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THE DEVELOPMENT OF SOIL LIMING STRATEGIES FOR IRRIGATION WITH ACID MINE DRAINAGE

By

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DECLARATION

I declare that the dissertation, which I hereby submit for the degree M.Sc. Soil Science at the University of Pretoria, is my own work and has not previously been submitted by me for a degree at this or any other tertiary institution.

Signed: VOD Moodley



Date: November 2023

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ABSTRACT

Alternative mine water management and treatment strategies are becoming important due to limitations placed on natural water resources. This is because of the high cost and energy requirements associated with treating mine water. Irrigation with gypsiferous mine-influenced waters has been well demonstrated and is indeed successful on a commercial scale and it is expected that large-scale rollout is eminent. An alternative mine water management and treatment strategy is to irrigate with untreated acid mine water (AMD) on soil that has been treated with liming material. Hence, the aim of this study is the development of soil liming strategies for irrigation with acid mine drainage. This has been investigated by undertaking titrations to quantify the additional acidity generated by Fe, Al, and Mn present in AMD and how this buffers the neutralising potential of hydrated lime. The first hypothesis states that iron is expected to have the most significant buffering influence on the neutralising potential of hydrated lime compared to aluminium and manganese as its oxidation, hydrolysis and precipitation is strongly acidifying. This hypothesis was accepted. It was demonstrated that Fe has the potential to buffer the neutralisation potential of hydrated lime because of two acid generating influences, namely the ferric and ferrous iron buffers with each of them influencing the potential of hydrated lime below a neutral condition. The titration experiments also showed that 2.96 mmol of acidity can be generated per mmol of Mn in solution, 2.56 mmol of acidity can be generated per mmol of Fe in solution and 3.36 mmol of acidity can be generated per mmol of Al in solution. These quantifications form the basis for the development of soil liming strategies for irrigation with AMD because it enables a determination of the amount of liming material needed to neutralize the acidity of AMD to be applied to soil. Neutralization tests were also done for this study to determine the influence of the abovementioned metals on the potential of varying particle size fractions of calcite and dolomite to dissolve and neutralise AMD. The second hypothesis states that iron will limit the potential of larger particle sizes of agricultural limestone to neutralise AMD to a greater extent than aluminium and manganese as these larger particles are likely to be armoured by iron precipitates. This hypothesis is rejected. It was shown that the dissolution of the larger particle size fractions of calcite and dolomite is specifically influenced by Al precipitates and then by Fe precipitates during the neutralization of AMD.

The former precipitate has a more prominent influence on restricting the potential of larger particle size fractions of calcite and dolomite to neutralize AMD. The latter precipitate further contributes to the armouring of the particles and a restriction in the dissolution of the medium and coarse agricultural limestone particle size fractions. The results of the neutralization tests show that neutralizing mine impacted water (AMD) is largely dependent on the particle size fraction of the liming material used. Decreasing the particle size fraction of calcite and dolomite increased their dissolution efficiency when used for neutralization. This facilitates the selection of an appropriate particle size fraction, applicable to neutralization of AMD for use as irrigation. Lastly, a soil column experiment was done to determine the potential of strategically liming soil with agricultural limestone to neutralise AMD to support a favourable rooting environment for crop growth. The final hypothesis for this study states that localising agricultural limestone within the top half of the soil profile improves the spatial contact with AMD and the potential for neutralization compared to incorporating limestone throughout the soil profile which reduces the spatial contact with AMD and the potential for neutralization. This hypothesis is rejected. It was shown that the placement position of the agricultural limestone within a soil profile does not have an influence on the neutralization of AMD to support a favourable rooting environment for crop growth. However, it is suggested that the type of agricultural limestone used in the soil profile, which can influence neutralization of AMD, is an important factor to consider. Therefore, it is recommended that liming materials with a slow dissolution efficacy be mixed throughout the soil profile. This is likely to increase the temporal contact between the liming material and AMD which contributes to a longer period to facilitate neutralization of the soil solution. The outcome of this study is used as a guideline for the development of soil liming strategies for irrigation with AMD as follows. 1) Calculate the total amount of acidity that Fe, Al, and Mn could generate as a neutral condition of the AMD is reached. 2) Utilise the appropriate size fraction of liming materials typically used in agricultural applications, which is calcite and dolomite. 3) Consider the influence of the dissolution efficacy of the agricultural limestone within a soil profile on neutralizing AMD. 4) Implement a monitoring program to track sulphate concentrations in the irrigation water as well as the soil moisture. 5) Incorporate an appropriate fertilizer management plan to address primary nutrient deficiency.

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CHAPTER 1: INTRODUCTION

1.1 Background

Coal mining operations and activities, which mainly occur in the Mpumalanga Province, are known contributors to the generation of Acid Mine Drainage, commonly referred to as AMD (Surender, 2009; Mathu, 2013). Pyrite (FeS_2), commonly associated with coal and gold resources, is oxidised when exposed to the atmosphere and water during mining (Shabalala et al, 2017). This process forms sulphuric acid and is environmentally threatening as it is responsible for the formation of AMD (Surender, 2009; Ochieng et al, 2010).

Anthropogenic factors threaten the earth's water resources with mining activities considered to be a key contributor. In addition, an increasing human population also exerts pressure on water resources for food production and domestic use. AMD can be released into natural water resources through seepage into groundwater or by direct discharge into surface water bodies such as streams and rivers, (McCarthy, 2011). Several incidents of flooding of underground mines and AMD discharge have been reported in South Africa including from the coal mining areas of Mpumalanga (Madiseng, 2019).

The Olifants River Catchment encompasses a significant portion of Mpumalanga's coal fields and has been polluted by active and closed mines in this area over several years. The receiving streams are contaminated with very high dissolved metal and salt loads and are characterised by low pH (The Water Wheel, 2011). Various dams and irrigation schemes are linked to the catchments in which coal is mined; therefore, management of water quality is crucial for long term sustainability.

Water is a precious resource that should be protected and used with extreme care. Beyond the obvious reason that most living organisms cannot function without it, the country depends on it for economic growth and development. South Africa is prone to water shortages and is one of the 30 driest countries globally, with the expectation that water demand will exceed supply as early as the year 2025 (Grewar, 2019). Many of the rivers in South Africa are heavily utilised, with few being in a satisfactory state.

Generally, the country's water infrastructure is in poor condition (Donnenfeld et al, 2018) and the high demand for water is attributed to the increase in the human population, urbanisation, and irrigated agriculture (Donnenfeld et al, 2018). Introducing AMD into the aquatic environment can toxify these systems, which can damage their ecology and degrade water quality (de Beer, 2005). However, there are strategies to prevent this, such as through proper storage and treatment of such waters (Akciil and Koldas, 2005).

Treatment of mine impacted water is commonly achieved through neutralization with hydrated lime ($\text{Ca}(\text{OH})_2$) and / or limestone (CaCO_3) in High-Density Sludge (HDS) treatment plants (Murdock et al, 1993; Johnson and Hallberg, 2005). Johnson and Hallberg (2005) further state that there are some disadvantages with this neutralization process such as:

- the production of gypseous water (dominated by calcium and sulphate ions) that is quite saline,
- financially demanding,
- produces sludge as a by-product with related disposal issues due to its potentially hazardous status.

Releasing neutralized mine water into catchments is unsustainable because of its saline character and high concentration of sulphate ions, which may increase salt loads in receiving water bodies (du Plessis, 1983; Madiseng, 2019). If this water is to be discharged, it may require additional desalinization treatment. This can be achieved by technologies such as reverse osmosis (RO), which has high operating costs and an excessively high energy footprint (van der Laan et al, 2014; Grewar, 2019).

Furthermore, the brine by-product from the RO process needs proper storage and further treatment. The advantage of this treatment technology, however, is that the water is converted to potable status, which enables domestic use. Due to the constraints placed on natural water resources, alternative mine water management strategies are vital.

An early steady-state chemical equilibrium modelling study by du Plessis (1983) directed interest towards using lime treated acid mine water for irrigation. It was theoretically demonstrated that the use of lime treated AMD for irrigated crop production is feasible, and the benefit of this approach is that it can minimize the salinity of catchment water bodies.

Lime and limestone treated mine water is rich in calcium and sulphate, and when used for irrigation, precipitates a significant amount of gypsum in the soil that is not considered deleterious to the terrestrial environment (du Plessis, 1983). The advantage of this approach is that water which has been neutralized by lime and / or limestone can be used without needing further treatment.

Based on the pioneering work of du Plessis in 1983, several researchers conducted field-scale trials to test the potential of neutralized acid mine water for irrigation. Their efforts successfully showed that it is practical to irrigate a variety of agricultural crops, which may be safely consumed (Jovanovic et al, 1998; Annandale et al, 2001).

An alternative approach is to directly irrigate with untreated acid mine water (van der Laan et al, 2014). This approach is in response to the rising water treatment costs making sustainable mine closure very expensive. It is also expected that the agricultural sector will consider utilising rehabilitated land and contaminated and/or low-quality water sources as irrigation for crop production as populations expand and more pressure is exerted on existing agricultural resources (McGladdery, 2019).

This has prompted investigations of soil preconditioned by alkaline materials such as hydrated lime or limestone as a form of passive treatment. If this approach is feasible, mine water treatment could well be revolutionised with expensive HDS plants not needed in many instances (van der Laan et al, 2014). Furthermore, an alternative mine water management strategy could be developed as well.

When AMD is neutralized with hydrated lime and/or calcium carbonates, transition metals are sequestered from the AMD by precipitating them, thereby reducing their soluble concentrations (Mackie and Walsh 2015, van der Laan et al, 2014). Increasing the pH of AMD enables the oxidation of metals, particularly ferrous iron, and manganese, and stimulates their hydrolysis and precipitation (Jones et al, 2014; van der Laan et al, 2014).

The oxidation converts the metals to their highest environmentally stable oxidation states (Rosso and Morgan, 2002), which has a buffering influence on the ability of the alkaline sources to increase pH (Sun et al, 2000; Totsche et al, 2006; Espana et al, 2006). The highest oxidation state of manganese is +7 and iron is +6. This buffering influence is caused by the metals, which generate additional acidity as they hydrolyse and precipitate.

Armouring can also occur when calcium carbonates are used as the neutralising substance because the metals precipitate as minerals, which can cover the surfaces of calcium carbonates and limit their neutralization efficiency (Skousen et al, 1999; Johnson and Hallberg, 2005; Cravotta et al, 2008; Cravotta and Trahan, 1999). Aziz et al (2008) mentions that the precipitation of iron minerals has a more significant armouring influence on limestone than other mineral precipitates. Furthermore, it is understood that the extent to which armouring influences the neutralisation efficiency of calcium carbonates is dependent on its particle size.

The armouring influence could have consequences when soil that has been preconditioned with calcium carbonate is used as a form of land treatment where soil deterioration could occur through acidification. Bearing in mind these consequences, the foundation of this dissertation is the development of soil liming strategies for irrigation with AMD.

A key assumption of this study that is precluded from the scope of the investigation is that crops will be able to grow and be productive under irrigation with acidic waters if the strategic liming can alleviate any influence of soil acidity and if crops are not susceptible to scorching.

This has been investigated by undertaking laboratory-based experiments against this background, considering calcium hydroxide (hydrated lime) and calcium carbonates (calcite and dolomite) in an aqueous environment to assess the potential of different sources of alkalinity to neutralise AMD.

The first phase of this study quantifies the additional acidity generated by Fe, Al, and Mn commonly found in AMD, and the extent to which this buffers the neutralising potential of hydrated lime.

The second phase determined the influence of the abovementioned metals on the potential of varying particle size fractions of calcite and dolomite (normally used in agriculture to ameliorate soil acidity) to dissolve and thereby neutralise AMD.

These two phases of the study provided guidance on the final phase, which determined the potential of strategically liming soil with agricultural limestone to neutralise AMD to support a rooting environment for crop growth. A soil column experiment was conducted to determine this potential.

1.2 Problem Statement and Research Questions

The oxidation of iron and manganese, and the hydrolysis and precipitation of these metals as well as aluminium during the neutralization of AMD generates acidity, which influences the efficiency of the liming materials used to treat this water. This may affect pH levels and the quantity of material required to neutralize the AMD and precipitate metals.

The armouring of calcium and calcium / magnesium carbonates may restrict their dissolution and neutralizing potential, which could have deleterious effects on a soil environment if AMD, which is applied as irrigation, is not sufficiently neutralized. Failure to achieve *in situ* neutralization of AMD applied as irrigation can be damaging to the soil environment and crop production.

When this acidic source infiltrates soil, protons (H^+ ions) may well act as a driver of mineral weathering. This promotes the dissolution of soil components, including clays, and increases the ionic concentration of aluminium and base cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) in the soil solution and seepage water (Garcia et al, 2008). Therefore, introducing AMD to the terrestrial environment can lead to soil acidification.

Soil fertility can be influenced as essential nutrients can be depleted due to cation leaching or release from the exchange complex (Agbenyeku et al, 2016). However, other elements could enrich the soil through their precipitation as different minerals or their adsorption.

There needs to be sufficient contact of the liming materials with the AMD applied to the soil for neutralization to occur. Therefore, the spatial placement of the liming material within the soil profile will be an important factor as this may influence the extent to which neutralization occurs and the impact on soil acidification, thus affecting the profile.

Based on this, the following questions need to be addressed to guide the development of soil liming strategies for irrigation with AMD:

- I. What influence do the acid generating abilities of Fe, Al and Mn have on the neutralization of AMD with hydrated lime?
- II. What influence do Fe, Al and Mn have on the neutralization of AMD with agricultural limestone of varying particle size fractions?
- III. What influence does spatial placement of agricultural limestone in a soil profile have on neutralizing AMD to support a favourable rooting environment for crop growth?

1.3 Hypotheses

The hypotheses for this study are:

- I. Iron is expected to have the most significant buffering influence on the neutralising potential of hydrated lime compared to aluminium and manganese as its oxidation, hydrolysis and precipitation is strongly acidifying.
- II. Iron will limit the potential of larger particle sizes of agricultural limestone to neutralise AMD to a greater extent than aluminium and manganese as these larger particles are likely to be armoured by iron precipitates.
- III. Localising agricultural limestone within the top half of the soil profile improves spatial contact with AMD and the potential for neutralization compared to incorporating the limestone throughout the soil profile which reduces spatial contact with AMD and the potential for neutralization.

1.4 Aim and Objectives

The principal aim of this study is the development of soil liming strategies for irrigation with AMD. This has been determined by undertaking phased laboratory-based experiments. The objectives of this study are to determine:

- I. The additional acidity generated by the precipitation of metals, which commonly occur in AMD like iron, aluminium, and manganese and the extent to which this buffers the neutralising potential of hydrated lime.
- II. The effect that these metals have on the potential of varying particle size fractions of calcite and dolomite to dissolve and enable neutralization.
- III. The potential of the placement position of agricultural limestone in a soil profile to neutralize AMD and support a favourable rooting environment for crop growth.

CHAPTER 2: LITERATURE REVIEW

2.1 Coal Mining and its Association with Acid Mine Drainage (AMD)

The discovery and rise of gold mining in the late 19th century in the well-known Witwatersrand Region of South Africa was the forerunner to the coal mining industry in the coalfields of the Mpumalanga Province. This region is famous for its intensive mining activity, which focuses on the exploration, extraction, and beneficiation of coal to supply local consumers as well as international markets (Fosso-Kankeu, 2016).

The coal mining industry is specifically geared towards providing the main source of energy in South Africa. Although there is pressure away from coal to renewables, coal fired power stations will supply much of our energy for the foreseeable future. Apart from being used for electricity generation by Eskom, it is also used as a feedstock to produce a large fraction of the country's liquid fuels and chemicals by Sasol (McCarthy, 2011; Mathu, 2013; Fosso-Kankeu, 2016; and Shongwe, 2017). In this regard, the South African economy is heavily dependent on the coal mining industry as it positively influences exports, domestic consumption, GDP, and employment (Shongwe, 2017).

Despite the economic benefits associated with this industry, coal mining activities are also damaging to the environment. This is attributed to air pollution through dust fall-out, emissions of particulate matter and toxic gases, and the degradation of biodiversity caused by clearing and stripping of lands in mine planning and establishment. There is also the physical and chemical deterioration of surface and ground water sources as well as land (Laisani and Jegede, 2019).

In any water constrained country, the quality of water determines its suitability for use. Surface and groundwater pollution is a common environmental issue that our country faces. This is evident in the upper reaches of the Olifants River Water Management Area, where extensive coal mining activities has resulted in poor quality water (Hobbs et al, 2008).

Coal mining activities, which include surface and underground mining operations, have considerable impact on the environment. One such impact is the exposure of sulphate containing minerals to the atmosphere, which produces acid through its oxidation. This acid is easily mobilised and can leach to the surrounding environment, which gives rise to the term acid mine drainage (AMD) (Ochieng et al, 2010; Llyod, 2002; Nkambule and Blignaut, 2012).

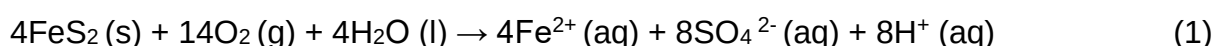
Therefore, the largest environmental liability attributed to the coal mining industry is the formation of AMD (Hobbs et al, 2008). Coal, and its associated geology, contain sulphate-bearing minerals, which produces AMD. An array of these minerals can occur depending on the mineralogy of the coal field. However, the most common mineral is pyrite (an iron sulphide mineral, FeS_2) globally regarded as the key precursor to the formation of AMD (Bailey, 2016).

Surface and underground mining methods expose significant rock masses to the atmosphere thus bringing large quantities of sulphide bearing minerals into contact with the atmosphere and the consequent generation of AMD (Akcil and Koldas, 2005; McCarthy, 2011; Shabalala et al, 2017). AMD can develop in opencast mine settings as well as underground workings of mines. The extent of this is usually insignificant when the mine is still operational and water levels are kept artificially low by pumping.

With the cessation of mining activities and the closure or abandonment of mines, pumping of water that has filled pits, voids or tunnels stops. The rebound of the water table or level can lead to contaminated water decanting at the surface and influencing groundwater bodies (Johnson and Hallberg, 2005).

2.2 The Basic Chemistry of AMD

The oxidation of pyrite principally leads to the formation of AMD. However, there are intermediate steps involved during the reaction process (Coetzee et al, 2007). The first step involves the oxidation of pyrite as shown by equation 1.

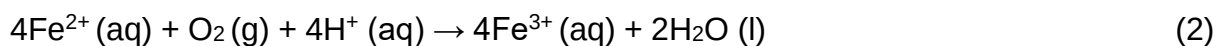


When pyrite is exposed to oxygen and water, oxidation occurs to form sulphate and ferrous iron (Fe^{2+}). During this reaction, water hydrolyses and generates hydrogen ions (H^+), which contribute to the acidity of the water (Johnson and Hallberg, 2005).

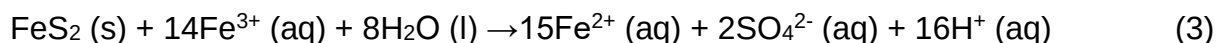
The dissolution of pyrite liberates hydrogen as well as sulphate ions, which can interact to form sulphuric acid. The formation of sulphuric acid strengthens the acidic nature of the water with the potential to increase the acidity of the drainage resulting in low pH levels.

It is common of AMD derived from pyrite to have a pH ranging between 2 and 4 (Skousen et al, 2019; du Plessis, 1983; Sheoran and Sheoran, 2006; Vahedian et al, 2014). The sulphuric acid is subsequently able to facilitate the dissolution of other mineral constituents by weathering them at faster rates compared to normal geological processes. This leads to an effluent of combined acidic nature with high metal and sulphate concentrations (de Beer, 2006).

The second phase in the formation of AMD involves the oxidation of ferrous to ferric iron (Fe^{3+}), which is illustrated by equation 2.



The oxidation of ferrous to ferric iron, is accelerated at low pH conditions by microbiological activity and consumes acidity during the oxidation reaction. This produces ferric iron, which becomes the main oxidant for pyrite dissolution that produces additional sulphate, ferrous iron, and hydrogen ions contributing to further acidity of the mine water (equation 3) (Akcil and Koldas, 2005).

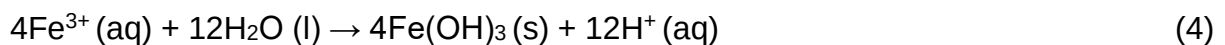


Below about a pH of 3, the oxidation of pyrite by ferric iron is about ten to a hundred times faster than by oxygen. It is commonly known that microorganisms like *Acidithiobacillus ferrooxidans* or *Leptospirillum ferrooxidans* obtain energy by oxidizing Fe^{2+} from sulphides to Fe^{3+} by catalysing this reaction (Bailey, 2016; Dold, 2014).

The final phase in the formation of AMD involves the hydrolysis and precipitation of ferric (Fe^{3+}) complexes (equation 4) and minerals, which are referred to as iron oxyhydroxides. Mine impacted waters that are rich in ferrous and ferric iron, can result in the precipitation of several iron minerals.

Ferrihydrite, or “yellow boy” as it is colloquially called because of its ochre appearance, can form and this precipitate is responsible for giving mine impacted water its distinctive rust-like appearance (de Beer, 2005). Additionally, schwertmannite, goethite, or jarosite can also precipitate, depending on the pH-Eh conditions and the availability of key elements like potassium. These secondary minerals like jarosite, schwertmannite and ferrihydrite are meta-stable and can gradually transform into goethite, a thermodynamically stable mineral phase.

The hydrolysis and precipitation of iron oxyhydroxides and, to a lesser degree, jarosite, will produce most of the acid in this process. If the pH is less than about 2, ferric hydrolysis products like $\text{Fe}(\text{OH})_3$ are not stable and Fe^{3+} will remain in solution (Dold, 2014). However, it is agreed that $\text{Fe}(\text{OH})_3$ does not exist and instead the first product to form is ferrihydrite $(\text{Fe}(\text{III})_{10}\text{O}_{14}(\text{OH})_2)$.



