller % of S and Ca. A corresponding increase in Mn is likely due to adsorption on precipitates.

Table 1A: SEM-EDS of Reacted solid residues of selected ratios.

Element	800CM	0.1F-60	0.1S-60	0.1F-360	0.1S-360	0.13F-60	0.13S-60
O	50.44	57.7	52.08	43.03	51.36	50.78	53.35
Mg	28.02	9.85	5.68	3.91	8.01	7.81	11.4
C	15.72	18.48	25.65	34.45	25.89	30.62	20.48
Al		5.83	8.3	6.95	7.32	5.84	6.47
Si	5.34	1.06	0.51	0.75	0.79	0.46	0.39
S		2.49	2.31	2.38	1.45	1.35	3.64
Ca			0.18		0.23		0.22
Mn					1.35		2.19
Fe		4.6	5.48	8.53	3.69	3.14	1.85

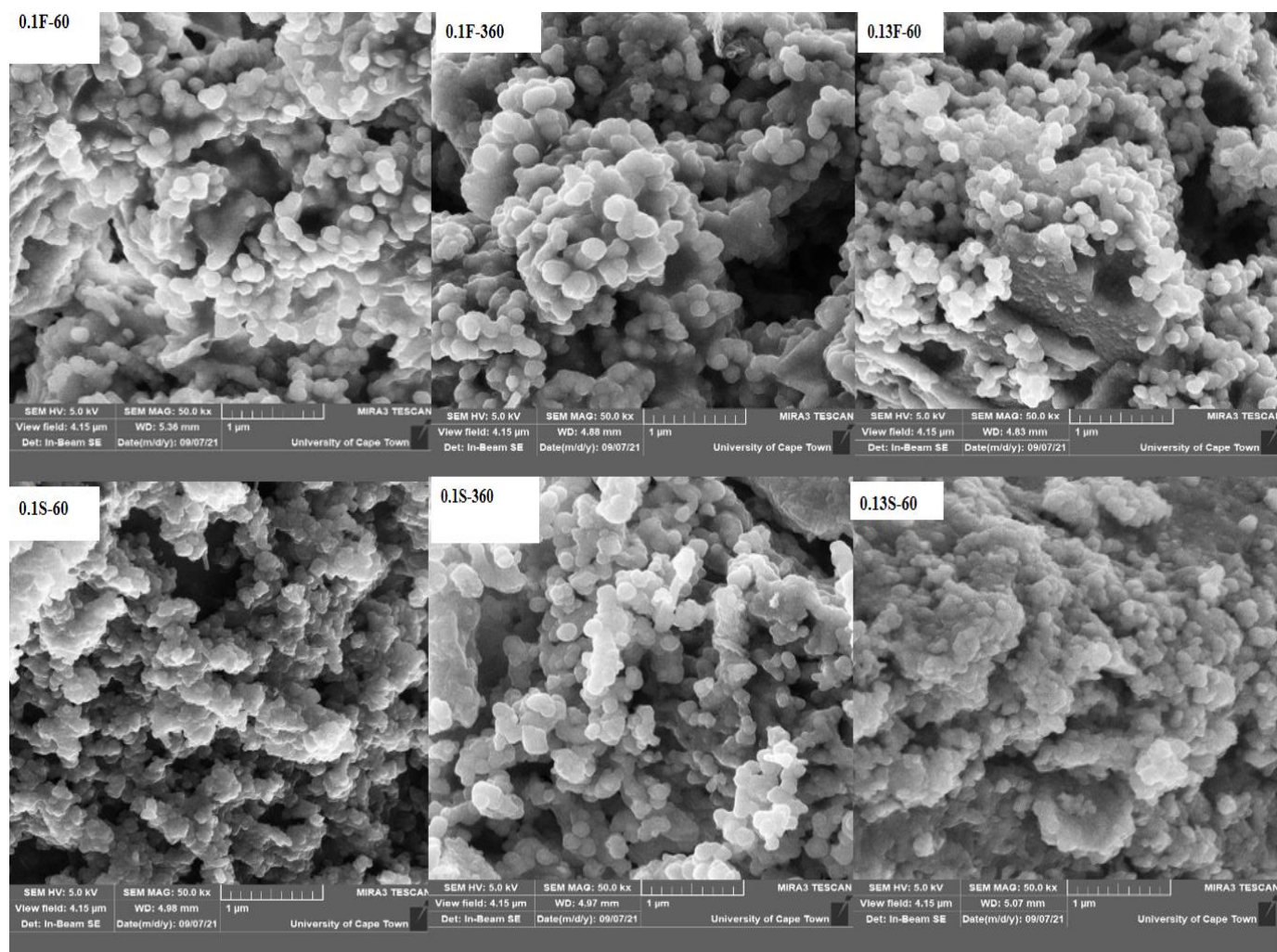


Figure 3A: SEM Images of solid residues obtained with flocculation and sonication (**0.1F-60**) Image of solid residues obtained after flocculating 0.1 g/100mL for 60 minutes (**0.1F-360**) Image of solid residues obtained after flocculating 0.1 g/100 mL for 360 minutes (**0.13F-60**) Image of solid residues obtained after flocculating 0.13 g/100 mL for 60 minutes (**0.1S-60**) Image of solid residues obtained after Sonicating 0.1 g/100mL for 60 minutes (**0.1S-360**) Image of solid residues obtained after Sonicating 0.1 g/100 mL for 360 minutes (**0.13S-60**) Image of solid residues obtained after Sonicating 0.13 g/100 mL for 60 minutes.