Besides the acidity commonly associated with AMD, toxicities of certain metals are a severe threat to the quality of the water. The oxidation of pyrite drives the acidic nature of mine water, which can dissolve other minerals. The water ultimately becomes contaminated showing common characteristics of AMD including high acidity levels, high salinity levels, high sulphate concentration as well as concentrations of potentially toxic metals and metalloids.

AMD usually contains high concentrations of iron, aluminium, and manganese as its dominant metal constituents. Other metals of environmental significance can also occur, which is dependent on the mineralogy of the associated geology and mineral deposit (Santomartino and Webb, 2007; Robb and Robinson, 1995; de Beer, 2005). It is important to acknowledge that the vast array of potential metals, high acidity, and high sulphate concentration associated with AMD, prohibits its release into the environment and makes it unlawful (Feng et al, 2004; Potgieter-Vermaak et al, 2006; Gitari et al, 2006).

2.3 The Management, Treatment and Potential Re-Use of AMD

Acid mine water can be considered a toxic effluent to natural environments, which is acidic and contains high metal and sulphate concentrations. One approach to lessen its impact on the environment is to manage it by containing it in specifically designed storage facilities (Trumm, 2010; Akcil and Koldas, 2005).

Typically, pollution control dams (PCDs) are used for this (Best practice guideline – A4: Pollution Control Dams, 2007). The purpose of these dams is to minimise the influence of polluted water on the surrounding environment. According to the Best practice guideline – A4: Pollution Control Dams (2007), these dams assist in:

- Reducing the extent of pollution by separating clean and dirty water.
- Capturing and retaining in PCDs, the dirty water contribution that cannot be discharged due to water quality constraints.
- Managing this water through recycling, re-use, evaporation and / or treatment.

Therefore, coupled with managing AMD, its treatment is equally important to prevent negative impacts on the environment. Improvement in its quality is possible through active and / or passive treatment systems. These systems aim at decontaminating the water to a desired quality, which authorises its discharge into the environment (Robb and Robinson, 1995; Kleinmann et al, 1998; Gaikwad and Gupta, 2007).

According to Johnson and Hallberg (2005), active treatment methods are the most utilised approaches to treat AMD in the mining industry because they are frequently used in operational as well as in post closure circumstances (Taylor et al, 2005). Although these systems are effective, they usually incur high capital and operational costs and exert financial pressure on mining companies.

Active treatment systems fall into two main categories: fixed plant and *in-situ*. The first category comprises conventional active treatment plants that are fixed in location and typically require pumping of AMD to the plant. *In-situ* active treatment approaches use portable land-based or water-based systems to conduct treatment within or adjacent to an affected water body (Taylor et al, 2005).

According to Taylor et al (2005), active systems use the following main chemical and physical processes during the treatment of AMD:

- pH control;
- electrochemical concentration;
- biological mediation (sulphate reduction);
- ion exchange;
- absorption or adsorption, and
- flocculation and filtration.

Active treatment is commonly referred to as chemical treatment (Kirby, 2014), because it involves adding inorganic alkaline reagents to the AMD (de Beer, 2005). This is done to control the pH of the water and increase it to levels that promote the precipitation of metals, often as hydroxide complexes (Taylor et al, 2005).

The successful implementation and sustainability of pH control and / or precipitation treatment systems requires the selection of a reagent appropriate for treatment (Taylor et al, 2005). Conventional alkaline reagents used for active treatment of AMD include (Saha and Sinah, 2018; Taylor et al, 2005):

- hydrated lime ($\text{Ca}(\text{OH})_2$);
- quicklime (CaO);
- caustic soda (NaOH);
- soda ash (Na_2CO_3);
- ammonia (NH_3);
- magnesium oxide or hydroxide ($\text{MgO}/\text{Mg}(\text{OH})_2$), and
- mineral carbonates (calcite, dolomite, magnesite and witherite).

While controlling pH is a common and cost-effective treatment method of AMD, there are some issues that should be considered with this approach. A particularly important consideration is the management of sludge generation (Johnson and Hallberg, 2005; Sukati et al, 2018; Taylor et al, 2005). This includes (Taylor et al, 2005):

- Disposal costs which can be as high as treatment costs;
- Possible re-mobilisation of unstable precipitates contained in treatment sludges, necessitating re-treatment of waters;

- Possible delay in sludge formation due to incomplete oxidation at the treatment site, resulting in off-site (downstream) deposition of sludge, and
- Downstream transport and deposition of sludge formed from in-situ treatment of AMD affected channels or streams.

Another potential issue is the desired end use of the water. If the effluent is used in agriculture, then the type of alkaline reagent used is an important consideration. In this instance, the use of sodium containing alkaline reagents is not advisable because of potentially excessive sodium concentrations in the irrigation water. This can negatively influence the physical properties of soil.

Discharging the treated water is unsustainable because of its saline character and high sulphate concentration, which can increase salt loads in the receiving environment (du Plessis, 1983; Madiseng, 2019). If this water is to be discharged, it may require additional desalinization treatment.

This can be achieved by technologies such as reverse osmosis (RO), which has high operating costs and an excessively high energy footprint (van der Laan et al, 2014; Grewar, 2019). The brine by-product from the RO process will also require proper storage and further treatment. However, the advantage of this treatment technology is that the water is converted to potable status, which enables domestic use.

Alternative mine water management and treatment strategies are vital due to the constraints placed on natural water resources coupled with the high cost and energy requirements associated with treating mine water. Since the late nineties, irrigation with gypsiferous mine influenced waters has been successfully demonstrated on a commercial scale, and large scale roll out is expected to be imminent.

One approach that has been suggested is to directly irrigate with untreated acid mine water on soil that has been treated with an alkaline reagent (van der Laan et al, 2014). This approach is in response to the rising costs of water treatment, making sustainable mine closure very expensive. If irrigating with AMD is a feasible option, it could potentially eliminate the need for treatment plants as well as the need for waste disposal measures.

Mine water management and treatment could be revolutionised, with active water treatment technologies becoming obsolete. It is also expected that the agricultural sector will consider utilising rehabilitated land and contaminated and / or low-quality water sources as irrigation for crop production, as populations expand, and more pressure is exerted on existing agricultural resources (McGladdery, 2019).

However, if irrigation with untreated AMD is not feasible, irrigation with neutralized water could still serve as an effective alternative for utilizing mine water without needing to treat it any further, thereby saving exorbitant financial and energy costs of RO (Madiseng, 2019).

2.4 Neutralizing AMD Using Hydrated Lime

Several alkaline reagents can be used as options to chemically treat AMD by neutralizing it. However, neutralization using hydrated lime is the most common reagent (Aube and Zinck, 2003; Aube and Lee, 2015; Maree et al, 2013). This is attributed to its efficiency in removing metals from AMD combined with the comparatively low costs to alternative reagents (Aube and Zinck, 2003).

The primary principle underpinning the treatment of AMD is linked to the insolubility of various metals under alkaline conditions. Therefore, by controlling the pH of the water to a predetermined endpoint, the metals begin to precipitate. The end-point pH referred to above depends on the chemical composition of the AMD and the metals it contains.

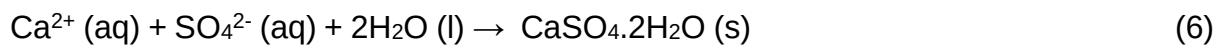
Where AMD contains iron, zinc, and copper, a pH of approximately 9.5 is required to enable the precipitation of these metals, whereas other metals like manganese, nickel and cadmium require a higher pH of approximately 11 (Aube and Zinck, 2003; Aube and Lee, 2015). Several metals can be precipitated by pH control including lead, aluminium, chromium-III, antimony, silver, selenium, thallium and beryllium (Taylor et al, 2005).

The first step in the neutralization of AMD involves the dissolution of hydrated lime. This increases the pH by supplementing hydroxide ions as described in reaction (5).



The increase in pH creates alkaline conditions, which decrease the solubility of most metals in AMD and enabling their precipitation. Due to metal precipitation, the resulting water quality contains very low residual metal loads. Similarly, as the metals precipitate the ionic balance is maintained through the solubilisation of calcium from the dissolution of hydrated lime (Aube and Lee, 2015).

This assists in the removal of additional sulphate ions through the partial precipitation of gypsum (equation 6), which is a by-product of the neutralization process (Aube and Zinck, 2003; Geldenhuys et al, 2003). However, the precipitation of gypsum is kinetically slow, and the water needs to be super-saturated with respect to gypsum (Aube and Lee, 2015).

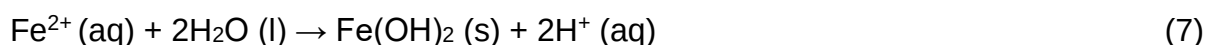


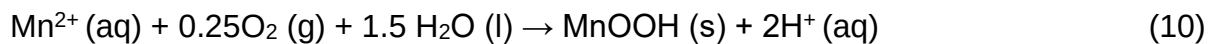
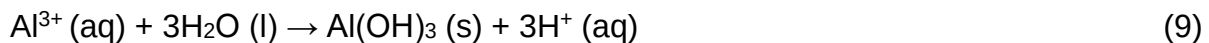
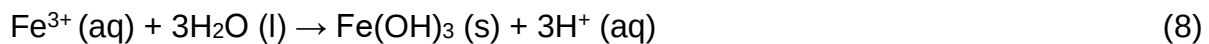
2.5 The Effect of Iron, Aluminium and Manganese on Neutralizing AMD

AMD usually contains significant concentrations of iron, aluminium and manganese as its primary metal constituents. According to Zipper et al (2018) and Pillay (2000) these metals act as a source of acidity when present in solution. This is attributed to their hydrolysable nature. As the pH of AMD is raised, hydroxide ions are available to react with each of the metals.

This causes hydrolysis reactions to occur, which converts the metals from a soluble to insoluble phase (Zipper et al, 2018). Theoretically, these reactions result in the precipitation of metal hydroxides (see equations 7 to 10), which removes the metals from solution. During this process H^+ ions are also released, which contributes additional acidity to the solution (Pillay, 2000).

This is commonly referred to as latent or mineral acidity (Taylor et al, 2005) and the potential of these metals to generate latent acidity constrains changes in pH that would otherwise occur in response to alkaline additions (Zipper et al, 2018). Therefore, the acid generating potential of these metals buffers the neutralization of AMD.





However, in acid-sulphate rich waters like AMD the precipitation of metals (specifically iron and aluminium) frequently occurs as hydroxysulphate minerals (Sanchez-Espana et al, 2016). During the precipitation of these minerals, the metals also hydrolyse and contribute acidity to the solution. However, the amount of acidity generated by the precipitation of hydroxysulphate minerals can differ from the acidity generated by the formation of metal hydroxides as shown in equations 7 to 9.

Equation 8 shows that the formation of an $\text{Fe}(\text{OH})_3$ has the potential to generate 3 mols of acidity during its formation. However, the first solid product likely to form is ferrihydrite which can generate about 7 times more acidity than the formation of $\text{Fe}(\text{OH})_3$. This is because the formation of ferrihydrite results in more water hydrolysis than the hypothesised product of $\text{Fe}(\text{OH})_3$. It should also be noted that nearly all the precipitates are non-crystalline, amorphous mixtures of many metals present in the AMD with several of the ions adsorbed and co-precipitating (Chermak et al, 2004; Zinck, 2006).

A generalized titration curve of AMD is provided below, which is divided into four phases. This curve conceptualises the buffering influence of Fe, Al and Mn on the neutralization of AMD (Uhlmann et al, 2004).

Phase I of the titration curve shows that as the pH increases from 2.55 to 2.9, the AMD shows a decrease in the free hydrogen ion concentration. The remaining alkalinity added is used for the deprotonation of hydrogen sulphate as well as for the homogeneous hydrolysis of iron (Uhlmann et al, 2004).

In phase II of the titration curve, the pH is buffered around 3 by the hydrolysis of Fe(III) with bound sulphate (Uhlmann et al, 2004). This causes the precipitation of iron hydroxysulphate minerals, which is typically schwertmannite (Botes & Steyn, 2022) in AMD. The precipitation of this amorphous mineral contributes latent acidity, which results in a plateau in the titration curve around a pH of 3.

This plateau shows the buffering influence of iron, as Fe(III), on neutralizing AMD and is referred to as the ferric iron buffer (Espana et al, 2006; Totsche et al, 2006). After the plateau, there is a weakly buffered transition where the pH increases to 4.3. In phase III of the curve, the pH is buffered between 4.3 and 5.5 due to the hydrolysis of Al with bound sulphate (Uhlmann et al, 2004).

This causes the precipitation of aluminium hydroxysulphate minerals, which is typically basaluminite or hydrobasaluminite (Sanchez-Espana et al, 2011). The precipitation of these amorphous minerals contributes latent acidity which results in the plateau in the titration curve. This demonstrates the buffering influence of aluminium on neutralizing AMD.

Phase IV of the curve shows that the pH increases relatively linearly around pH of 5.5. According to Uhlmann et al (2004) the precipitates were minor and mainly contained manganese oxides. The buffering mechanism in this phase was coupled to the solid phase; if precipitates were removed, the pH increase was steeper. This implies that, less alkalinity had to be added, and buffering was much less effective.

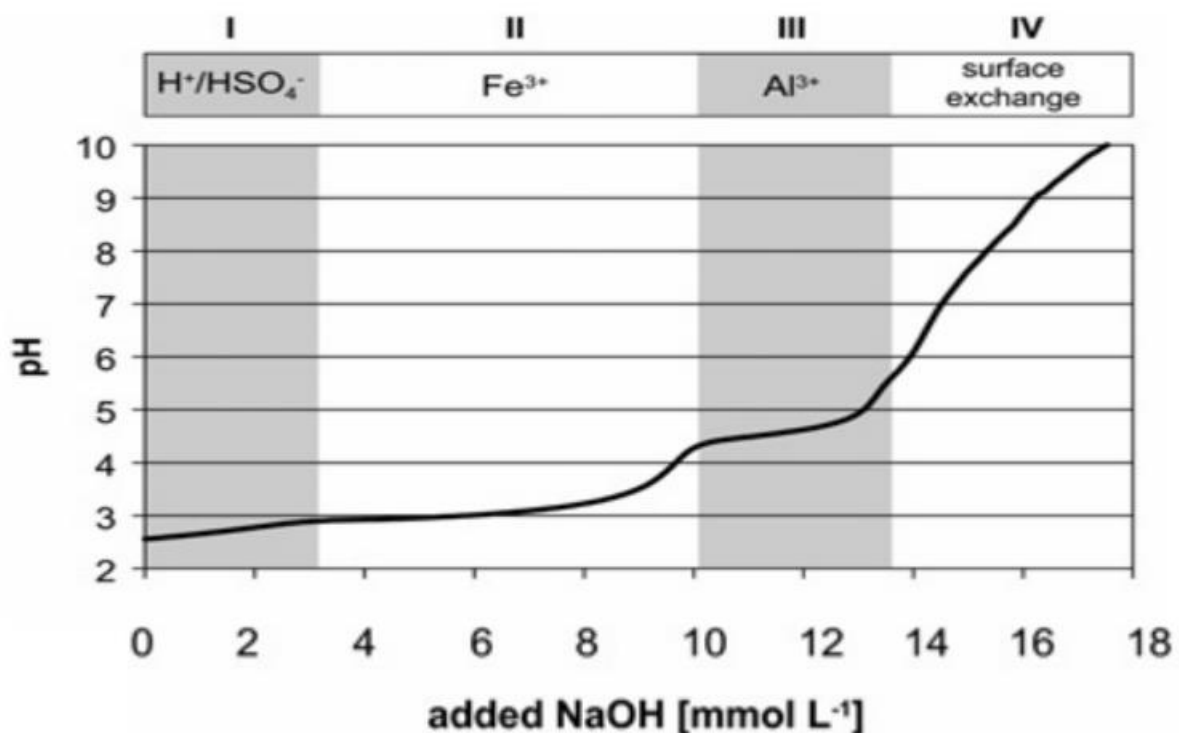


Figure 2.1: Generalised titration curve to conceptualise the buffering influence of Fe, Al and Mn on the neutralization of AMD (Adapted from Uhlmann et al, 2004).

2.6 The Effect of Armouring of Limestone on Neutralizing AMD

According to Maree and du Plessis (1994), limestone can be considered as an alternative source of alkalinity to neutralize AMD. Using calcite or dolomite as a neutralizing agent is supported by financial saving benefits, accessibility, safety, and ease of handling (Potgieter-Vermaak et al, 2005; Seodigeng et al, 2017). The disadvantages of this reagent are slow dissolution kinetics and decreased neutralizing effectiveness with time (Seodigeng et al, 2017).

The decreased neutralizing efficacy is attributed to its inclination to being armoured by metal precipitates and gypsum. This develops an external coating of Al^{3+} , Fe^{3+} , Mn^{2+} and SO_4^{2-} based scales, which impede transport of reactants and products between the surfaces of limestone and the AMD (Skousen et al, 2000; Watten et al, 2005).

Neutralizing AMD with limestone removes acidity, which automatically favours metal precipitation reactions to occur. Treating AMD in this manner will inevitably cause the precipitation of ferric minerals around limestone grains, which armour their surfaces. Aluminium precipitates can also armour the surfaces of limestone grains in this manner (Santomartino and Webb, 2007).

Limestone grains encapsulated by metal precipitates are less effective at neutralising AMD than uncoated grains because armouring constrains the rate at which the solid limestone is dissolved by acidic ions. While armoured limestone can still cause a rapid increase in the pH of AMD this diminishes with time, and the neutralisation rate declines logarithmically (Santomartino and Webb, 2007).

A coating of metal hydroxide can decrease the reactivity of limestone by a factor of 2.5 to 5, depending on its thickness. Over time this can lead to the failure of limestone to treat AMD (Santomartino and Webb, 2007). The effect of armouring of limestone by metal precipitates and gypsum reduces its expectancy to neutralize AMD.

These influences can be partially overcome by methods that lessen the presence of oxygen during treatment, enlarge the reactive surface area of the limestone by pulverisation and / or by providing sufficient agitation for the continuous abrasion of armoured surfaces within the system (de Beer, 2005; Masindi et al, 2022).

2.7 The Impact of Mining Activities on Soil

Mining activities can disrupt natural environments in numerous ways. This is caused by changing landscapes, depositing large amounts of hazardous waste materials, and discharging polluted water as well as expelling atmospheric effluents, which negatively impact air, water, soil quality and biodiversity (Warhate et al, 2006; Benidire et al, 2021).

Mining activities disrupt soil components, which includes soil horizons and structure, soil microbe populations and nutrient cycles that are important for sustaining a healthy ecosystem (Sheoran et al, 2010). Major impact is noted in soils around mining zones (particularly in sulphide-rich mining areas) like collieries, which are attributed to the discharge of AMD (Benidire et al, 2021; Warhate et al, 2006).

This can cause the formation of acid sulphate soils in coal mining areas because of the inflow of mine impacted water that is enriched with sulphates (Mitrakova et al, 2023). Soils which are exposed to AMD are physically deteriorated by becoming structurally unstable and highly prone to erosion (Row-Chowdhury et al, 2015). This is attributed to the decomposition of organic matter and the weathering of silicate minerals, which leads to a loss of mineral structure in soil (Zhang et al, 2014).

In addition, they are also chemically impaired, which is mainly attributed to their acidification, salinization and contamination by heavy metals, trace elements, hydrocarbon compounds and other toxic substances (Benidire et al, 2021). As a result, acidifying soil by exposing it to AMD is regarded as the main driver of its degradation.

This has several consequences for the quality of soil as it results in the reduction of its fertility status through the mobilization of base cations and depletion of essential macronutrients in the soil (Zhang et al, 2014; Agbenyeku et al, 2016). Acidic ions in the soil solution (H^+ ions) displace cations through exchange reactions from their binding sites which acidifies the soil. Coupled with soil acidification, an increase in the solubility and mobilization of heavy metals and toxic elements can occur and be released from soils (Kunhikrishnan et al, 2016; Zhang et al, 2014).

The presence of these and other toxic metals contaminates soil and can result in crop toxicity problems, which poses a risk to vegetation growing in these areas. This can affect food quality and safety and pose a risk to humans and animals who might consume such crops (Khan et al, 2008).

One of the largest environmental liabilities attributed to the coal mining industry is the formation of AMD. Strategies exist to contain and chemically treat this water, but the disadvantage is that it is very expensive and energy intensive. A potential alternative to mine water management and treatment is to irrigate with untreated acid mine water on soil that is preconditioned by alkaline materials like limestone. This has prompted this study, which is the development of soil liming strategies for irrigation with acid mine drainage. A three phased assessment is needed to develop these strategies against the literature that was reviewed.

The first assessment is the quantification of the additional acidity generated by metals like iron, aluminum, and manganese during their oxidation, hydrolysis, and precipitation, which buffers the neutralization of AMD. This will be achieved by a titration experiment.

The second assessment is the effect of Fe, Al and Mn on the potential to armour varying particle size fractions of agricultural limestone during neutralization of AMD as the armouring of agricultural limestone may restrict its dissolution and neutralizing potential. This will be achieved by conducting an aqueous neutralization test.

These two assessments guide the third assessment, which considers the potential of strategically liming soil with agricultural limestone to neutralise AMD and support a favourable rooting environment for crop growth. A soil column experiment will be conducted to determine this potential.

A key assumption of this study that is precluded from the scope of the investigation is that crops will be able to grow and be productive under irrigation with acidic waters if the strategic liming can alleviate any influence of soil acidity and if crops are not susceptible to scorching.

CHAPTER 3: NEUTRALIZATION OF ACID MINE DRAINAGE BY CALCIUM HYDROXIDE IN AN AQUEOUS ENVIRONMENT

3.1 Introduction

The study consisted of laboratory-based experiments in three phases. The purpose of the phased approach was to fulfil the principal aim of the study, which was the development of soil liming strategies for irrigation with AMD. This chapter details the first phase of the experiments, which addressed the following research question:

What influence does the acid generating ability of Fe, Al and Mn have on the neutralization of AMD with hydrated lime?

The experiment intended to quantify the additional acidity generated by metal oxidation, hydrolysis and precipitation and show how this influences the neutralization of AMD with hydrated lime. This was achieved by assessing the acid generating influence (referred to as buffering) of iron, aluminium and manganese on the potential of hydrated lime to establish a neutral condition. For this experiment, a pH range between 7 and 7.5 was used to represent a neutral condition, appropriate for the development of soil liming strategies for irrigation with AMD.

Titration were done to assess the acid generating influence of the metals on the neutralizing potential of hydrated lime. The acid metal solutions (referred to as AMD) were titrated with a $\text{Ca}(\text{OH})_2$ solution until a neutral and alkaline condition was established with a final solution pH of between 10 and 11.

A potential concern is that the relatively short reaction period of the experiment could have led to only partial oxidation of some of the metal cations during the titrations. This could have resulted in high concentrations of the metals being present in the solution after the titration was terminated. This residual concentration means that further acidity might well have been generated over time and that incomplete oxidation, hydrolysis as well as precipitation of the metals could occur.

This possibility is particularly linked to the first pH range of between 7 and 7.5 (neutral condition), which is considered appropriate for the development of soil liming strategies for irrigation with AMD.

However, taking the solution to higher pH levels can accelerate the oxidation kinetics and potentially overcome this challenge. Thus, reaching the pH range of between 10 and 11 (alkaline condition) forced hydrolysis of the metals during the titration experiment as well as facilitated their oxidation and precipitation during the relatively short reaction period of the experiment to quantify the acidity that each metal cation could generate.

3.2 Description and Preparation of the Synthetic AMD Solutions

To resemble the sulphate acidity signature of AMD, dilute sulphuric acid (7 mM) was used as the basis for the synthesis of the various AMD solutions for this study. The dilute sulphuric acid was also used as the control solution because it does not contain high metal concentrations.

The following acidic solutions were used and will be referred to as AMD for this study. The AMD solutions were synthesised using the following sulphate salts: Ferrous sulphate ($\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$) to produce the AMD-Fe solution, manganous sulphate ($\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$) for AMD-Mn and aluminium sulphate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$) for the AMD-Al solution. These sulphate salts were also used to synthesise a solution that contained all the metals referred to as AMD-Fe-Al-Mn.

It was decided to use these salts because most mine affected waters have high metal concentrations, and these salts were soluble enough to achieve such concentrations when the AMD solutions were synthesised in a laboratory. Water quality data provided by a colliery (whose details are protected for confidentiality purposes) in the Mpumalanga Province, was utilised to guide the concentrations used in the various AMD solutions.

The experiment focused on determining the influence of the acid generating potential of specifically Fe, Al, and Mn on the neutralisation of AMD with hydrated lime. In the experiment, the influence of each metal cation was determined. Actual mine impacted water usually contains all these cations, and others, therefore making the individual influence of each cation, complex to determine and identify. To overcome this challenge, the approach decided upon was to synthesise solutions that contained specific metal cations.

The solutions used were as follows:

- A control solution of dilute sulphuric acid.
- Three AMD solutions, namely AMD-Fe, AMD-Al, and AMD-Mn - each with a single acid generating metal cation - to assess their effect on an individual basis.
- An AMD solution containing all three metals to assess their combined effect. This triple metal solution referred to as AMD-Fe-Al-Mn represents the condition most likely to be encountered as most mine impacted waters would typically contain all three metals.

Solutions with the different metal cations at the same molar concentration (mol.L^{-1}) were prepared. This approach allowed for the control of the concentration of the metal cations in the different AMD solutions; the assessment of their buffering influence on the neutralization of AMD with hydrated lime; and an unbiased assessment of the quantity of acidity that each metal cation could generate during the titrations.

The water quality data from the colliery was divided into wet and dry seasons to compare the metal concentrations of both seasons to establish a common molar concentration for the different metals. To achieve this, the 25th, 50th and 95th percentile metal values of both seasons were determined. Analysis of the data showed that the 50th percentile (or median concentration) for each metal in both seasons was comparable. The median concentration of both seasons was 4 mM for Fe, 6 mM for Al and 1 mM for Mn.

The median concentrations of Fe and Al were averaged to obtain the concentration of each metal in the different AMD solutions, which was found to be 5 mM. This was decided on because they were identified as the main metal cations based on their abundance in the water quality data provided by the colliery.

The 5th percentile of each season was used to determine the pH, which was found to be approximately 2. This was used as the reference pH value for all the acidic solutions. Table 3.1 provides the molar and mass concentrations for each metal present in the AMD solutions. Table 3.2 shows the sulphate concentration and ionic strength for each solution used in the study.

The ionic strength of each solution was calculated by the equation below:

$$\mu = \frac{1}{2} \sum_{i=1}^n c_i z_i^2$$

where μ is the ionic strength (mol.L^{-1}), c_i is the molar concentration (mol.L^{-1}) of the ion and z_i is the charge of the ion.

Table 3.1: Molar and mass concentrations for each metal present in the synthesized AMD solutions.

Metal cation	Molar concentration (mM)	Mass concentration (mg.L^{-1})
Fe (as Fe^{2+})	5	280
Al (as Al^{3+})		135
Mn (as Mn^{2+})		275

Table 3.2: The sulphate concentration and ionic strength of each solution.

Solution	Sulphate concentration (mg.L^{-1})	Ionic strength (mol.L^{-1})
Control	672	0.021
AMDFe	1153	0.041
AMDAI	2113	0.096
AMDMn	1153	0.041
AMD-Fe-Al-Mn	3074	0.14

Note: the AMD solution that has all three metals contains them at a molar concentration of 5 mM per metal. Thus, the total metal concentration for this solution is 15 mM.

Bulk solutions were prepared and stored in 20 litre high density polyethylene (HDPE) containers which were kept closed to reduce oxidation. The control solution (dilute sulphuric acid, 7mM) was prepared by adding 0.14 mole of H_2SO_4 to 20 litres of deionized water. This resulted in a measured pH of 2 for the control solution.

The AMD solutions were prepared as prescribed for the control solution above to resemble the acidity signature of AMD as well as establishing a pH of approximately 2 for each synthetic mine water. The required amount of salt(s) needed to synthesise specific AMD solutions was then added (See Appendix A1).

A calibrated consort C830 pH meter measured the pH of all the solutions a day after they were synthesised. Table 3.3 shows the initial pH value of each solution. Table 3.4 shows the mass of each sulphate salt(s) required to synthesise the AMD solutions. The slight difference observed between the initial pH of the various AMD solutions could be attributed to the different types of sulphate salt(s) used to synthesise each solution as well as the differences in the mass of each required to prepare the AMD solutions.

Table 3.3: Initial pH values of the solutions used in the experiment which were measured 24 hours after their synthesis.

Solution	Initial pH
Control	2
AMD-Fe	1.99
AMD-Al	2.01
AMD-Mn	2.08
AMD-Fe-Al-Mn	2.08

Table 3.4: The AMD solutions used in the experiment and the mass of sulphate-salt(s) required to synthesise each one.

Solution	Sulphate salt(s) required to synthesise solution	Mass of salt(s) (g) required to synthesise 20 litres of solution
AMD-Fe	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	27.803
AMD-Al	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	33.322
AMD-Mn	$\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$	22.307
AMD-Fe-Al-Mn	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + \text{MnSO}_4 \cdot 7\text{H}_2\text{O}$	83.432

Note: The solution AMD-Fe-Al-Mn is the consolidation of the mass of salts required for each individual solution

3.3 Quantifying Metal Acid Generating Potentials and their Influence on Buffering the Neutralising Potential of Hydrated Lime.

This experiment assessed the acidity generated by iron, aluminium and manganese when AMD was neutralized by hydrated lime due to their ability to oxidise to higher valences (primarily for iron and manganese), hydrolyse and consequently precipitate. The approach considered appropriate was the identification of plateaus along titration curves for each of the AMD solutions used for the study. Due to the resultant acidity produced, these pH plateaus demonstrate the buffering influence of the metals on neutralization.

3.4 Methodology

The experiment was conducted in the Soil Science Laboratory located in the Department of Plant and Soil Sciences at the University of Pretoria. Titrations were used to conduct the neutralization experiment, which was facilitated by magnetic stirrer plates to enable the mixing and oxidation of the solutions during the experiment. A 10 mM hydrated lime solution was used as the titrant, while each acidic solution served as the titrand for all the titrations that were undertaken.

The volume of the hydrated lime solution required to neutralize the control solution (7 mM sulphuric acid) reflected the initial acidity of each solution. This also isolated the acidity (attributed to sulphuric acid) from the acidity generated by the metal cations when the AMD solutions were neutralized because the AMD solutions also contained the same concentration of sulphuric acid as the control solution to establish their initial acidic character.

The titration of the control solution involved adding 6 ml increments of the titrant to 50 ml of the 7mM sulphuric acid solution. The solution was stirred for 5 minutes to ensure homogenization and aeration during the titration. Thereafter, the solution was removed from the magnetic stirring plates and allowed to stabilize for 5 minutes before its pH was measured.

This process provided the volume of hydrated lime solution required to reach a neutral condition as well as the volume required to establish the reference pH range used for the titrations (pH of between 10 and 11).

The procedure used for the titration of the control solution was repeated for the titrations involving the various synthetic AMD solutions to a pH value of between 7 and 7.5 (neutral condition) and between 10 and 11 (alkaline condition). Fifty millilitres of the AMD solution (which essentially contained 0.25 millimol of metal(s)) were pipetted to each 250 ml Erlenmeyer flask. Six ml increments of the hydrated lime solution were titrated to each flask while the solutions were being stirred using the magnetic stirrer plates. The contents of each flask were stirred for 5 minutes to ensure homogenization and enable oxidation during the titrations.

Thereafter, the solutions were removed from the plates and allowed to stabilize for 5 minutes before their pH was measured. This procedure was repeated until a neutral condition and alkaline condition were reached for each set of titration.

Total soluble metal concentration in each synthetic AMD solution was analysed after reaching neutral and alkaline conditions by inductively coupled plasma atomic emission spectroscopy (ICP-OES) to measure the residual concentration of metals in the solution. This determined whether a significant amount of additional acidity could still be generated over time, and the extent to which the initial concentration of metals had been removed.

3.5 Interpretation of the pH Value

The measured pH of each replicate for a specific solution reflects the negative decadic logarithm of the hydrogen ion (proton) activity as follows (Wolkersdorfer, 2020):

$$\text{pH} = -\log_{10}\{\text{H}^+\}$$

Wolkersdorfer (2020) states that errors can occur when calculating the arithmetic mean or average from pH value measurements, which is caused by not considering the logarithmic character of the pH measurements. Therefore, it is suggested that the pH values must first be converted into the activity of the hydrogen ions (protons), which can then be used to determine the mean or average hydrogen ion activity (Wolkersdorfer, 2020).

The proton activity can be calculated as follows:

$$\{\text{H}^+\} = 10^{-\text{pH}}$$

For this study the mean solution pH was expressed by determining the mean proton activity of each solution as follows:

$$\{H^+\}_{AVERAGE} = \{(10^{-pH \text{ Rep1}} + 10^{-pH \text{ Rep2}} + 10^{-pH \text{ Rep 3}}) \div 3\}$$

Thereafter, the mean solution pH was determined according to the mean proton activity as follows:

$$\text{Mean solution pH} = -\log_{10}\{H^+\}_{AVERAGE}$$

The mean solution pH values were used to develop the titration graphs for all solutions used in this experiment. See Appendix A2 for the titration data for each solution.

3.6 Results and Discussion

3.6.1 Quantifying the Acid Generating Potentials of Metals During the Neutralization of AMD.

The titration of the control solution showed that 0.74 mmol of OH^- (hydroxide) was required to reach a neutral condition. This implies an acidity signature of 0.74 mmol H^+ . The AMD solutions also contained the same concentration of sulphuric acid as the control. Therefore, the minimum titratable acidity for each AMD solution should be 0.74 mmol H^+ . However, this was not the case because more calcium hydroxide was required to neutralize the AMD solutions in comparison to the control solution (Table 3.5).

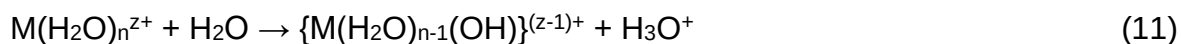
During neutralization of the AMD solutions, additional acidity was generated by each solution therefore needing an excess volume of hydrated lime as seen in Table 3.5. This shows that the AMD solutions have an initial acidity as well as the potential to generate additional acidity during their neutralization, which will be referred to as the metal acid generating potential (MAGP).

Table 3.5: The excess volume of $\text{Ca}(\text{OH})_2$ required to reach a neutral condition for each acidic solution used.

Solution	Total titrant volume required for neutralization (ml)	Excess volume (ml)
Control	37	0
AMD-Fe	69	32
AMD-Al	79	42
AMD-Mn	48	11
AMD-Fe-Al-Mn	108	71

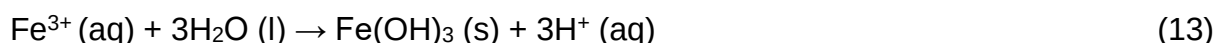
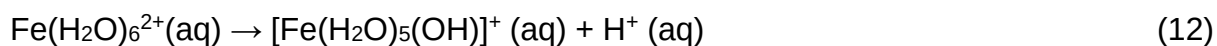
Note: The excess volume was calculated by subtracting the total titrant volume required for neutralization of the control solution from the titrant volume required for neutralization of each AMD solution.

The MAGP of the AMD solutions is allied with the oxidation, hydrolysis, and consequent precipitation of the various metals from the solutions. A generic model of the hydrolysis reaction is provided below (equation 11) where M is the respective hydrolysable cation, n is the co-ordination number and z is the charge of the cation. The model states that as the cation begins to hydrolyse, it acts as a source of protons thereby donating acidity (Pillay, 2000).



However, oxidation can occur, which changes the valence of some cations like Fe(II) and Mn(II). In the case of iron, some Fe(II) is expected to oxidise to Fe(III) which consumes acidity. However, the residual Fe(II) can hydrolyse as well as the Fe(III) and both can act as sources of protons that generate acidity. This is demonstrated by equations 12 and 13 below.

The first reaction shows the hydrolysis of Fe(II) in which one of the water molecules surrounding the cation is split and releases a proton (generates 1 mole of acidity per mole of Fe^{2+} that is hydrolysed). The second equation is a summary of the first three hydrolysis reactions of ferric iron. It shows that Fe(III) reacts with three water molecules to form a ferric hydroxide precipitate and produces 3 protons (generates 3 moles of acidity) during the process.



The excess volume of titrant presented in Table 3.5 signifies extra alkalinity which was needed to neutralize the additional acidity generated by the metals in the AMD solutions due to their oxidation and hydrolysis. This causes the precipitation of the metals in the AMD solutions which is more acidifying than solution oxidation and hydrolysis, which results in additional acidity being produced.

For the titrations, 50 ml of the various AMD solutions were used. The solutions with a single metal had an initial concentration of 5 mM for each metal. Therefore, it should follow that there would be 0.25 millimol of metal present in the 50 ml aliquots used. Table 3.6 below provides a quantification of the additional acidity that each AMD solution was able to generate when a neutral condition was achieved, in the instance that 1 litre of the various solutions were used.

Table 3.6: The additional acidity that each AMD solution generated because of metal oxidation and precipitation during neutralization with $\text{Ca}(\text{OH})_2$.

Acidic solution	Amount of metal present (mM.L^{-1})	$\text{Ca}(\text{OH})_2$ required for neutralisation (mM.L^{-1})	Excess $\text{Ca}(\text{OH})_2$ required (mM.L^{-1})	Additional acidity generated ($\text{mM H}^+.\text{L}^{-1}$)	Sum acidity ($\text{mM H}^+.\text{L}^{-1}$)
Control	0	7.4	0	0	14.80
AMD-Fe	5	13.8	6.4	12.8	27.60
AMD-Al		15.8	8.4	16.8	31.60
AMD-Mn		9.6	2.2	4.4	19.2
AMD-Fe-Al-Mn	15	21.6	14.2	28.4	43.2

Note: The excess base required was calculated by subtracting the $\text{Ca}(\text{OH})_2$ required for neutralisation of the control from the $\text{Ca}(\text{OH})_2$ required for neutralisation of each AMD solution. The additional acidity generated by the metals in each AMD solution is equal to excess alkaline material required. The sum acidity of each AMD solution is equal to the $\text{Ca}(\text{OH})_2$ required for neutralization.

According to the additional acidity generated by the oxidation and precipitation of the metals in the AMD solutions in Table 3.6, a preliminary acid generating potential of each metal present in the various AMD solutions can be quantified from the titrations for the various AMD solutions.

The titration experiment provides the preliminary acid generating potential of the metals as follows:

- One millimole of ferrous iron generated an additional 2.56 millimole of acidity,
- The same amount of aluminium generated an additional 3.36 millimole of acidity and
- One millimole of manganous manganese generated an additional 0.88 millimole of acidity.

From the titration experiment, it is noted that the preliminary acid generation potential associated with manganese is the least when a neutral condition was achieved. This was anticipated as the ratio between the quantity of manganese and the acidity which it can generate is nearly 1:1. Mn can oxidise to higher valence states and the observed ratio suggests that only a portion of the initial Mn oxidised during the titration as neutrality was reached, which allowed a slight amount of hydrolysis to occur and acidity generation.

Alternatively, the acid generating potential of Mn may begin to occur once a neutral condition is established and its acid generating potential is likely to extend beyond neutrality. Furthermore, considering that the pK_a for Mn^{2+} is about 10, it suggests that partial oxidation occurred when reaching a neutral condition for the AMD-Mn solution. This implies that higher pH levels as well as a longer reaction period could be required to facilitate the complete oxidation and precipitation of Mn.

Ferrous iron showed the second greatest potential to generate acidity during neutralization. However, ferrous iron will be oxidised (like Mn), and oxidation would convert Fe^{2+} to Fe^{3+} . In doing so, the resultant Fe^{3+} ions would then be able to hydrolyse as presented in Equation 13 above and generate acidity too. From this equation, 1 mol of Fe(III) can generate 3 mol of acidity in the process of precipitating as a ferric hydroxide mineral. This is in addition to the 4 mols of acidity generated per mole of Fe for hydrolysis which implies that 7 moles of acidity could be generated.

The titration of the ferrous iron solution in this experiment (AMD-Fe) showed that 2.56 mol of acidity was generated instead. The slight difference in the expected acid generation could be due to the partial oxidation of Fe(II). This suggests that there is still a presence of residual Fe(II) in solution, which could generate acidity over time during its precipitation.

However, another possibility is that a Fe(III) hydroxysulphate mineral had precipitated as opposed to a Fe(III) hydroxide which generates 3 mols of acidity during its formation. The relatively short reaction period observed in the experiment may have also resulted in the abovementioned difference between the preliminary quantification of acid generating potential for Fe and that provided by equation 13.

However, this possibility can be addressed by accelerating the oxidation kinetics in reaching higher pH levels. Thus, by reaching a pH range of between 10 and 11, Fe(II) may have been forcefully oxidised to Fe(III) and its hydrolysis facilitated during the titration experiment.

Aluminium, however, showed the greatest potential to generate additional acidity during neutralization. This is primarily linked to its hydrolysis and precipitation as there is no associated oxidation coupled with it. The following reaction shows the acid generating potential for Al(III):



The titration of the aluminium solution in this experiment showed that 3.36 mol of acidity was generated when a neutral condition was reached. This is slightly more than that expected from the abovementioned reaction (reaction 14) which suggests that most of the aluminium had precipitated during the titration. The difference in the expected acid generation could be due to the re-solubilization of Al as a neutral condition was reached, which required an excess amount of base to re-precipitate it before the titration was terminated.

The treatment with all the metals present in solution (typical of actual AMD) required the greatest excess alkalinity for neutralization due to the combined contributions of each metal. However, the sum of the individual acid contributions from each metal is more than that obtained for the combined solution (of all three metals) according to the titration for this solution. This could be due to co-precipitation of metals when the triple metal solution was titrated, which would decrease the concentration of metals in the solution, consequently reducing the total acid generating potential of this synthetic AMD.

3.6.2 Review of the Preliminary Metal Acid Generating Potentials and their ability to Generate Further Acidity

The total soluble metal concentration in each AMD solution was determined by ICP-OES after reaching a neutral condition (pH between 7 and 7.5) and an alkaline condition (pH between 10 and 11). This was done to measure the residual / or final metal concentration in each solution to ascertain if a significant amount of additional acidity could still be generated after reaching either condition, as well as to review the preliminary quantification of acid generating potential of each metal. See Appendix A3 for the ICP-OES data for the metal concentrations in the various solutions after reaching a neutral and alkaline pH.

The extent to which metals were removed from the solutions was assessed by quantifying the remaining metal concentration in the AMD solutions after the titrations. The metals were removed from the AMD solutions by oxidation (primarily for Fe and Mn), followed by their hydrolysis and precipitation. This is facilitated by increasing the pH of the solutions.

It is also understood that when metal is removed from the solution, acidity is generated during the oxidation, hydrolysis and precipitation process. Therefore, quantifying the proportion of metal removed assists in reviewing the preliminary acid generating potential for each metal as shown in section 3.6.1.

This premise is based on the significance of the final metal concentration in each AMD solution after reaching either of the abovementioned pH levels as well as the amount of acidity that could be generated. It is recommended that future work considers the possibility of the precipitates or floc which formed, to generate additional acidity. This is suggested because of the relatively short reaction time allowed for the titration experiments in this study.

An analysis of variance (ANOVA) was conducted to assess any significant differences between the final metal concentrations in each of the AMD solutions after reaching a neutral and an alkaline condition. The mean of the final metal concentration in each AMD solution after reaching each condition was compared using a Tukey HSD Post Hoc test at a significance level of $\alpha=0.05$. This was achieved using IBM SPSS 28 statistical software.

Table 3.7 shows the average final metal concentration present in each AMD solution after reaching a neutral condition. It also shows the extent to which Fe, Al and Mn was removed from each solution. The final metal concentration was determined by averaging the measured total soluble metal concentration (determined by ICP-OES) in each triplicate of the various AMD solutions. The percentage removed was determined by subtracting the final concentration from the initial, then dividing by the initial concentration and multiplying by 100.