Table 2A: Chemical Composition of reacted solid residues from selected calcined magnesite ratios.

Element	800°C	0.1F-60	0.1S-60	0.13F-60	0.13S-60
MgO	100.00	16.785	9.864	14.94	18.249
Al ₂ O ₃	0.146	14.084	24.13	18.972	17.884
SiO ₂	2.25	0.337	0.709	0.947	0.881
S		7.935	6.73	4.826	5.830
CaO	0.994	0.449	0.51	1.075	0.879
Fe ₂ O ₃	0.123	14.724	14.389	9.864	9.488
K ₂ O	0.052	0.027	0.025	0.026	0.017
TiO ₂	0.022	0.029	0.087	0.017	0.036
Cr	0.022	0.029	0.031	0.014	0.014
Sr	0.005		0.002	0.004	0.003
Cu	0.001		0.005	0.007	0.04
Ni	0.016	0.020	0.023	0.040	0.047
MnO	0.013	0.086	0.262	0.530	1.024
Mo				0.001	0.001
Cl	0.056	0.029	0.034	0.034	0.051
Zr	0.001		0.002	0.0	0.002
V	0.012	0.037	0.033	0.033	0.029

Table 3A: Chemical composition of product water for optimization of time and dosage

Sonication										
Element	AMD	Time			dosage					
		30	60	180		0.2	0.6	1.2		
pH	2.25	9.62	9.04	8.3		8.15	9.76	10.09		
Fe	43.85	0.033	0.023	0.035		0.017	0.019	0.12		
Al	70.0	0.026	0.7	0.161		2.7	0.022	0.191		
Mn	20.8	0.004	0.004	0.007		7.6	0.007	0.049		
Zn	2.21	0.002	0.004	0.0024		0.003	0.001	0.006		
SO ₄ ²⁻	3820									
Flocculation										
pH	2.25	10.28	10.34	9.78		8.21	9.7	9.63		
Fe	43.85	0.026	0.09	0.028		0.011	0.19	0.0002		
Al	70.0	0.3	0.04	0.296		2.7	0.02	0.0009		
Mn	20.8	0.008	0.003	0.038		4.6	0.005	0.001		
Zn	2.21	0.007	0.004	0.0026		0.001	0.007	BDL		
SO ₄ ²⁻	3820									

Table 4A: p value and % removal for major elements during optimization of calcination temperature (temperature 800 °C)

sonication		Flocculation	P Value
pH	9.63	10.3	0.1274
Element	% removal	% removal	
Fe	99.9	99.9	0.5961
Al	99.5	99.8	0.9192
Mn	99.9	99.9	0.0981
SO ₄ ²⁻	65.2	64.4	0.0003

Table 5A: p value and % removal for major elements during optimization of contact time (time 30 minutes)

sonication		Flocculation	P Value
pH	9.62	10.28	< 0.0001
Element	% removal	% removal	
Fe	99.9	99.9	0.5961
Al	99.5	99.6	0.021
Mn	99.9	99.9	> 0.999
SO ₄ ²⁻	64.3	64.4	0.7665

Table 6A: p value and % removal for major elements during optimization of dosage (dosage 0.6 g/ 100 mL)

sonication		Flocculation	P Value
pH	9.76	9.7	
Element	% removal	% removal	
Fe	99.9	99.6	0.0373
Al	99.9	99.9	0.8832
Mn	99.9	99.9	> 0.9999
SO ₄ ²⁻	65.6	68.1	0.0012

Table 7A: p value and % removal for major elements during variation of pH and dosage (0.1g / 100 mL for 60 minutes)

sonication		Flocculation	P Value
pH	4.23	4.29	0.0171
Element	% removal	% removal	
Fe	98.65	97.1	0.0002
Al	56.02	53.42	0.0021
Mn	2.6	1	0.0017
SO ₄ ²⁻	28.1	55.41	< 0.0001

Table 8A: p value and % removal for major elements during variation of pH and dosage (0.13 g/ 100 mL for 60 minutes)

sonication		Flocculation	P Value
pH	6.52	6	0.1274
Element	% removal	% removal	
Fe	99.8	99.96	0.0014
Al	99.9	99.94	0.6239
Mn	63.6	16.5	< 0.0001
SO ₄ ²⁻	52.98	55.8	0.0464

Table 9A: p value and % removal for major elements during variation of pH and dosage (0.1 g/ 100 mL for 360 minutes)

sonication		Flocculation	P Value
pH	6.4	4.74	< 0.0001
Element	% removal	% removal	
Fe	99.95	96.2	< 0.0001
Al	99.9	99.95	0.750
Mn	1.9	5.3	< 0.0001
SO ₄ ²⁻	0.07	54	< 0.0001

Table 10 A: p value and % removal for major elements during variation of pH and dosage (0.13 g/100 mL for 360 minutes)

sonication		Flocculation	P Value
pH	7.15	6.15	< 0.0001
Element	% removal	% removal	
Fe	99.9	99.9	0.2417
Al	99.7	99.9	0.0369
Mn	32.0	18.89	0.008
SO ₄ ²⁻	12.8	45.0	< 0.0001