Table 3.7: The concentration of metals in each AMD solution after establishing a neutral condition (pH between 7 and 7.5).

Solution	Samples analysed	Metal present	Initial concentration (mg.L ⁻¹)	Final concentration (mg.L ⁻¹)	Std. Dev	Percentage removed
AMD-Fe	3	Fe	280	0.42 ^{NS}	0.30	99.85
AMD-Al		Al	135	0.45 ^{NS}	0.034	99.67
AMD-Mn		Mn	275	140.43*	21.49	49.09

*Note: NS indicates there is no significant difference in the mean final metal concentration between the AMD-Fe and AMD-Al solutions at the 0.05 level. * Indicates that there are significant differences in the mean final metal concentration between the AMD-Mn and AMD-Fe as well as the AMD-Mn and AMD-Al solutions at the 0.05 level.*

Table 3.7 shows that most of the aluminium was removed during neutralization of the AMD-Al solution. The removal of Al was mainly achieved through its hydrolysis during the titration and its consequent precipitation as an aluminous mineral. Reaching a neutral condition facilitated the removal of 99.67% of the initial aluminium concentration from the AMD-Al solution and resulted in a final concentration of 0.0167 mM (0.45 mg.L⁻¹), which was left in solution.

The preliminarily quantified acid generating potential associated with Al during neutralization showed that 1 millimole of Al generated 3.36 millimole of acidity. Based on this quantification the abovementioned final Al concentration could generate an additional 0.056 mM of acidity. Therefore, the potential of the final amount of Al to further produce additional acidity after reaching a neutral condition (pH between 7 and 7.5) can be deemed negligible.

This implies that the preliminary quantification of acid generating potential of Al can be accepted because once a neutral condition is achieved, most of the Al in solution is removed, thereby reducing its potential to produce high amounts of additional acidity.

Similarly, most of the iron initially present in solution was removed during the neutralization of the AMD-Fe solution. Its removal is attributed to the oxidation of ferrous to ferric iron, followed by the hydrolysis of ferric iron and its precipitation as a ferric mineral. Reaching a neutral condition facilitated the removal of 99.85% of the initial iron concentration from the AMD-Fe solution and resulted in a final iron concentration of 0.0075 mM (0.42 mg.L^{-1}), which was left in the solution. This implies that much more acidity should have been generated if all ferrous iron was oxidised and precipitated as oxyhydroxides. Thus, it is assumed that Fe precipitates which formed may show the potential to generate further acidity overtime.

The preliminary quantification of acid generating potential of Fe during the titration of the AMD-Fe solution showed that 1 millimole of Fe generated an additional 2.56 millimole of acidity during its precipitation. This implies that the abovementioned final Fe concentration could generate an additional 0.019 mM of acidity through its precipitation. Therefore, the potential of Fe to produce a high amount of additional acidity after neutralization occurred can be deemed negligible.

The residual iron in solution after reaching a neutral condition as well as the amount of acidity that this concentration could generate is negligible. This implies that the preliminarily quantified acid generating potential of Fe is acceptable because once a neutral condition is achieved, most of the Fe in solution is removed which also nullifies its potential to produce a significant amount of acidity.

Neutralizing the AMD-Mn solution enabled only partial removal of the initial manganese present in this solution. Like iron, this metal cation can oxidise to higher valences like Mn(III) and Mn(IV) with the former valence state being able to hydrolyse and precipitate. Reaching a neutral condition facilitated the removal of 49% of the initial Mn in the AMD-Mn solution and resulted in a final concentration of 2.56 mM (140.43 mg.L^{-1}).

It was mentioned earlier that manganese generated the least acidity during neutralization. It was also stated that partial oxidation occurred when reaching neutrality. The significant amount of Mn present in solution (51%) after neutralization provides the evidence to support that only a portion of the initial Mn was able to oxidise to Mn(III) as a neutral condition was reached.

This suggests that Mn is likely to only start hydrolysing and generating additional acidity when a neutral condition is achieved. Therefore, the acid generating potential of Mn is also likely to be greater than the preliminarily quantified amount shows (0.88 mmol of acidity per mmol of Mn in solution). This suggests that buffering influence attributed to the acid generation potential of Mn begins when a neutral pH is obtained and that its influence extends through a neutral range (pH between 7 and 7.5). Therefore, the acid generating potential of Mn requires further investigation. It is also suggested that higher pH levels are necessary to remove most Mn from solution because of its partial oxidation. Thus, the pH level required to facilitate complete removal of Mn from solution is an important parameter.

Tables 3.8 shows the final metal concentration present in each AMD solution after reaching an alkaline condition (pH between 10 and 11). It also provides the extent to which Fe, Al and Mn was removed from each solution after reaching this condition.

Table 3.8: The concentration of metals in each AMD solution after establishing an alkaline condition (pH between 10 and 11).

Solution	Samples analysed	Metal present	Initial concentration (mg/L)	Final concentration (mg/L)	Std. Dev	Percentage removed
AMD-Fe	3	Fe	280	0.86*	0.14	99.70
AMD-Al		Al	135	0.18*	0.0078	99.87
AMD-Mn		Mn	275	0.0023*	0.0015	99.99

*Note: * indicates that there are significant differences between the mean final metal concentration in the AMD solutions at the 0.05 level.*

Table 3.8 shows that the residual concentration of aluminium in the AMD-Al solution after reaching an alkaline condition (pH between 10 and 11) is less than the concentration reported when a neutral condition was achieved (Table 3.7). Thus, more Al was removed (99.87%) upon reaching a higher pH level, with an insignificant concentration of Al left in solution. Therefore, the amount of additional acidity which could be generated from this concentration is negligible.

Reaching an alkaline condition resulted in a slightly higher final iron concentration in solution as opposed to neutralizing the AMD-Fe solution. This was found to be 0.015 mM (0.86 mg/L), which is double the final Fe concentration when neutrality was reached. The acid generating potential of the residual amount of Fe in solution after reaching an alkaline condition is 0.039 mM of acidity.

This acid generating potential is nearly double the potential that the remaining iron concentration in solution could produce at a neutral condition. The two-fold increase of the final iron concentration of the AMD-Fe solution and its associated acid generating potential, which occurred when the solution reached an alkaline condition, is attributed to the solubility of ferric iron. As the pH of the AMD-Fe solution begins to increase, the oxidation of ferrous to ferric iron is facilitated (Sun et al, 2000).

However, ferric iron solubility is controlled by pH and ferric iron will become less soluble as pH increases. At a pH of greater than 3.5 to 4, ferric iron becomes insoluble, and its precipitation is enabled. Furthermore, if the pH increases beyond 8, ferric iron can solubilise (Aube and Lee, 2015).

Therefore, the slight increase in the remaining iron concentration when the AMD-Fe solution reached a pH of between 10 and 11 could be attributed to the solubilisation of ferric iron in solution. This is because the ferric minerals which formed are amphoteric and dissolve at higher pH levels.

Reaching a higher pH of between 10 and 11 facilitated the removal of 99.99 % of the Mn from the AMD-Mn solution. However, neutralizing the AMD-Mn solution enabled partial removal (49%) of the initial manganese concentration from this solution. The removal of Mn at an alkaline pH condition is attributed to the oxidation of residual Mn(II) to Mn(IV) oxides. This supports the assertion that the pH level required to facilitate complete Mn removal from solution is a very important parameter and that highly alkaline conditions are needed.

Table 3.9 shows the final concentration of metals present in the solution which contains all three metal cations (AMD-Fe-Al-Mn) after reaching a neutral and alkaline condition. Neutral conditions resulted in the complete removal of iron; removal of most of the Al (99.96%) and the partial removal (48.5%) of Mn from the solution. However, the alkaline condition removed nearly all the Fe (99.99%), Al (99.94%) as well as Mn (99.98%) from the solution.

It is also noted that the final concentration of Fe and Al in Table 3.9 is lower than the final concentration obtained when the AMD solutions, which only contained these metal cations, reached a neutral (Table 3.7) and alkaline (Table 3.8) condition. This difference could be the result of the co-precipitation of metals as the AMD-Fe-Al-Mn solution reached under these pH conditions. However, it may also show that the presence of Mn influences the extent to which Fe and Al are removed from solution.

Table 3.9: The concentration of metals in solution after establishing a neutral condition (pH between 7 and 7.5) and an alkaline condition (pH between 10 and 11).

Solution	pH level reached	Initial concentration (mg/L)			Final concentration (mg/L)		
		Fe	Al	Mn	Fe	Al	Mn
AMD-Fe-Al-Mn	7 – 7.5	280	135	275	0	0.054	141.62
	10 – 11				0.015	0.077	0.066

The final metal concentrations were determined by ICP-OES. This method of analysis accounts for the total soluble metal concentration and is unable to differentiate between species and oxidation states. In other words, using an ICP-OES cannot distinguish between the proportion of ferrous and ferric iron that remains in solution, but provides the total concentration. Neither can it distinguish between the various species of Mn in solution.

To determine the proportion of residual Fe(II) in solution, a spectrophotometric determination for ferrous iron can be undertaken using the 1.10 phenanthroline method. By quantifying this concentration, it would be feasible to quantify the extent to which ferrous iron had oxidised to ferric iron. By coupling a spectrophotometric analysis with an ICP-OES analysis the amount of residual ferric iron in solution can be quantified.

Similarly, to determine the proportion of residual Mn(II) in solution, a spectrophotometric determination for dissolved manganese can be undertaken using either the persulphate, PAN, or porphyrin methods. By measuring the concentration of Mn(II) in solution, the extent to which manganese was oxidised can be determined.

However, the focus of this experiment was to quantify the additional acidity generated by metal oxidation, hydrolysis and precipitation during neutralization as well as to assess the buffering influence of iron, aluminium, and manganese on the potential of hydrated lime to neutralize AMD. As these metals oxidise and precipitate, they can generate acidity and become insoluble.

Therefore, the ICP-OES analysis to measure the total soluble concentration of the different metals in solution was considered sufficient as it provided the quantification of both the extent to which the initial concentration of metals had been removed and the remaining metals in solution (which could facilitate the analysis of whether a significant amount of additional acidity could still be generated). Furthermore, it assisted in reviewing the preliminary quantification of the acid generating potential of the metals during the titration experiment as well as ascertaining the importance of solution pH on the removal of Mn.

Understanding and acknowledging that Fe, Al and Mn can generate additional acidity during neutralization is important in considering a strategy to lime soil for irrigation with AMD. The findings can be used as a reference for the quantity of acidity that iron and aluminium can generate as neutrality is achieved.

A review of the acidity that manganese can generate because of its high concentration present in solution after reaching a neutral condition will be discussed later in this chapter. It is assumed that Mn only started to hydrolyse when a neutral condition was achieved and that the additional acidity it can generate is likely to extend through a neutral pH range.

If the acidic contribution of these metals in a liming strategy is ignored, it is definite that the amount of alkalinity (liming material) required to neutralize AMD will be insufficient when applied to soil. The consequence could be an unfavourable rooting environment for crop growth due to soil acidification.

Therefore, water quality data must be perused to consider the contribution of each of the abovementioned metals to generating acidity. Care must be taken that water quality is not merely corrected for the pH of the irrigation water used, that is the pH of the AMD but also to consider its acidity.

The next section describes how the abovementioned metals buffer the neutralizing potential of hydrated lime because of the additional acidity they generate during neutralization. This will be demonstrated through comparing the titration graphs for each of the AMD solutions with the control as shown in Figures 3.5 A - D below.

3.6.3 Assessing the Buffering Influence of Iron, Aluminium and

Manganese on the Potential of Hydrated Lime to Neutralize AMD.

The control solution (sulphuric acid) with no metals present, shows a plateau in the slope of its curve between a pH of 2 and 3.44. This plateau indicates a buffering influence caused by a strong acid (sulphuric acid) and the second hydrolysis reaction of H_2SO_4 , which has a $\text{pK}_2 = 1.98$ (Nordstrom, 2020). Additionally, below a pH of 3, most of the sulphate in solution would be present in the bisulphate form (HSO_4^-) and as the titration with $\text{Ca}(\text{OH})_2$ proceeds the bisulphate deprotonates which has a pK_a of 2 and exhibits a buffering influence.

At a pH of 3.44, the control solution shows a sharp increase in the slope of its titration curve. Below this pH, the slope was relatively flat. However, above this pH, the slope became drastically steeper. It is suggested this pH value shows an inflection point, which marks the end of the buffering influence that is attributed to the second hydrolysis reaction of H_2SO_4 and bisulphate deprotonation.

Figure 3.1 shows the titration graphs which demonstrate the buffering influence of A) iron; B) aluminium; C) manganese and D) a combination of all three metals on the neutralization potential of hydrated lime. All the titration curves for the AMD solutions follow the buffering influence of the control solution (between a pH of 2 and 3.44) in the beginning of the titration as explained above. Thereafter, the buffering influence of each of the metals occur in certain pH ranges where the slope of the titration graph for the AMD solutions plateaus and will be elaborated on below.

Figure 3.1 A. shows two more plateaus in the slope of the AMD-Fe graph. The first occurs between a pH of 2 and 3.50, and the second smaller plateau is observed between a pH of about 5 and 5.76.

Figure 3.1 B. also demonstrates two additional plateaus in the slope of the AMD-Al graph between a pH of 4.27 and 4.64 and between a pH of about 9 and 9.39.

Figure 3.1 C. shows two more plateaus in the slope of the AMD-Mn graph. The first occurs between a pH of 7 and 7.78 whereas the second occurs between a pH of 11 and 11.60.

Lastly, Figure 3.1 D. shows four additional plateaus in the slope of the combined metal solution graph. The first occurs between a pH of 4.28 and 4.71, the second flattening occurs at a pH between 5.73 and 5.89, the third flattening occurs at a pH between 6.91 and 7, and the last flattening or plateau occurs at a pH between 10.50 and 11.

Table 3.6 showed the additional acidity that each metal generated because of their oxidation, hydrolysis and precipitation during neutralization with $\text{Ca}(\text{OH})_2$. The hydrolysis pathway is essential for removing metals from solution (Potgieter- Vermaak et al, 2006; Lakovleva et al, 2015).

The removal is achieved by increasing the pH of the solution to conditions where the metals cannot persist in their soluble phase (Aube and Lee, 2015). Through the hydrolysis pathway, additional acidity is generated (Watzlaf et al, 2004) as the metals precipitate, which buffers the neutralizing potential of hydrated lime and causes the plateaus of the titration graphs for the metal solutions as seen in Figure 3.1 A - D.

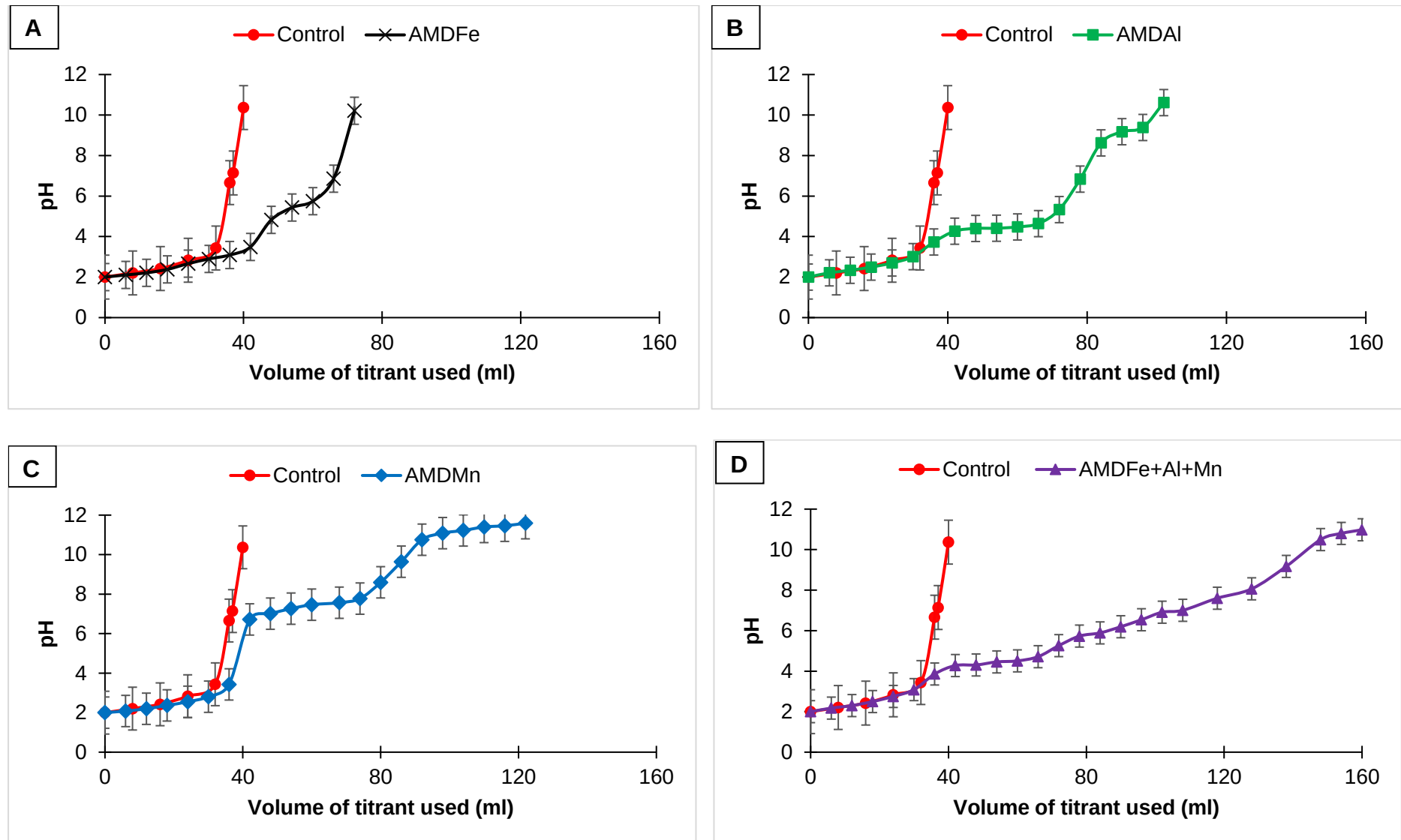


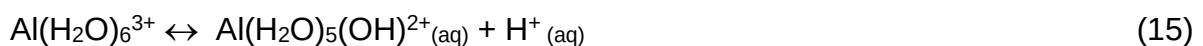
Figure 3.1: The buffering influence that metals commonly present in AMD have on the neutralization potential of hydrated lime.

The following section will detail the buffering influences of iron, aluminium, and manganese individually on the neutralization of AMD with hydrated lime, followed by the influence of all three metals in combination. The discussion will start by considering the influence of the AMD-Al solution.

Aluminium buffering

Aluminium influences the neutralizing potential of hydrated lime between a pH of 4.27 and 4.64 (see Figure 3.1 B.) The buffering in this pH range occurs because the precipitation of an aluminium hydroxide mineral starts which generates acidity. The solubility of aluminium decreases above a pH of 4 (Caraballo et al, 2019; Nordstrom, 2020), which facilitates its hydrolysis and consequent precipitation as an aluminous mineral species (Caraballo et al, 2011).

The hydrolysis of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ occurs at about a pH of 4.5 to 5 and can generate acidity as per the reaction below:



As this pH is reached, quantities of soluble Al^{3+} can hydrolyse and precipitate from solution and it is suggested that the buffering influence, which occurs between a pH of 4.27 and 4.64, is attributed to a combination of hydrolysis and precipitation. During the titration of the AMD-Al solution with hydrated lime, a white gelatinous substrate began to develop when it had reached a pH of about 4 (Figure 3.2). This substrate represents the precipitation of an aluminium hydroxysulphate mineral from solution, which requires the aggregation or clustering of polymeric Al species complexed with sulphate ions (Sanchez-Espana, 2016). It is also possible that it is a mixture of aluminium hydroxide and hydroxysulphates.

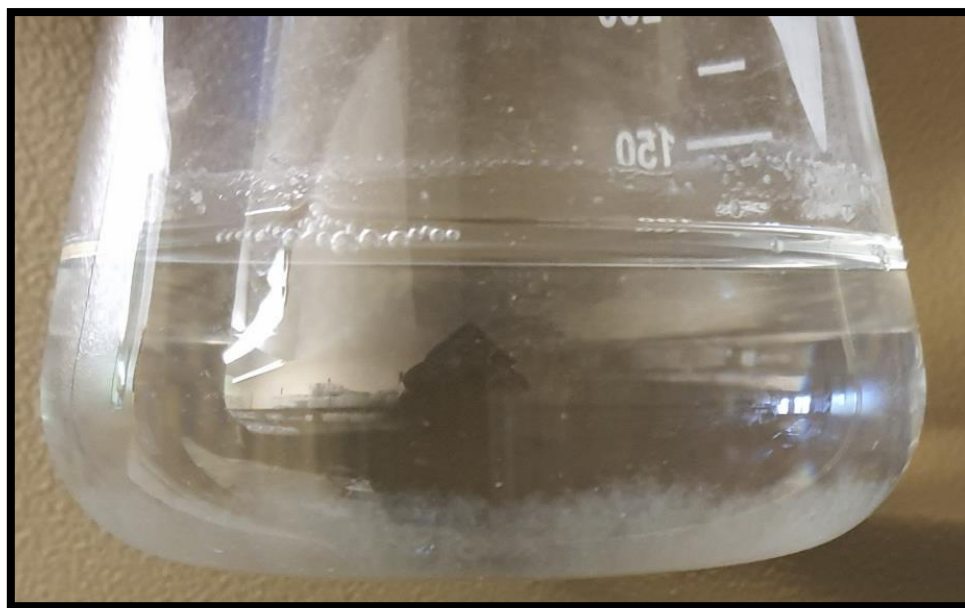


Figure 3.2: The white gelatinous substrate that developed in the AMD-Al solution after its pH was increased to 4.

The buffer, which is attributed to the hydrolysis of $\text{Al}(\text{H}_2\text{O})_6^{3+}$ as well as the formation of the white gelatinous substrate, is caused by the acidity generated due to the precipitation of hydrobasaluminite (an aluminium hydroxysulphate mineral), according to Caraballo et al (2019) who found that a whitish precipitate, which forms at a pH of between 4 to 5 in an aluminium sulphate rich solution, is likely to be hydrobasaluminite.

Hydrobasaluminite is a metastable and nearly amorphous mineral phase, which can dehydrate and irreversibly re-crystallise to poorly crystalline basaluminite ($\text{Al}_4(\text{SO}_4)(\text{OH})_{10.5}\text{H}_2\text{O}$) (Bigham and Nordstrom, 2000). Several aluminium precipitates could form as aluminium hydroxide and hydroxysulphate phases such as aluminite, meta-aluminite, microcrystalline gibbsite, alunite and as mixtures of phases (Nordstrom, 2020). However, Sanchez-Espana et al (2011) found that the most frequent aluminium precipitate likely to form in sulphate rich acidic solutions (such as AMD) is hydrobasaluminite as per the reaction:



From this equation, as hydrobasaluminite precipitates, acidity will be generated. It is this additional acidity that has the buffering influence on hydrated lime to neutralize the acidic solution.

This influence contributes to the flattening in the slope of the AMD-Al graph between a pH of 4.27 and 4.64 (Figure 3.1 B). The buffering influence persists until the bulk of the initially soluble aluminium has been removed by precipitation and the additional acid generation becomes negligible.

The precipitation of hydrobasaluminite generates a lower amount of acidity when compared to the acidity generated by the precipitation of an aluminium hydroxide mineral. The preliminary acid generating potential quantified for Al in the titration experiment is more than the amount of acidity generated by the precipitation of either of the abovementioned minerals. This suggests that a combination of aluminium hydroxysulphate and aluminium hydroxide minerals precipitated as the AMD-Al solution reached a neutral condition.

At a pH of 5.33, the slope of the graph for the AMD-Al solution, begins to steepen positively. Thus, this pH level is symbolic of an inflection point and suggests that all the Al^{3+} has been hydrolysed and precipitated in solution and marks the end of the Al buffering influence. The neutralizing potential of hydrated lime will not be buffered until this state is reached, and the pH of the solution can continue to increase to neutrality (Nordstrom, 2020).

Figure 3.1 B also shows the brief flattening of the graph for the AMD-Al solution above a neutral condition (between a pH of about 8.60 and 9.39) which partially buffered the potential of hydrated lime to further increase pH. This will temporarily make the slope of the titration curve steep because of alkalinity release and is attributed to the dissolution of aluminous hydroxide precipitates, which solubilizes aluminium (as Al^{3+}) (Lovett, 1992) and occurs at a pH above 8 to 9 (Balintova and Petrilakova, 2011). This results in additional alkalinity to form aqueous aluminate which caused the partial buffer.

Iron buffering

Iron influenced the neutralizing potential of hydrated lime between a pH of 2 and 3.50, which is marked by the flattening of the slope of the AMD-Fe titration curve (see Figure 3.1 A). The control solution also shows a flattening within this pH range, but the influence of the AMD-Fe solution is slightly extended.

This implies that iron can generate acidity at an early stage that could be caused by the oxidation of Fe^{2+} to Fe^{3+} which is facilitated by rapidly increasing the pH of the solution and through aeration caused by stirring the solution during the titration. The plateau between a pH of 2 and 3.50 is due to the buffering by a strong acid and Fe(III) hydrolysis and precipitation. The buffering by the second hydrolysis of H_2SO_4 has a pK_2 of 1.98, which is close to the pK_a of 2.19 for Fe(III), so that their influences would overlap (Nordstrom, 2020).

During the titration of the AMD-Fe solution, it was observed that ferrous iron (Fe^{2+}) oxidised to ferric iron (Fe^{3+}), which occurred as the pH of the solution reached 3. This was observed by the development of a yellow-orange colour of the solutions, commonly referred to as ferrihydrite (de Beer, 2006; Balintova and Petrilakova, 2011) and as the pH of the solution increased its colour intensified (Figure 3.3).



Figure 3.3: The oxidation of Fe^{2+} to Fe^{3+} marked by the development of a yellow orange colour, followed by the precipitation of Fe^{3+} .

The development of this ochre tint in solution is ascribed to the hydrolysis and precipitation of Fe(III). Its solubility is also regulated by pH, and at a pH between 3 and 3.5, ferric iron cannot exist in the soluble phase and will precipitate as ferric minerals due to its hydrolysis, thereby generating acidity (Bailey, 2016).

Such precipitation will create a buffering influence and can be identified as the ferric (Fe(III)) iron buffer that occurs at a pH of 3 (Espana et al, 2006; Totsche et al, 2006). In the case of a sulphate rich solution (like AMD) the most likely ferric mineral to precipitate would be schwertmannite as per the following equation (Espana et al, 2006):



As Fe^{3+} hydrolyses and precipitates to form schwertmannite, some acidity is generated shown as the flattening in the graph of the AMD-Fe solution occurring at a pH between 2 and 3.50. This is a result of the oxidation of ferrous to ferric iron followed by the additional acidity generated as the ferric iron hydrolyses and precipitates (eq. 17).

The slope of the titration curve for the AMD-Fe solution exhibits a slight increase after a pH of 3.50, before it flattens off for the second time at a pH between 5 and 5.75. The change in the slope of the graph at a pH of 3.50 marks an inflection point. It also suggests that the buffering influence that is credited to the hydrolysis and precipitation of Fe(III) has ended, in other words the end of the Fe(III) buffer.

Due to the narrow range of pH-Eh conditions in which ferric iron is soluble, not all the initially available Fe^{2+} can be fully converted to Fe^{3+} by oxidation. Therefore, it is possible, that there is still a presence of iron as Fe^{2+} in solution. This manifests itself as the second buffering influence, which occurred between a pH of 5 and 5.75 (see Figure 3.1 A) implying that this is influenced by the first hydrolysis of Fe^{2+} , which occurs at a pH of 6 (eq. 18) attributed to the ferrous iron (Fe(II)) buffer.



As this pH is reached, soluble Fe^{2+} still present in the solution will hydrolyse. The slope of the graph for the AMD-Fe solution experiences an increase after a pH of 5.75. This marks another inflection point and the end of the ferrous buffer.

The slope of the graph increases more steeply after a pH of 6.87. This suggests a third inflection point that is attributed to the precipitation of some residual Fe^{2+} as $\text{Fe}(\text{OH})_2$. As the pH of the solution increases, the solubility of the residual ferrous iron decreases (Totsche et al, 2006) and facilitates its precipitation.

Iron buffering is one of the most common buffers of acid mine water because pyrite (an iron bearing sulphide mineral) serves as the precursor to its formation. Totsche et al (2006) found there are two types of iron buffers, namely the ferric Fe(III) and ferrous Fe(II) buffers that can influence AMD.

This supports the observations of this experiment: two buffering influences were noted for the iron containing solution (AMD-Fe) at a pH between 2 and 3.49 (because of the ferric buffer) and a pH between 5 and 5.75 because of the ferrous iron buffer with both buffers occurring below neutrality.

The preliminary acid generating potential quantified for Fe in the titration experiment is less than the amount of acidity generated by the precipitation of an iron(III) hydroxysulphate mineral (like schwertmannite) and an iron(III) hydroxide. The difference in the amount of acidity is suggested to be attributed to the presence of some ferrous iron in solution which could not hydrolyse during the precipitation of $\text{Fe}(\text{OH})_2$ and subsequently generate acidity when the AMD-Fe solution reached a neutral condition.

Manganese buffering

Manganese influenced the neutralizing potential of hydrated lime between a pH of 7 and 7.78 as seen by the plateau in the slope of the AMD-Mn titration curve (see Figure 3.1 C.). Initially Mn(II) was observed to generate the least acidity during neutralization, and it was thought that partial oxidation had occurred when reaching a neutral condition. This is based on the residual concentration of Mn in solution after reaching a neutral condition. Furthermore, it was mentioned that the hydrolysis and buffering influence of manganese begins once a neutral condition is achieved and that its acid generating capability could be more significant than the preliminary quantification showed as its buffering influence is likely to extend beyond neutrality.

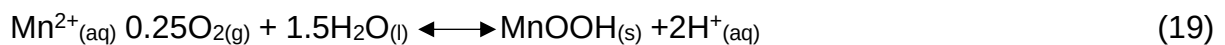
Examining the titration graph for the AMD-Mn solution in Figure 3.1 C shows that there is a buffering influence occurring when neutrality is reached. Therefore, it appears that Mn has a larger acid generating potential than initially quantified because a total of 0.37 mmol of hydrated lime was required to overcome the buffering influence. This implies that 1 mM of manganese has the potential to generate 2.96 mM of acidity as opposed to 0.88 mM as preliminarily quantified for this metal in section 3.6.1.

The removal of Mn(II) is difficult due to its high solubility over a wide pH range and the slow oxidation kinetics required to precipitate as manganese oxides (Tobiason et al, 2016; Aguiar et al, 2010). The oxidation state of Mn also plays a role in its distribution, mobility, and accumulation in water.

Manganese can occur in several oxidation states as: 2⁺, 3⁺, 4⁺, 6⁺ and 7⁺ (Li et al, 2019). The most common state is Mn(II) in water with a pH of less than 7, the higher oxidation states of Mn(III,IV) exist at higher pH values and redox potentials, while Mn (VI) and (VII) do not occur in most natural waters (Li et al, 2019) and tend to precipitate out of solution like Fe³⁺.

The oxidation of Mn(II) is said to be kinetically inhibited at a circumneutral pH range (Christenson et al, 2016) and its conversion to oxide forms in water does not occur without the involvement of hydroxide. Hydroxide precipitation can remove Mn(II) by increasing pH as this reduces its solubility (Li et al, 2019).

Therefore, Mn(II) would firstly need to be converted to an intermediate form before proceeding to a manganese (IV) oxide (Lovett, 1992). It is proposed that through this intermediate conversion, some of the manganese would hydrolyse to Mn(III) oxyhydroxide and subsequently generate acidity (eq. 19) (Rob and Robinson, 1995):



The acid generating potential quantified for Mn in the titration experiment is more than the amount of acidity generated by the precipitation of an Mn(III) hydroxide mineral as shown in the equation above. The difference in the amount of acidity is suggested to be attributed to the slow oxidation kinetics as Mn²⁺ is oxidised to Mn³⁺ which can hydrolyse and subsequently generate additional acidity when the AMD-Mn solution reached a neutral condition.

The intermediate conversion of Mn(II) to Mn(III) is thought to be responsible for the buffer that occurs between a pH of 7 and 7.78 in Figure 3.1 C due to the initiation of Mn hydrolysis. This buffer is suggested to be the result of the precipitation of a metastable Mn(III) oxyhydroxide mineral phase like β-MnOOH (Watzlaf,1987).

The slope of the graph for the AMD-Mn solution increases after a pH of 7.78 before plateauing for the second time. This pH level represents an inflexion point, which marks the end of the intermediate conversion of Mn(II) to Mn(III).

At a pH of between 11 and 11.60, there is another flattening in the slope of the AMD-Mn graph. It was previously mentioned that the conversion of Mn(II) in water does not occur without the involvement of an intermediate hydroxide form before proceeding to a manganese (IV) oxide. Also, manganese is soluble over a wide pH range, and it is likely that only a portion of it would have converted as explained above and that there is residual Mn(II) in solution.

Increasing pH by hydrated lime supplements the solution with calcium and hydroxide ions with the latter causing the increase in pH. Once neutrality is passed, the solution would shift toward a progressively alkaline condition in which hydroxide ions become available and can complex with Mn(II).

Furthermore, reaching these alkaline pH levels indicates that the oxidation kinetics are accelerated, which facilitates the conversion of residual Mn(II) to Mn(IV). This process is known to require significant amounts of alkalinity to convert the soluble manganese to Mn(IV) oxides. Thus, through this process, residual manganese can be precipitated and oxidised to Mn(IV) oxides and would consume alkalinity until its presence in solution is minimal (Rob and Robinson, 1995; Aguiar et al, 2010).

This implies that the second buffering influence, which occurs between a pH of 11 and 11.60, is triggered by the removal of residual Mn(II) through its oxidation to Mn(IV) oxides, as opposed to the generation of additional acidity by the remaining Mn(II) in solution.

Buffering through the presence of Fe, Al and Mn

When all three metals were present in solution (typical of actual AMD) the first plateau in the slope of the graph for the combined metal solution occurred between a pH of 2 and 3.86. This is caused by the combined buffering influence of the second hydrolysis reaction of H_2SO_4 and bisulphate deprotonation (buffering by a strong acid) as well as the ferric (Fe(III)) iron buffer.

The second plateau occurred between a pH of 4.28 and 4.71 which is caused by the buffering influence of aluminium. After the pH of 4.71, the slope increased to a pH of 5.73. This change in slope shows an inflection point marking the end of the aluminium buffer.

A third flattening occurs very briefly at a pH between 5.73 and 5.89. This is attributed to the ferrous iron buffer. After the pH of 5.89, the slope of the graph increased to a pH of 6.91, which shows another inflection point and the end of the ferrous iron buffer.

Similarly, a fourth flattening occurred very briefly between a pH of 6.91 and 7 which is attributed to the intermediate conversion of Mn(II) to Mn(III) oxyhydroxide. After the pH of 7, the slope increased to a pH of 10.50.

The final flattening occurred in the slope of the AMD-Fe-Al-Mn graph at a pH of between 10.50 and 11. This can be put down to the removal of residual Mn(II) through its oxidation to Mn(IV) oxides.

Overall, the buffering observed when all three metals are present in solution is not as pronounced as the individual influence of each metal. This is likely to be caused by the co-precipitation of metals as the AMD-Fe-Al-Mn solution was neutralized. This would decrease the concentration of the metals in solution as well as their ability to buffer neutralization. This agrees with Chermak et al (2004) and Zinck (2006) that stated that nearly all the precipitates which form are non-crystalline, amorphous mixtures of many metals present in the AMD with several of the ions adsorbed and co-precipitating.

3.7 Conclusion

The titrations show that Fe, Al and Mn contribute additional acidity during neutralization of the AMD solutions and this acid generating potential is attributed to the oxidation, hydrolysis and consequent precipitation of the metals. This influences the neutralizing potential of hydrated lime and buffers its potential to increase the pH of the acid metal solutions to a neutral condition and a level that is considered appropriate for the development of soil liming strategies for irrigation with AMD.

The following quantifications can be used as a guide to determine the total amount of acidity that iron, manganese, and aluminium can potentially generate as a neutral condition is achieved. This can assist in determining the amount of alkalinity required to neutralize this acidity thus forming the basis for the development of soil liming strategies for irrigation with AMD.

The titrations in this experiment provide the following acid generating potentials for the metals as follows:

- 2.96 millimole of acidity (as H^+) could be generated per millimole of manganese that is present in solution.
- 2.56 millimole of acidity could be generated per millimole of iron that is present in solution, and
- 3.36 millimole of acidity could be generated per millimole of aluminium that is present in solution.

Recognizing that Fe, Al and Mn can generate additional acidity during the neutralization of AMD is important in considering a strategy to lime soil for irrigation with mine impacted water. Ignoring the acidic contributions of these metal cations in a liming strategy could lead to an inadequate amount of alkalinity (liming material) required to neutralize AMD applied to soil.

This could lead to an unfavourable rooting environment for crop growth through soil acidification. Therefore, water quality data must be carefully perused to consider the individual contribution of each of the abovementioned metals to generate acidity, and not merely corrected for the pH of the irrigation water used (that is the pH of the AMD).

The results of the titrations of the AMD solutions showed that Fe has two buffering influences on the neutralization potential of hydrated lime. The first occurs between a pH of 2 and 3.49 and the second occurs between a pH of approximately 5 and 5.75. Both buffers occurred below neutrality. Aluminium has one buffering influence on the neutralizing potential of hydrated lime, which occurs between a pH of 4.27 and 4.64. This influence is primarily attributed to the hydrolysis of Al as there is no oxidation associated with this metal. The second influence occurs above neutrality; therefore, its influence is omitted.

Manganese has a buffering influence which occurs at a pH of between 7 and 7.77, which coincides with a neutral condition. This implies that the acid generating influence associated with Mn is initiated once neutrality is reached. The abovementioned buffering influence is a result of the intermediate conversion of Mn(II) to Mn(III) through its oxidation, followed by its hydrolysis and precipitation.

The second influence associated with Mn(II) occurs between a pH of 11 and 11.59, well above neutrality, and due to the removal of residual Mn(II) through its oxidation to Mn(IV) oxides. This is known to require significant amounts of alkalinity while not generating significant additional acidity.

Based on the findings of this chapter, the hypothesis, which states that Fe is expected to have the most significant buffering influence on the neutralization potential of hydrated lime compared to Al and Mn as its oxidation and hydrolysis is strongly acidifying, is accepted.

It has been demonstrated that Fe has the potential to buffer the neutralisation potential of hydrated lime because of two acid generating influences, namely the ferric and ferrous iron buffers. The titration experiment showed that each of them influenced the neutralization potential of hydrated lime below the neutral condition. The ferric iron buffer is attributed to the oxidation of Fe^{2+} to Fe^{3+} , followed by the hydrolysis and precipitation of Fe^{3+} , which occurs between a pH of 2 and 3.49. Thereafter, the influence of the ferrous iron buffer occurs due to the hydrolysis and precipitation of residual Fe^{2+} , which occurs between a pH of about 5 and 5.75.

CHAPTER 4: NEUTRALIZING ACID MINE DRAINAGE USING AGRICULTURAL LIMESTONE OF VARYING PARTICLE SIZE FRACTIONS.

4.1 Introduction

The previous chapter focused on quantifying the additional acidity generated through the oxidation, hydrolysis, and precipitation of Fe, Al and Mn present in AMD and evaluated how this buffered the neutralizing potential of hydrated lime. The findings of the third chapter are an important aspect of the study as it lays the foundation for the development of soil liming strategies for irrigation with AMD. By quantifying the amount of acidity that these metals can potentially generate during the neutralization of AMD, a determination of the corresponding amount of alkalinity to neutralize the acidity is possible.

Liming soil to neutralize AMD used for irrigation will require the use of an alkaline material that is appropriate for use in agriculture to neutralize the acidity of this water. Soil ameliorants capable of neutralizing acidity include agricultural lime and different types exist like carbonates, oxides, and hydroxides. The choice of agricultural lime is normally determined by its reactivity and cost which includes price per ton, transportation, handling, and application (FERTASA handbook, 2016).

The use of oxides and hydroxides in agriculture like slaked and hydrated lime is not recommended due to their caustic nature, which makes it difficult to store and handle. Additionally, the use of excessive amounts of these materials can result in very high soil pH levels which can negatively affect soil through the rapid decomposition of organic matter (FERTASA handbook, 2016) and can cause certain nutrient deficiencies as well as toxicities.

The most utilised type of agricultural lime by crop producers is carbonates which include calcitic (CaCO_3) and dolomitic ($\text{CaMg}(\text{CO}_3)_2$) limestone. One of the primary factors which determine their reactivity is the fineness of the particles, that is their particle size. Finer particle size fractions are expected to have a larger specific surface area which increases contact between the limestone and acidic ions. This improves the dissolution of the limestone and facilitates neutralization efficiency.

When calcitic or dolomitic limestone (carbonates) are used to neutralize AMD, metals like Fe, Al and Mn in the water precipitate as minerals which can cover their surfaces and is referred to as armouring. This can limit the neutralizing efficiency of the limestone by encapsulating it and restricting its dissolution. The extent to which armouring influences the neutralization efficiency of limestone is dependent on its particle size and its susceptibility to armouring increases as its particle size becomes larger. Thus, the armouring of agricultural limestone could have negative consequences when soil that has been preconditioned with this material is used to neutralize AMD, where soil deterioration could occur through acidification.

This chapter is aimed at determining the influence of Fe, Al and Mn on the neutralization of AMD with calcitic and dolomitic limestone of varying particle size fractions which are appropriate for use in agriculture. The effectiveness of the different particle size fractions of agricultural limestone in neutralizing various AMD solutions was assessed where AMD could be used as irrigation on soil that is preconditioned with these amendments. This was done to identify an applicable size fraction of agricultural limestone to be used in the development of soil liming strategies for irrigation with AMD.

pH versus time curves (see Figures 4.4 and 4.5) were also plotted to visualise the influence of Fe, Al and Mn on the neutralization of AMD with the various particle size fractions of the agricultural limestone. This determines the influence that the metals can have on restricting neutralization due to the potential armouring of their surfaces, which limits their dissolution and consequently buffers neutralization.

4.2 Methodology

In chapter three of this study, the additional acidity generated by Fe, Al and Mn was quantified. These findings are important to the aim of this experiment and were used to guide its approach. The findings showed that additional acidity was produced by each of the metal cations as follows:

It was demonstrated that in the short term:

- 2.96 millimole of acidity could be generated per millimole of manganese that is present in the solution.
- 2.56 millimole of acidity could be generated per millimole of iron, and

- 3.36 millimole of acidity could be generated per millimole of aluminium that is present in solution.

Therefore, when attempting to neutralize solutions that contain these metals, it is necessary to consider their acid generating potential and not only the initial amount of acidity that is present in the solution, as indicated by solution pH. This approach would ensure the inclusion of the corresponding amount of alkalinity or liming material required to neutralize the total (net) acidity of the AMD solutions. However, to accurately determine the total amount of liming material needed for neutralization, it is recommended that a quantification of the extent of the armouring of the surfaces of the liming material is also required.

The solutions used for this experiment were the same as those used previously and are summarised as follows:

- Dilute sulphuric acid as the control solution
- Three AMD solutions, which contained a single metal to assess each one's influence individually, referred to as AMD-Fe, AMD-Al and AMD-Mn.
- One AMD solution, which contained a mixture of all three metals to assess their combined effect. This combined metal solution, referred to as AMD-Fe-Al-Mn, represents the condition most likely to be encountered as AMD would typically contain all three metals.

The control solution was represented by 7 mM sulphuric acid and had an initial pH of 2. All the AMD solutions contained 7 mM of sulphuric acid to provide their acidity signature and contained 5 mM of each metal. These solutions had a pH of approximately 2. Furthermore, each of the solutions had an initial acidity of 14.8 mM H^+ .

Calcite and dolomite represent the types of agricultural soil amendments (referred to as agricultural limestone) appropriate for the study. The calcite was kindly donated by Mr L. Pistorius and sourced from Danielskuil in the Northern Cape. The sample comprised a mixture of coarse particles, that was pulverised to obtain the required particle size fractions for the experiment. Commercially available dolomitic limestone was used in the experiment, which was obtained from Mr L. Nonyane at the Future Africa Campus of the University of Pretoria.

The particle size fractions that were used are provided in the table below. These size fractions followed the guidelines for the use of limestone in agriculture provided by Watling et al (2010):

1. Particles that are smaller than 0.3 mm are 100% effective,
2. Particles between 0.3 to 0.85 mm are 60% effective, and
3. Particles larger than 0.85 mm are the least effective.

The effectiveness, referred to above, is in relation to the capacity of these different size fractions to ameliorate soil acidity. The chosen size fractions were also practical for laboratory work appropriate to the available sieve sizes. Portions of each type of agricultural limestone were sieved through a series of Star Screen Test Sieves. Aliquots of the pulverised limestone were added to the series of sieves, sealed with a lid, and placed on a mechanical vibrating table to shake the sieves to separate the limestone into various particle sizes.

Table 4.1: Particle size fractions of the agricultural limestone used for the study.

Particle fraction	Size fraction (mm)
Coarse	1 – 2
Medium	0.25 – 0.50
Fine	< 0.25

The total Ca and Mg concentrations of each type of limestone was determined by a nitric acid microwave digestion coupled with an ICP-OES analysis (see Appendix A4, table A4.1 for the total Ca and Mg contents). This was used to determine the weight contribution of calcium and magnesium in each of the particle size fractions of the calcite and dolomite used in this study (See Table 4.2 and 4.3).

Both tables show that there are differences between the weight contributions of Ca and Mg in each particle size fraction for both types of limestone. The differences could be attributed to the rate of dissolution for each particle size fraction during the acid digestion. It is also possible that the analytical technique used to determine the total calcium and magnesium contents is not suitable for a chemical assay regarding limestone. Alternatively, an X ray fluorescence (XRF) analysis could be a more suitable technique for an elemental analysis of the agricultural limestone.

Table 4.2: The weight contribution (%) of Ca and Mg of each particle size fraction of calcite used in the neutralization experiment

Weight contribution (%)	Calcite particle size fraction		
	1 – 2 mm	0.25 – 0.50 mm	< 0.25 mm
Calcium	51	55	55
Magnesium	16	15	11

Table 4.3: The weight contribution (%) of Ca and Mg of each particle size fraction of dolomite used in the neutralization experiment

Weight contribution (%)	Dolomite particle size fraction		
	1 – 2 mm	0.25 – 0.50 mm	< 0.25 mm
Calcium	26	24	23
Magnesium	26	26	25

4.2.1 Experimental Approach

A neutralization test was undertaken using 250 ml Schott flasks and a reciprocal shaker to mix and agitate the solutions during the experiment. Each flask was filled with 100 ml of the various acid solutions discussed to ensure adequate headspace for mixing in the flasks. To compensate for the metals' acid generating contributions, the total acidity of each metal solution was calculated according to equation 20.

This enabled the determination of the corresponding molar amount of alkalinity required for neutralization. This amount can be estimated following an acid-base accounting approach (equation 21). However, it should be noted that this amount does not compensate for the impact of armouring of the limestone surfaces on neutralization.

$$\text{Total acidity (mol.L}^{-1}\text{)} = \text{Acid}_{\text{initial}} + \text{Acid}_{\text{generated by metal hydrolysis}} \quad (20)$$

$$\text{Total alkalinity (mol.L}^{-1}\text{)} = \text{Total acidity (mol.L}^{-1}\text{)} \quad (21)$$

Table 4.4 provides a quantification of the total acidity for all the solutions used in this experiment as determined in Chapter 3 of the study. 100 ml aliquots of each solution were used in this test and the total acidity for this specific volume of the different solutions was:

- Control – 1.48 mmol H⁺
- AMD-Fe – 2.76 mmol H⁺
- AMD-Al – 3.16 mmol H⁺
- AMD-Mn – 2.96 mmol H⁺
- AMD-Fe-Al-Mn – 5.92 mmol H⁺

Table 4.4: The sum acidity for each of the solutions as measured in Chapter 3 of the study.

Solution	Initial acidity (mmol H ⁺ .L ⁻¹)	Acid generating potential of metals (mmol H ⁺ .L ⁻¹)	Total acidity (mmol H ⁺ .L ⁻¹)
Control	14.8	-	14.8
AMD-Fe		12.8	27.6
AMD-Al		16.8	31.6
AMD-Mn		14.8	29.6
AMD-Fe-Al-Mn		44.4	59.2

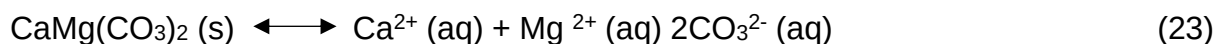
The total alkalinity required to neutralize the total acidity of the abovementioned solutions are the same according to equation 21. This assumes that 1 mol of carbonate is required per mol of acidity present in solution. Therefore, the total amount of alkalinity per solution can be converted to a theoretical amount of calcitic and dolomitic limestone which contains the necessary amount of alkalinity to neutralize each solution. This was calculated by considering the theoretical dissolution reactions of each type of limestone.

In the case of calcite its dissolution reaction is:



From equation 22, one mole of calcite can release a mole of carbonate upon its dissolution. Thus, the amount of calcitic limestone needed to neutralize each solution is the same as the total amount of carbonate alkalinity required for each of the solutions.

The dissolution reaction associated with dolomite is:



Equation 23 shows that one mole of dolomite can release two moles of carbonate when it dissolves. Therefore, the amount of dolomitic limestone needed to neutralize each solution is equivalent to half of the total amount of alkalinity (as carbonate) required for each solution.

The table below shows the total alkalinity for each type of limestone to neutralize the total acidity of the different solutions as well as the amount of calcitic and dolomitic limestone which contains the required amount of alkalinity. The mass of each type of limestone was determined by multiplying the total alkalinity required per limestone by the molar mass of analytical grade calcite ($100.09 \text{ g}\cdot\text{mol}^{-1}$) and dolomite ($184.41 \text{ g}\cdot\text{mol}^{-1}$) respectively. The mass of each type of limestone was determined assuming that each type of limestone has a 100% reactivity. It should be noted that if the reactivity is less, the mass of each type of limestone would be more.

The calculated weight of each type of limestone was the same for each particle size fraction used in the experiment. After weighing the calculated mass of calcitic and dolomitic limestone for each particle size fraction, it was added to the Schott flasks which contained 100 ml of the various solutions. The contents of the flasks were mixed at intermittent periods during the experiment.

The pH of the solutions was measured after every 48 hours using a calibrated Consort C830 pH meter until they had all reached a neutral condition (pH between 7 and 7.5). If this condition could not be achieved after a 720-hour reaction period, the experiment was terminated.

Table 4.5: The total alkalinity requirement for each type of limestone and the estimated amount of each to neutralize 100 ml of each solution.

Solution	Total acidity (mmol H ⁺)	Total carbonate alkalinity (mmol CO ₃ ²⁻) per limestone type		Mass (g) of each type of limestone which contains the required amount of alkalinity (as CO ₃ ²⁻)	
		Calcite	Dolomite	Calcite	Dolomite
				(CaCO ₃)	(CaMg(CO ₃) ₂)
Control	1.48	1.48	0.74	0.148	0.136
AMD-Fe	2.76	2.76	1.38	0.276	0.253
AMD-Al	3.16	3.16	1.58	0.316	0.290
AMD-Mn	2.96	2.96	1.48	0.296	0.272
AMD-Fe-Al-Mn	5.92	5.92	2.96	0.592	0.545

Five acidic solutions, two types of limestone and three particle size fractions were used in this experiment. This provided a total of 30 treatment options. Each treatment option was replicated thrice to allow for statistical analysis of the data. Examples of a few treatment options used for the experiment are as follows:

AMD-Fe-Calcite-Coarse treatment:

For the particle size fraction of 1 – 2 mm, it was estimated that 100 ml of the AMD-Fe solution will require 0.276 grams of calcite (see Table 4.5).

AMD-Fe-Dolomite-Medium treatment:

- For the particle size fraction of 0.25 – 0.50 mm, it was estimated that 100 ml of the AMD-Fe solution will require 0.253 grams of dolomite.

After termination of the neutralization test, aliquots were taken from the various solutions, which were treated with each of the particle size fractions of calcite and dolomite and analysed with ICP-OES. The analysis included a measure of the calcium (Ca^{2+}) and magnesium (Mg^{2+}) concentrations (mol.L^{-1}) of the solutions treated with calcite and dolomite respectively (See Appendix A4, tables A4.3 and A4.6).

The presence of calcium and magnesium in the solutions was a result of the dissolution of the agricultural limestone used. Therefore, by determining the amount of Ca and Mg present in solution after the test ended, the dissolution efficiency of the various particle size fractions of calcite and dolomite was determined. This facilitates a quantification of the effectiveness of each particle size fraction of calcitic and dolomitic limestone in neutralizing the various acid solutions.

The dissolution efficacy of each particle size fraction of calcitic limestone was calculated by dividing the equilibrium aqueous Ca concentration (mmol.L^{-1}) after 30-day equilibration period, obtained by ICP analysis (Calcium $M_{\text{equilibrium}}$) by the amount of Ca^{2+} (mol) present in the required amount of calcite used to neutralize each solution (Calcium M_{initial}) (see equation 24).

Similarly, the dissolution efficacy of each particle size fraction of dolomitic limestone was calculated by dividing the equilibrium aqueous Mg concentration (mmol.L^{-1}) after 30-day equilibration period, obtained by ICP analysis (Mg $M_{\text{equilibrium}}$) by the amount of Mg^{2+} (mol) present in the required amount of dolomite used to neutralize each solution (Mg M_{initial}) (see equation 25).

$$\% \text{ Calcitic Limestone dissolution} = \frac{\text{Ca}M_{\text{Equilibrium}}*V}{\text{Ca}M_{\text{Initial}}} \times 100 \quad (24)$$

$$\% \text{ Dolomitic Limestone dissolution} = \frac{\text{Mg}M_{\text{Equilibrium}}*V}{M_{\text{Initial}}} \times 100 \quad (25)$$

Note that V is the volume of each solution used in the neutralization test (100 ml).

Refer to Appendix A4 for a summary of the amount of calcium and magnesium present in the required amount of calcitic and dolomitic limestone used to neutralize each of the solutions (Table A4.2 and A4.4) as well as the calcium and magnesium concentrations present in the solution after the test ended (Table A4.3 and A4.5). See Appendix A4 for an example calculation of equation 24 and 25 respectively.

The presence of Fe, Al and Mn can influence the dissolution of the various particle size fractions of the agricultural limestone by restricting its dissolution through armouring of its surface. It was decided that the measured amount of calcium in each solution treated with the various particle size fractions of each type of agricultural limestone be used to assess this influence. This is because each particle size fraction of the agricultural limestone used has higher calcium than magnesium content (Table A4.1 Appendix A4).

An analysis of variance (ANOVA) assessed significant differences between calcium concentrations within solutions treated with the various particle size fractions of agricultural limestone. The means were compared using the Tukey HSD – Post Hoc test at a significance level of $\alpha = 0.05$ (see Figures 4.2 and 4.3).

Neutralization curves were also plotted to visualise the influence of Fe, Al and Mn on buffering the neutralization of AMD with the various particle size fractions of the agricultural limestone. This evaluates the influence of these metals on the possible occurrence of armouring of the surfaces of the varying particle size fractions of calcite and dolomite which restricts their dissolution during neutralization.

4.3 Results and Discussion

4.3.1 The Dissolution Efficiency of the Various Particle Size Fractions of Agricultural Limestone Used for Neutralization.

Table 4.6 provides a quantification of the dissolution efficiency of each of the particle size fractions of calcite and dolomite used to neutralize the various acidic solutions. Each solution was treated with the calculated theoretical amounts of calcite and dolomite required to neutralize its total acidity (Table 4.5).

In the case of the control solution (dilute sulphuric acid) the dissolution efficiency of each particle size fraction of calcite and dolomite is more than 50 %. Therefore, at least half of the amount of calcite and dolomite that was required to neutralize this solution had dissolved during the experiment. This implies that the dissolution of the various particle size fractions was not significantly influenced and can be regarded as efficient in terms of neutralising this solution.

The differences observed in the dissolution efficiencies of the various particle size fractions is attributed to the rate at which they dissolved. This is affected by the particle size of the limestone and the fine (<0.25 mm) size fraction for each type of limestone showed the highest dissolution efficiency. This is attributed to its larger specific surface area, which increased the contact between its surface and acidic ions in the control solution which enabled quicker dissolution of the agricultural limestone.

Table 4.6: Average dissolution (%) of the particle size fractions of calcite and dolomite used to neutralize the various acid solutions.

Solution	Dissolution (%)					
	Calcite particle sizes			Dolomite particle sizes		
	Coarse (1 – 2 mm)	Medium (0.25 – 0.50 mm)	Fine (< 0.25 mm)	Coarse (1 – 2 mm)	Medium (0.25 – 0.50 mm)	Fine (< 0.25 mm)
Control	53	62	63	62	66	73
AMD-Fe	61	65	88	82	86	96
AMD-Al	47	70	76	77	94	95
AMD-Mn	42	46	46	48	46	49
AMD-Fe-Al- Mn	31	37	50	51	57	60

The quantified dissolution efficiency of each particle size fraction of calcite and dolomite with the iron rich acid solution (AMD-Fe) is also regarded as effective. However, the decrease in the dissolution of the coarse (1 – 2 mm) and medium (0.25 – 0.50 mm) particle size fractions of the agricultural limestone from that of the fine (<0.25 mm) size fraction raises a question about their dissolution efficiency during neutralization of this solution.

The differences imply that the dissolution of the coarse size fraction of calcite and dolomite, and the medium size fraction of each was limited with the former size fraction of each being the most influenced. This shows that the presence of iron in the solution has most likely impacted the effectiveness of the abovementioned size fractions of the agricultural limestone to dissolve and neutralize the solution.

The impact can be caused by a lower specific surface area of the surfaces of these particle size fractions which dissolves more slowly than the fine particle size fraction. The slower dissolution rate of the coarse and medium particle size fractions of calcitic and dolomitic limestone can favour the armouring of their surfaces by iron precipitates as a longer period is needed for their dissolution, which enables the coating of their surfaces and can restrict dissolution. In addition, the dissolution efficiency of the coarse calcite size fraction suggests that the armouring by iron precipitates has a greater influence on its dissolution and neutralizing potential than the coarse dolomite size fraction.

Just as with the AMD-Fe solution, the quantified dissolution efficiency of, particularly, the coarse particle size fraction (1 - 2 mm) of the agricultural limestone from the dissolution of the medium and fine size fractions raised a query regarding its dissolution during the neutralization of the AMD-Al solution. In the case of the coarse calcite fraction, less than half of the amount of calcite that was required to neutralize this solution had dissolved during the experiment.

This implies that the dissolution efficiency of this particle size fraction of calcite can be regarded as ineffective in terms of neutralising the aluminium rich acid solution. However, in the case of the coarse dolomite fraction more than half of the amount of dolomite that was required to neutralize this solution had dissolved. This suggests that it is effective in neutralizing the solution.

The differences in the dissolution efficiencies of the coarse size fraction from the medium and fine size fraction of each type of limestone shows that the presence of aluminium in the solution has most likely impacted their dissolution. This could also be caused by a lower specific surface area of this particle size fraction which dissolves more slowly than the other size fractions. The slower dissolution rate of the coarse calcitic and dolomitic limestone can be conducive to the possible armouring of their surfaces by aluminium precipitates as a longer period is needed for their dissolution which influences their reactivity.

It is also noted that the dissolution efficiency of the coarse calcite fraction is lower than the coarse dolomite fraction (just as with the AMD-Fe solution). This indicates that its dissolution is limited owing to the presence of aluminium in the solution because of the likely armouring of the surfaces of the coarse calcite fraction by aluminium precipitates, which is more prominent than with the coarse dolomite fraction.

The AMD-Fe and AMD-Al solution show similar trends regarding the dissolution of the different particle size fractions of each liming material used for neutralization. Both metals have an influence on the dissolution of particularly the coarse particle size fraction. However, it is noted that the metals have a greater influence on limiting the dissolution and consequent neutralizing potential of the coarse calcite fraction. This demonstrates that calcite is likely more prone to being armoured by iron and aluminium precipitates than dolomite.

Furthermore, when focus is placed on neutralizing acidic solutions which contain iron and aluminium (like AMD), the particle size fraction of the liming material used becomes an essential consideration.

In the case of the manganese rich acid solution (AMD-Mn), the dissolution efficiencies of the calcite particle size fractions used to neutralize the AMD-Mn solution are nearly identical and less than half of the amount of calcite which was used had dissolved during the experiment. Similarly, are the dissolution efficiencies of the various particle size fractions of dolomite. This suggests that the presence of Mn in solution does not influence the dissolution of the various particle size fractions of calcite and dolomite used for neutralization.

The previous chapter showed that manganese has a buffering influence caused by its acid generating potential. This influence occurs once a neutral condition is reached, and its influence extends over a pH range that coincides with neutrality. This implies that the various particle size fractions of calcite and dolomite would undergo sufficient dissolution to reach a neutral condition before their dissolution and neutralization potential is influenced by the potential armouring of their surfaces by manganese precipitates.

In the case of the AMD-Fe-Al-Mn solution the dissolution of the coarse and medium particle size fractions of calcite is regarded as ineffective. The reactivity of primarily the coarse calcite fraction shows that its dissolution during neutralization is severely limited and can be attributed to the presence of Fe and Al, which is likely to have armoured this particle size fraction.

However, the dissolution efficiency of the dolomite particle size fractions can be regarded as effective. The decrease in the dissolution of the coarse and medium-size fractions from the dissolution of the fine fraction generated interest during the neutralization of the AMD-Fe-Al-Mn solution. This demonstrated that the dissolution of the coarse and medium dolomite size fractions is limited owing to the presence of Fe and Al in the solution, which is likely to have armoured the surfaces of these size fractions as with the coarse and medium particle size fractions of calcite.

Decreasing the particle size fraction of both liming materials increased the dissolution efficiency of calcite and dolomite used for the neutralization of the control, AMD-Fe, AMD-Al and AMD-Fe-Al-Mn solutions. However, the particle size fractions of calcite and dolomite used for the neutralization of the AMD-Mn solution did not affect the dissolution of the liming materials.

The fine particle size fraction of each liming material (particle size of less than 0.25 mm) was the most effective size fraction used for neutralization. This implies that, of the particle size fractions considered in this study, the fine particle size fraction is the most appropriate to use for the neutralization of acid metal solutions like AMD, but finer fractions would most likely be even better.

The increase in the dissolution efficiency associated with decreasing the particle size fraction of the liming materials was a result of an increase in the total available surface area of the liming materials. This has a favourable influence on the rate of acid neutralization (Sun et al, 2000), which catalyses the dissolution kinetics and implies that more calcite and dolomite can dissolve at a faster rate (van Tonder et al, 1994) leading to an increase in the availability of alkaline ions (CO_3^{2-}) required for neutralization.

Each of the dolomite particle size fractions used in this study showed an overall higher dissolution efficiency compared to the calcite particle size fractions during the neutralization of the acid solutions. The difference between the reactivity of the various particle size fractions of calcite and dolomite could be due to a greater proportion of carbonate, in the dolomitic limestone used for this experiment.

4.3.2 The Restriction in the Dissolution of the Various Particle Size Fractions of Agricultural Limestone as Influenced by the Presence of Fe, Al and Mn.

The calcium concentration within specific solutions obtained from the ICP-OES analysis was compared to identify if observed differences were statistically significant after treatment with calcite (Figure 4.1) and dolomite (Figure 4.2) of the various particle size fractions used. See Appendix A4 Table A4.5 for the concentration data.

This was done to confirm the restriction in the dissolution of the different particle size fractions of the agricultural limestone as influenced by the presence of metals in the different solutions.

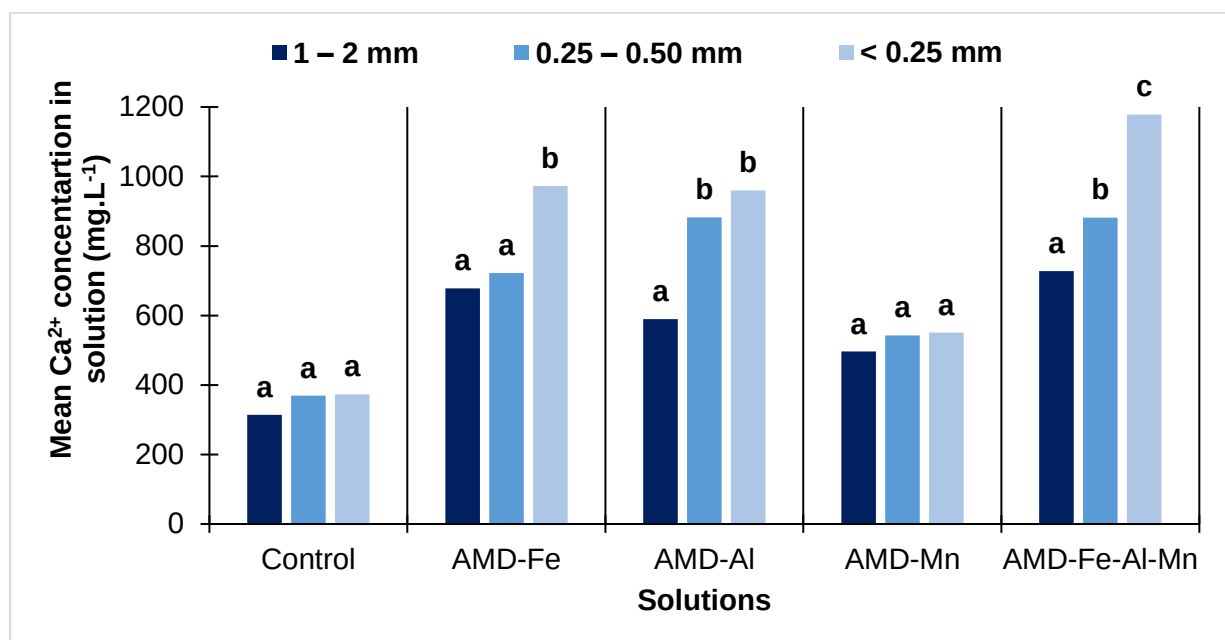


Figure 4.1: The mean equilibrium calcium concentration in each solution treated with coarse (1 – 2 mm), medium (0.25 – 0.50 mm) and fine (< 0.25 mm) particle size fractions of calcite after 30 days of reaction. (Note: The mean calcium concentration for a specific solution with the same letter is not significantly different at $\alpha = 0.05$).

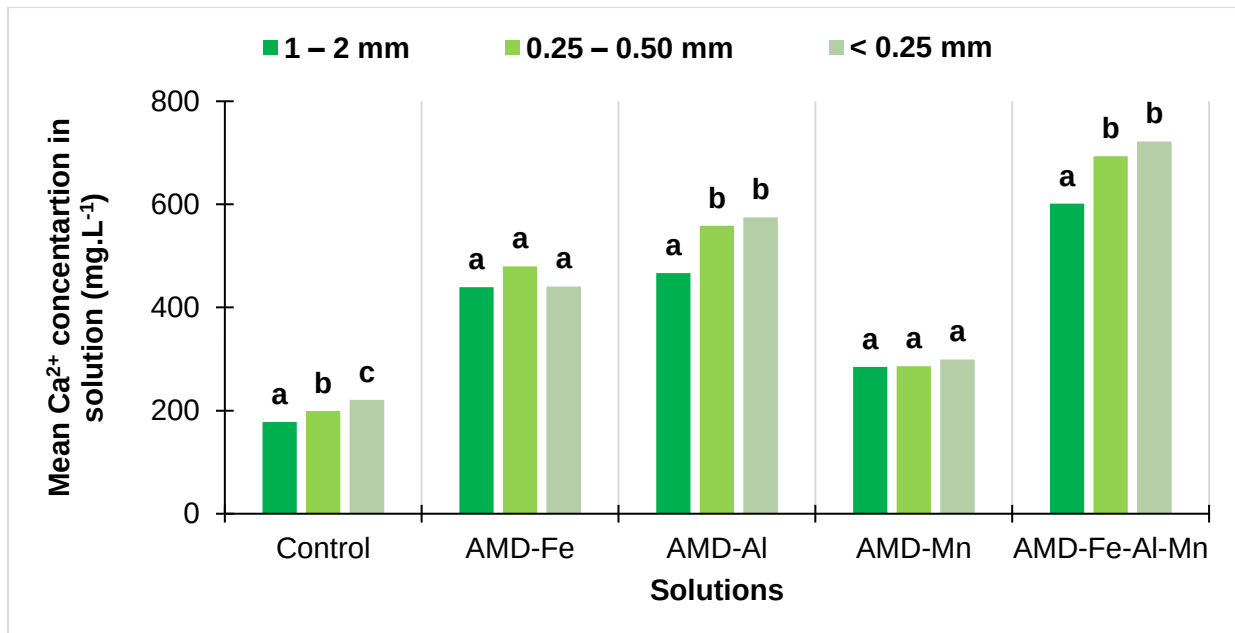


Figure 4.2: The mean equilibrium calcium concentration in each solution treated with coarse (1 – 2 mm), medium (0.25 – 0.50 mm) and fine (< 0.25 mm) particle size fractions of dolomite after 30 days of reaction. (Note: The mean calcium concentration for a specific solution with the same letter is not significantly different at $\alpha = 0.05$).

Treating the control solution with the coarse (1 - 2 mm), medium (0.25 - 0.50 mm) and fine (< 0.25 mm) calcite size fractions (Figure 4.1) did not show any significant differences in their calcium concentrations. This confirms that the dissolution of each particle size fraction of calcite was not significantly restricted by the control solution during the neutralization period. However, the calcium concentrations in the control solution, which were treated with the same particle size fractions of dolomite (Figure 4.2) are all significantly different.

The differences are thought to be caused by the rate at which they dissolved or the armouring of their surfaces which could have stopped dissolution. The fine dolomite fraction is likely to have dissolved more quickly in comparison to the coarse and medium fractions.

The slower dissolution rates associated with the coarse and medium dolomite fractions could have favoured the conditions leading to the precipitation of gypsum. It is suggested that the dissolution rate of the larger particle size fractions to be the rate-controlling step (Offeddu et al, 2015) which is either diffusion or surface controlled. In the case of sparingly soluble minerals like dolomite, it is surface controlled. This implies that the slow dislodgement of ions in the mineral limits dissolution. Therefore, as the coarse and medium dolomite size fractions dissolved, the solution at the coarse/medium dolomite-solution interface could become supersaturated with respect to gypsum.

This is likely to have favoured its precipitation at specific surface localities at which this condition presides, leading to the armouring of these sites (Offeddu et al, 2015). The armouring then impedes dissolution and restricts the release of calcium from the coarse and medium dolomite fractions. This could cause the observed differences in the calcium concentrations present in the control solution, after equilibration, from each dolomite particle size fraction.

The AMD-Fe solution showed significant differences between the concentrations of calcium after treatment with the coarse and fine particle size fractions, as well as the medium and fine size fractions (Figure 4.1). The observed differences confirm that the dissolution of the coarse and medium particle size fractions was influenced during neutralization and that the presence of Fe had caused a restriction in their dissolution, particularly for the coarse fraction.

However, no significant differences between the concentrations of calcium in this solution were observed after being treated with the coarse, medium, and fine particle size fractions of dolomite (Figure 4.2). This confirms that Fe did not severely restrict the dissolution of the various particle size fractions of dolomite in comparison to its impact on the dissolution of calcite.

Similarly, the concentrations of calcium in the AMD-Al solution, treated with the coarse and fine particle size fractions of calcite as well as the coarse and medium size fractions of calcite, are significantly different (Figure 4.1). This confirms that the dissolution of primarily the coarse fraction was influenced by the presence of Al in this solution consequently causing the restriction in its dissolution.

The extent of the difference between the calcium concentrations in the solution after treatment with the various particle size fractions indicates that coarse calcite was specifically unable to neutralise the AMD-Al solution or increase its pH to an appropriate level.

Similarly, significant differences between the concentrations of calcium in the AMD-Al solution, which was treated with the coarse and fine particle size fractions of dolomite as well as the coarse and medium size fractions of dolomite is noted (Figure 4.2). This confirms that the dissolution of the coarse particle size fraction was influenced by the presence of Al in solution and had caused the restriction in the dissolution of this particle size fraction.

However, the extent of the difference in the calcium concentrations between the dolomite particle size fractions is not as great as when calcite was used. This indicates that the dissolution of coarse dolomite was only partially restricted during neutralization.

Treating the AMD-Mn solution with the coarse, medium, and fine particle size fractions of calcite and dolomite did not show any significant differences between the Ca^{2+} concentrations in this solution. This implies that the dissolution of the various particle size fractions of both types of limestone was not significantly restricted by the presence of Mn in solution during the neutralization period.

The mean calcium concentrations in the AMD-Fe-Al-Mn solution treated with coarse, medium, and fine particle size fractions of calcite are all significantly different. The extent of the differences confirms that the dissolution of the coarse and medium particle size fractions had mainly been restricted during neutralization. The former size fraction was severely restricted in its dissolution and unable to neutralize the solution or establish an appropriate pH. The latter fraction displayed a limited restriction in its dissolution during neutralization.

Similarly, the mean calcium concentrations in the AMD-Fe-Al-Mn solution treated with coarse, medium, and fine particle size fractions of dolomite are all significantly different. However, the extent of the differences in the calcium concentrations is not as significant as when calcite was used.

The restriction in the dissolution of the varying particle size fractions of calcite and dolomite shows that the efficacy of the fine particle size fraction (< 0.25 mm) was the greatest during neutralization of the various acid solutions. This implies that it has the greatest neutralizing potential and would be the most appropriate size fraction to use when AMD is used as irrigation on soil that is preconditioned with these amendments.

The next section evaluates the influence of Fe, Al, and Mn on the occurrence of armouring of the surfaces of the particle size fractions of calcite and dolomite. Neutralization curves (Figures 4.4 and 4.5) are provided to visualise the influence of these metals on neutralizing AMD using coarse (A. 1 – 2 mm), medium (B. 0.25 – 0.50 mm) and fine (C. < 0.25 mm) particle size fractions of agricultural limestone. See Appendix 4 Tables A4.6 to A4.10 for the neutralization data for each of the solutions treated with the various particle size fractions of calcite and dolomite.

4.3.3 The Influence of Fe, Al, and Mn on Armouring of the Various Particle Size Fractions of the Agricultural Limestone Used for Neutralization.

Both figures (4.4 and 4.5) show that when the control solution (dilute sulphuric acid) was neutralized by the various particle size fractions of calcite and dolomite, each particle size fraction was able to increase the pH of this solution to a neutral condition (pH between 7 and 7.5).

The fine particle size fraction (< 0.25 mm) of both types of limestone was the most efficient in neutralizing the control solution. However, when coarse and medium particle size fractions of calcite and dolomite were used, there was a temporary lag in neutralization. This lag results in a longer period required to reach a neutral condition.

The lag in neutralization observed for the coarse (Figures 4.4 & 4.5 A) and medium particle size fractions of calcite and dolomite (Figures 4.4 & 4.5 B) is attributed to the total available surface area that can dissolve and neutralize the acidity signature of the control. Larger particle size fractions have a smaller surface area in contact with acidic ions in the solution.

This means that less material can dissolve, therefore needing a longer reaction period for neutralization. However, decreasing the particle size of the limestone, increases the total surface area of the alkaline material. This results in a higher availability of material, which can dissolve and neutralize the acidity signature of the control solution at a faster rate.

The coarse particle size fraction needed the longest reaction period with calcite requiring 504 hours and dolomite 432 hours to reach neutrality. The medium particle size fraction followed with calcite requiring 384 hours and dolomite 336 hours; while the fine particle size fraction of both types of limestone required 240 hours to reach a neutral condition. The fine particle size fraction therefore has the shortest reaction period.

The shorter reaction periods observed for the coarse and medium particle size fractions of dolomite in comparison to the period required for the same size fractions of calcite could be due to a greater proportion of calcium carbonate than magnesium carbonate, in the dolomitic limestone.

The neutralization curves (Figures 4.4 & 4.5) confirm that the control solution does not have a significant influence on the dissolution of the various particle size fractions of calcite or dolomite. This also indicates that the influence of gypsum precipitation on the surface of the various particle size fractions of the limestone is minor. What is crucial, however, is the time allowed for neutralization especially if coarser and less reactive particle size fractions are used.

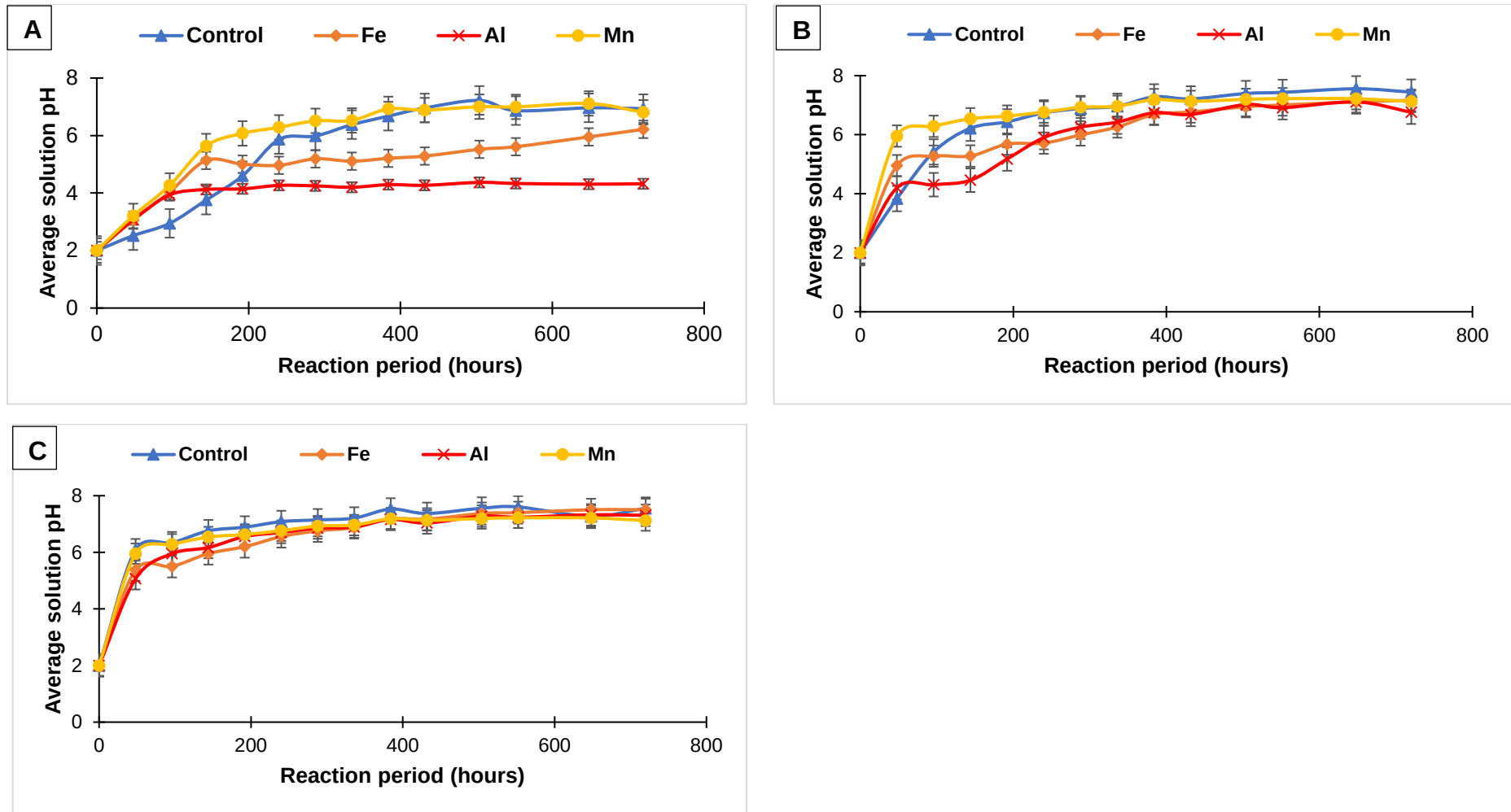


Figure 4.3: The influence of Fe, Al and Mn on the potential occurrence of armouring of the surfaces of various particle size fractions (A. 1 – 2 mm, B. 0.25 – 0.50 mm and C. < 0.25 mm) of calcite used to neutralize the AMD solutions.

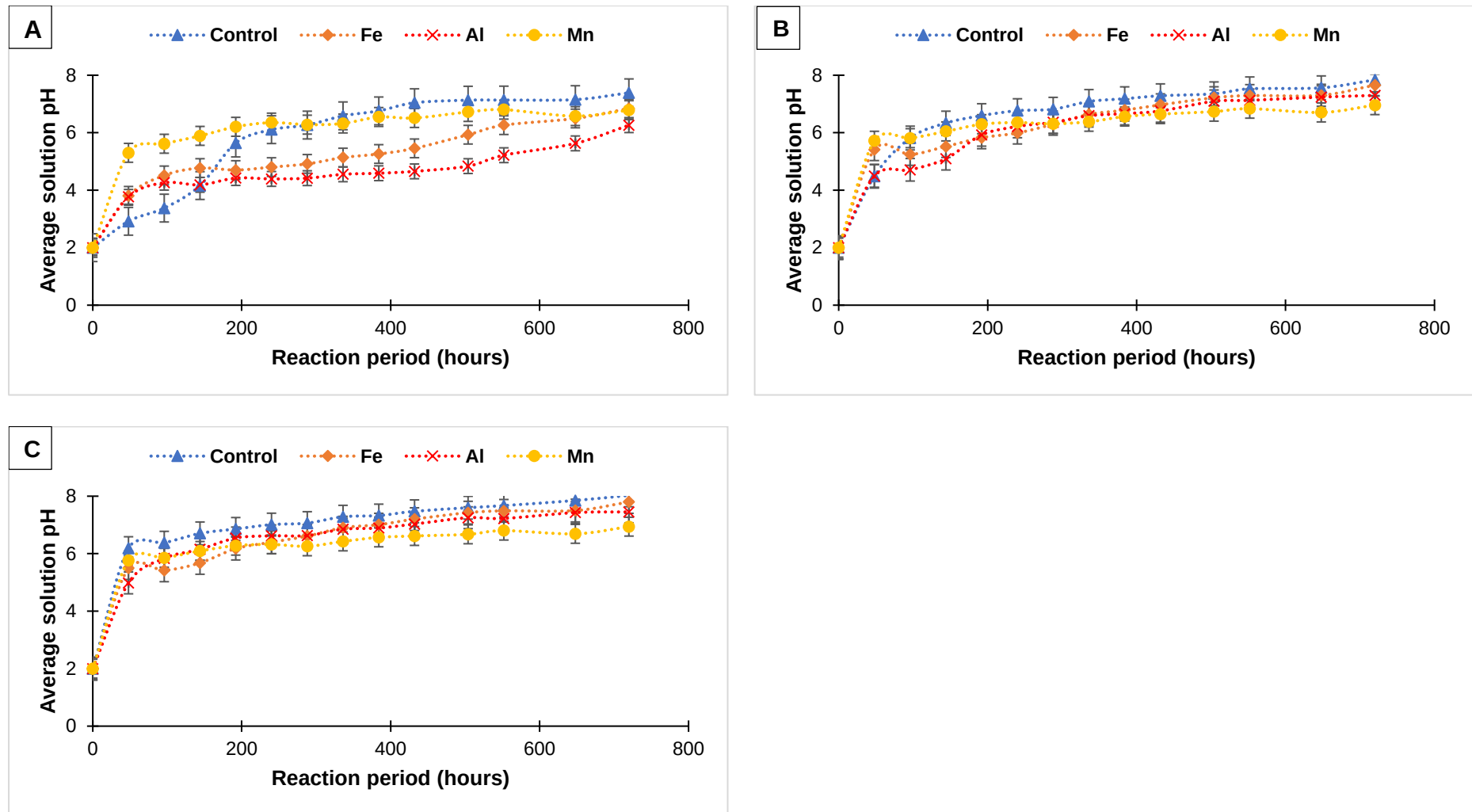


Figure 4.4: The influence of Fe, Al, and Mn on the potential occurrence of armouring of the surfaces of various particle size fractions (A. 1 – 2 mm, B. 0.25 – 0.50 mm and C. < 0.25 mm) of dolomite used to neutralize the AMD solutions.

The AMD-Fe solution demonstrated that the presence of iron in solution caused a temporary restriction in the dissolution of coarse (Figure 4.3 and 4.5 A.) and medium (Figure 4.3 and 4.5 B.) particle size fractions of calcite and dolomite, thus influencing neutralization of the solution. The restriction is represented by the plateauing in the neutralization curve of this solution at a certain pH range.

The plateauing of the neutralization curve of the AMD-Fe solution that was treated with the coarse particle size fraction of calcite occurred when the solution reached a pH of 5 and ended when the pH of the solution reached approximately 5.5. The restriction in the dissolution of this particle size fraction extended over a period of 360 hours. Also, treating the AMD-Fe solution with coarse calcite did not allow for its neutralization as the final pH of the solution was 6.21 after reacting for a period of 720 hours.

Similarly, coarse dolomite was also unable to neutralize the AMD-Fe solution and the final pH of the solution after reacting for a period of 720 hours was 6.84. Iron restricted the dissolution of coarse dolomite as represented by the plateau, which occurred when the solution reached a pH of 4.5 and extended until the solution reached a pH of 5. The restriction in the dissolution of this particle size fraction extended over a period of 192 hours.

The AMD-Fe solution had a slight influence on the dissolution of the medium particle size fraction of calcite and dolomite as represented by the short plateauing of the neutralization curve of this solution (Figure 4.3 and 4.5 B.).

The plateau occurred when the solution reached a pH of 5 and ended when its pH was 5.5. The restriction in the dissolution of the medium calcite and dolomite size fraction extended for 96 hours. Treating the AMD-Fe solution with medium calcite and dolomite allowed for a neutral condition to be established despite the temporary restriction in its dissolution.

The fine particle size fraction of both types of limestone was not influenced by the presence of Fe in the solution as each size fraction of limestone neutralized the solution. The fine calcite fraction achieved a final pH of 7.51 and dolomite a final pH of 7.80. This size fraction also required the shortest period to neutralize the solution, which was achieved after 384 hours, and achieved the highest final pH of the size fractions used for the neutralization test.

The plateaus on the neutralization curve of the AMD-Fe solution demonstrates that the dissolution of mainly the coarse particle size fractions of calcite and dolomite were restricted. The dissolution of the medium size fraction of both types of limestone was only slightly influenced and was able to neutralize the solution.

Treating the solution with the limestone removes the acidity of the solution, increases the solution pH, and allows Fe precipitation reactions to occur (Santomartino and Webb, 2007). Fe precipitation results in the removal of iron from solution which causes the restriction in the dissolution of the coarse particle size fractions of calcite and dolomite as demonstrated by the plateaus on the neutralization curves.

Coarse particle fractions have smaller available surface areas which negatively influences the rate of acid neutralization with longer periods required to remove acidity from the solution. However, the zones or areas of solution closely surrounding the coarse particles indicate significantly higher pH conditions than the rest of the solution. These zones will favour the oxidation of ferrous to ferric iron and the precipitation of Fe minerals like lepidocrocite and goethite (Jones et al, 2014) if the pH in these areas is greater than 4.5 (Bailey, 2016). This occurs via heterogeneous nucleation, which is a surface-induced precipitation process.

Through the process of heterogeneous nucleation, the surface of the coarse calcite acts as the centre upon which Fe minerals can precipitate, develop, and grow. This encapsulates the surface of the coarse calcite fractions with a Fe precipitate coating that is commonly referred to as armouring (Hammarstrom et al, 2003; Ziemkiewicz et al, 1997).

The Fe armouring forms a diffusion barrier between the surface of the coarse calcite and the solution thus restricting its dissolution and limiting the rate at which the solid limestone is attacked by protons and neutralizes acidity (Santomartino and Webb, 2007).

The armouring of the surface of, particularly, the coarse calcite and dolomite size fractions by iron precipitates is likely to be responsible for hindering the neutralization process that resulted in the plateau in the neutralization curves of the AMD-Fe solution as shown in Figure 4.3 and 4.5 A. Although these particle sizes were armoured and were able to facilitate the further increase in pH, they were unable to establish a neutral condition for the AMD-Fe solution within the period allocated for the experiment.

The AMD-AI solution demonstrated the influence of aluminium present in solution on the coarse and medium particle size fractions of calcite and dolomite to neutralize the solution. The aluminium in solution caused a:

- restriction in the dissolution of the coarse calcite fraction (Figure 4.3 A.),
- temporary restriction in the dissolution of coarse dolomite fraction (Figure 4.4 A.) due to a lower dissolution rate which required a longer period to reach equilibrium and,
- slight restriction in the dissolution of the medium particle size fraction of calcite and dolomite (Figure 4.3 and 4.5 B.).

The influence is due to restricting the dissolution of the abovementioned particle size fractions as represented by the plateauing in the neutralization curve of this solution. The plateauing of the neutralization curve for the AMD-AI solution that was treated with the coarse particle size fraction of calcite occurred when the solution reached a pH of 4. Treating the AMD-AI solution with coarse calcite did not allow for its neutralization and the final pH of the solution was 4.32 after reacting for a total of 720 hours. The plateau also remained level and the restriction of the dissolution of the coarse calcite fraction was permanent.

Aluminium restricted the dissolution of coarse dolomite as represented by the plateau, which occurred when the solution reached a pH of approximately 4 and ended when the solution reached a pH of 4.84. The restriction lasted for a period of 408 hours after which the pH increased to a final value of 6.26.

The AMD-AI solution had a slight influence on the dissolution of the medium particle size fraction of calcite and dolomite as represented by the brief plateauing of the neutralization curve of this solution (Figure 4.3 and 4.5 B.). The plateau that influenced the dissolution of the medium calcite fraction occurred when the solution reached a pH of 4 and ended at a pH of 4.5.

The restriction in the dissolution of this size fraction lasted for 96 hours. Similarly, the plateau that influenced the dissolution of the medium dolomite fraction occurred when the solution reached a pH of 4.5 and ended at a pH of 4.71 lasting for 48 hours. However, the medium calcite and dolomite fractions were able to neutralize the AMD-AI solution and required 504 hours to reach a neutral condition.

The fine particle size fraction of both types of limestone was not influenced by the presence of Al in the solution as each size fraction of limestone neutralized the solution. Fine calcite achieved a final pH of 7.31 and dolomite a final pH of 7.45.

The plateaus on the neutralization curve of the AMD-Al solution demonstrate that the dissolution of the coarse particle size fractions of calcite and dolomite was restricted. Though coarse dolomite showed a restriction in its dissolution, this was temporary and led to an increase in solution pH. It is also possible that if more time was allowed, the solution could have eventually reached a neutral condition.

Using coarse calcite to neutralize the AMD-Al solution was unsuccessful because its dissolution was severely restricted thus failing to neutralize the solution. This is due to the strong adhesion of Al oxyhydroxide and hydroxysulphate precipitates on the surface of the coarse calcite fraction (Palomino-Ore et al, 2019), which could have armoured its surface (Cravotta and Trahan, 1999) like the influence of Fe on this size fraction).

Armouring of the coarse calcite prevented the transfer of ions to and from the calcite causing a restriction in dissolution and neutralization by ion diffusion through the Al precipitate coating. As the neutralization experiment continued, it is probable that the thickness of the Al precipitate coating continued to increase through its growth, which caused it to become an increasingly effective barrier to ion transport (Palomino Ore et al, 2019). This caused the restriction in the dissolution of the coarse calcite fraction, which led to its failure to neutralize the AMD-Al solution or increase its pH to a suitable level. This is supported by the low dissolution efficiency (47%) that was calculated for the coarse calcite fraction during neutralisation of the AMD-Al solution (Table 4.6).

The AMD-Mn solution did not have an influence on any of the particle size fractions of calcite used for neutralization. This implies that Mn does not significantly restrict the dissolution of the coarse, medium, and fine calcite during neutralization. The coarse calcite fraction was able to neutralize the AMD-Mn solution and required 504 hours, whereas the medium and fine calcite fractions required 384 hours to reach a neutral condition.

The coarse, medium, and fine dolomite particle size fractions were unable to neutralize the AMD-Mn solution. Each size fraction established a circum-neutral condition after the experiment was terminated and the final pH of the solution, after reacting with the various particle size fractions of dolomite, was between 6.7 and 6.9. Figure 4.4 A to C does not show any signs of the restriction in the dissolution of the dolomitic particle size fractions, which also implies that Mn does not restrict its dissolution during neutralization. However, it is probable that the abovementioned size fractions of dolomitic limestone may have been able to neutralize the AMD-Mn solution over a longer period.

4.3.4 Neutralizing the AMD-Fe-Al-Mn Solution with the Various Particle Size Fractions of Calcite and Dolomite.

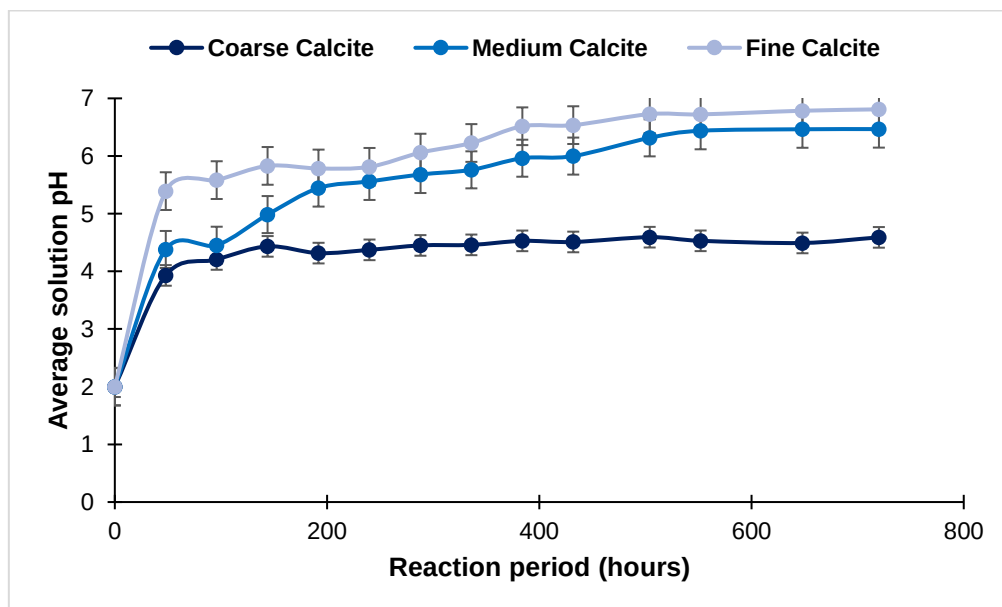


Figure 4.5: The influence of the various particle size fractions of calcite on the neutralization of the AMD solution which contains all three metal cations.

Figure 4.5 shows that treating the AMD-Fe-Al-Mn solution with the coarse calcite fraction, with a particle size of 1 – 2 mm, was unsuccessful in neutralizing the solution and could not increase its pH to an appropriate level. The dissolution of this particle size fraction was severely restricted as represented by the plateauing on its neutralization curve.

The plateau occurred when the solution reached a pH of approximately 4 and remained so for the duration of the neutralization experiment (720 hours). This means that the surface of the coarse calcite was coated or armoured thus restricting the dissolution of this particle size fraction.

As explained in section 4.3.3 above, the presence of aluminium in solution resulted in the restriction in the dissolution of the coarse calcite fraction which occurred once a solution pH of 4 was achieved. It was explained that the restriction in its dissolution is a result of the armouring of the coarse calcite surface by Al precipitates and, as the experiment continued, the thickness of the Al precipitate coating increased, which caused it to become an increasingly effective barrier to ion transport (Palomino Ore et al, 2019). This caused the complete restriction in the dissolution of the coarse calcite fraction leading to its failure to neutralize the solution or increase its pH to a suitable level.

The medium calcite fraction, with a particle size between 0.25 - 0.50 mm, underwent a very short restriction in its dissolution, which occurred when the solution reached a pH of 4.38 and ended at a pH of 4.45. Thereafter, the pH of the solution increased to 5.78 when another temporary restriction in dissolution occurred until the solution reached a pH of 6. The medium calcite fraction was also unable to neutralize the solution but achieved a final pH of 6.47.

The presence of aluminium and iron in solution demonstrated an influence on the medium calcite fraction when used for neutralization as explained in section 4.3.3. This influence caused a temporary restriction in the dissolution of the abovementioned particle size fraction of limestone as indicated by the two plateaus. The first plateau demonstrates the restriction because of the armouring of the surface of the medium calcite fraction by aluminium precipitates, and the second is attributed to armouring by iron precipitates.

The combined influence partially hinders neutralization and consequently limits the neutralization potential of the medium calcite fraction. It is proposed that a longer reaction period could have led to a neutral condition when the AMD-Fe-Al-Mn solution was neutralized using the medium calcite size fraction.

The fine calcite fraction, particle size < 0.25 mm, was temporarily restricted in its dissolution, which occurred between a pH of 5.39 and 5.81. The pH of the solution was able to increase to a circum-neutral level thereafter. The final pH achieved was 6.81 and was the highest pH overall for the various calcite particle size fractions. The temporary restriction in the dissolution of this size fraction could be the result of the settling of the precipitates (which form in solution) onto the bed of fine calcite in the solution rather than armouring of its surface by Fe precipitates. This can fill the interstitial spaces between the calcite particles and solution thus reducing contact and restricting its neutralization capacity (Palomino Ore et al, 2019; Santomartino and Webb, 2007).

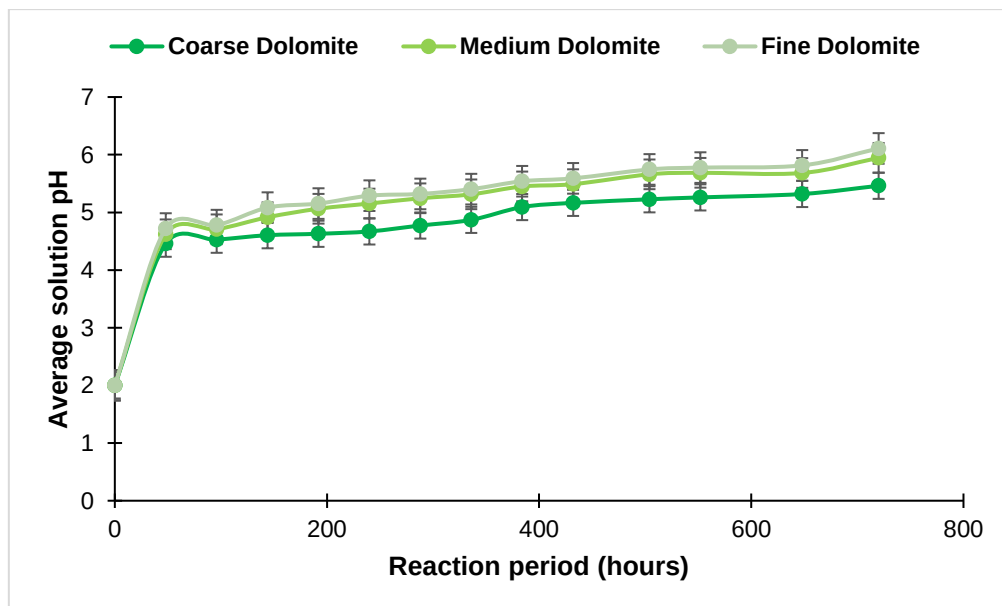


Figure 4.6: The influence of the various particle size fractions of dolomite on the neutralization of the AMD solution which contains all three metal cations.

Treating the AMD-Fe-Al-Mn solution with the coarse dolomite fraction was unsuccessful in neutralizing the solution and could not increase its pH to an acceptable level. The dissolution of this particle size fraction was restricted as represented by the presence of two plateaus on its neutralization curve.

The first plateau occurred when the solution reached a pH of 4.46 and continued for 288 hours until its pH was 4.87. The pH of the solution then increased to 5.09 when the second plateau commenced that lasted for a period of 336 hours to a final pH of 5.46 before the experiment was concluded.

The plateaus on the neutralization curve associated with the coarse dolomite fraction imply that the dolomite surface was also likely to be armoured by Al and Fe precipitates, which restricted its dissolution, hindered neutralization, and consequently limits its neutralization potential.

The medium and fine dolomite fractions were also unable to neutralize the solution that contains all three metals. A final pH of 5.95 was achieved when using the medium particle size fraction, and a slightly higher pH of 6.11 when fine dolomite was used. Their neutralization potential seems to overlap as shown by the curves in Figure 4.5 and a restriction in the dissolution of these size fractions occurs between a pH of approximately 5 and 5.5. The surface of the medium fraction is likely to have been armoured by Fe precipitates during neutralization.

The fine dolomite fraction is unlikely to have been armoured by Fe precipitates. Rather the potential settling of the precipitates onto the bed of fine dolomite in the solution reduced the contact between the particles and solution and caused a restriction in neutralization. However, it is possible that the medium and fine particle size fractions of dolomitic limestone may have been able to neutralize the solution that contains all three metals over a longer period.

4.4 Conclusion

Decreasing the particle size fraction of calcite and dolomite increased their reactivity when used for neutralization of the AMD solutions. Calcitic and dolomitic limestone with the finest texture (particle size of less than 0.25 mm) was the most reactive size fraction overall. This particle size fraction was also the most effective at dissolution during neutralization of the AMD solutions.

The increase in reactivity is a result of a larger total surface area which results in a higher availability of material in contact with the solution to neutralize acidity. As the particle size of the limestone decreases, its total available surface area increases, which has a positive influence on the rate of dissolution and acid neutralization.

Therefore, the fine particle size has the greatest neutralizing potential and is the most appropriate size fraction to use where AMD is used as irrigation on soil that is preconditioned with agricultural limestone. However, finer particle will probably react even better.

Neutralizing mine impacted water (AMD) is dependent on the particle size fraction of the agricultural limestone used. Utilizing inappropriate size fractions of calcite and dolomite influences their neutralization potential. This is caused by the presence of metals in the water. The metals precipitate as minerals as the pH of the solution increases, which can cover (armour) the surfaces of the agricultural limestone, prevent their dissolution, and limit their neutralization potential.

Neutralizing an acidic solution that contained the following metals (commonly present in AMD) showed that:

Manganese

Did not appear to restrict the dissolution of the varying particle size fractions of calcite and dolomite used during the neutralization experiment.

Iron

Restricted the dissolution of the coarse and medium particle size fractions of calcite and dolomite most likely due to the armouring of the surface of the limestone particles by Fe precipitates.

Iron caused a temporary restriction of the dissolution of the coarse (1 – 2 mm) and medium (0.25 -0.50 mm) particle size fractions of calcite and dolomite. The restriction was more prominent, however, for the coarse fraction of both types of limestone.

Aluminium

Permanently restricted the dissolution of the coarse calcite fraction most likely due to the armouring of the surface of the limestone particles by Al precipitates. However, the coarse dolomite fraction was only temporarily restricted. A slight restriction in the dissolution of the medium particle size fraction of calcite and dolomite was demonstrated.

Neutralizing an acidic solution that contained all three metals (typical of AMD) using the following treatments showed that:

Coarse calcite fraction (1 – 2 mm)

Was not feasible as the complete restriction in its dissolution occurred most likely due to the armouring of its surface by Al precipitates.

Medium calcite fraction (0.25 – 0.50 mm)

Achieved a pH level of 6.48 while also undergoing a temporary restriction in its dissolution due to the probable armouring of its surface by aluminium and iron precipitates.

Fine calcite fraction (< 0.25 mm)

Resulted in the highest pH and was able to achieve a circum-neutral level (pH of 6.81). Its dissolution was temporarily restricted most likely due to the settling of mainly Fe precipitates (which form in solution) onto the bed of fine calcite in the solution rather than armouring of its surface. This can fill the interstitial spaces between the calcite particles and solution, thus reducing contact and restricting its neutralization capacity.

Coarse dolomite fraction

Could not increase the pH to an acceptable level as its dissolution was restricted due to the likely armouring of its surface by Al and Fe precipitates.

Medium dolomite fraction

Could not increase the pH to an acceptable level and underwent a restriction in its dissolution most likely due to the armouring of its surface by primarily Fe precipitates.

Fine dolomite fraction

Achieved a pH of 6.11, but also was temporarily restricted in its dissolution similarly to the fine calcite fraction.

The findings indicate that aluminium and iron, limits the potential of the larger particle size fractions of agricultural limestone to neutralize AMD. This is caused by a restriction in the dissolution of the medium and coarse particle size fractions because of the probable armouring of their surfaces by Al and Fe precipitates.

Based on these findings, the hypothesis which states that Fe will limit the potential of larger particle sizes of agricultural limestone to neutralise AMD to a greater extent than Al and Mn as these larger particles are likely to be armoured by iron precipitates is rejected. It is shown that Al had a greater limitation on the dissolution of the larger particle size fractions of calcite and dolomite during the neutralization of AMD.

Recommendation

It is suggested that to determine suitable liming rates for a specific mine water using a specific liming material, that a dynamic neutralization test be conducted in contrast to a static test as presented in this chapter.

A dynamic neutralization test involves applying the necessary amount of a specific type of limestone of a certain particle size fraction which contains the required amount of alkalinity to neutralize the acidity generated by Fe, Al and Mn in a mine impacted water and to then monitor neutralization of the solution until a restriction in the dissolution potential of the liming material occurs. Thereafter, increments of the liming material should be added to the solution until the restriction in its dissolution and neutralization potential is overcome. This method is suggested to account for the influence of the acid generating potential of the metals in AMD as well as their influence on armouring the surface of a specific particle size fraction of the liming material used during neutralization.

CHAPTER 5: NEUTRALIZING ACID MINE DRAINAGE IN STRATEGICALLY LIMED SOIL COLUMNS TO SUPPORT A ROOTING ENVIRONMENT FOR CROP GROWTH

5.1 Introduction

The third chapter in this study showed that Fe, Al and Mn which are metals commonly present in AMD contribute additional acidity during its neutralization. This is attributed to the oxidation, hydrolysis and consequent precipitation of these metals. Their acid generating ability influences neutralization of AMD and buffers increases in pH that are considered appropriate for the development of soil liming strategies for irrigation with AMD. The findings of the third chapter enable a quantitative determination of the amount of acidity that these metals can potentially generate during the neutralization of AMD. This facilitates a determination of the corresponding amount of alkalinity to neutralize the acidity and lays the foundation for the development of soil liming strategies for irrigation with AMD.

The fourth chapter showed that Fe and Al in AMD restrict the dissolution and neutralizing efficacy of calcitic and dolomitic limestone of varying particle size fractions, which are appropriate for use in agriculture. The findings of the chapter help in selecting an applicable size fraction of agricultural limestone where AMD could be used as irrigation on soil that is preconditioned with these amendments and further contributed to the development of soil liming strategies for irrigation with AMD.

These two phases of the study guide this chapter which determines the potential of strategically liming soil with agricultural limestone to neutralise AMD. To neutralize the acidity introduced by leaching AMD through a soil column, the agricultural limestone must be in contact with the acid solution, which facilitates its dissolution and potential for neutralization to occur.

A common approach to amending soil acidity in agriculture is the mixing of calcitic or dolomitic limestone with soil through cultivation. This technique is generally practised in annual cropping systems like grain farming (FERTASA Handbook, 2016). In these systems, the liming material is usually spread over the soil surface. Thereafter discing occurs, which incorporates the alkaline substance within the root zone (top 20 – 35 cm of soil).

Incorporating the limestone throughout the soil profile increases the temporal contact with AMD and could be expected to improve the chance for neutralizing acidity. However, there is cause for concern. Preferential flow paths occurring within the soil profile may decrease the spatial contact between the leaching AMD and limestone thus lessening the potential for neutralization.

Therefore, an alternative placement position may need to be considered, which involves localising the agricultural limestone in the top half (top 5 – 10 cm) of the soil profile. Immediate contact between percolating AMD and the limestone is made feasible by concentrating the liming material at the top half of the soil profile. This is intended to facilitate quicker dissolution of the limestone to direct neutralization. However, this is mostly reliant on the particle size fraction of the limestone used, appropriate to neutralize AMD.

A soil column experiment was conducted to assess the influence of agricultural limestone in two placement positions in a soil profile on neutralizing AMD and whether a favourable rooting environment for crop growth would be supported. A key assumption of this study that is precluded from the scope of the investigation is that crops will be able to grow and be productive under irrigation with acidic waters if the strategic liming can alleviate any influence of soil acidity and if crops are not susceptible to scorching.

It is hypothesised that localising agricultural limestone within the top half of the soil profile will improve contact with AMD and the chance for neutralization compared to incorporating the limestone throughout the soil profile which lessens contact with AMD and the chance for neutralization.

5.2 Materials and Methodology

5.2.1 Introduction

The experiment was conducted at the Soil Science Laboratory, Department of Plant and Soil Sciences, University of Pretoria. It focused on a soil column experiment to assess the influence of the placement of fine textured (<0.25 mm) calcitic and dolomitic limestone in two positions in a soil profile on neutralizing AMD and whether this would support a favourable rooting environment for crop growth.

The placement positions in the experiment were as follows:

1. Incorporating the agricultural limestone within the root zone of the profile (that is mixed throughout the soil profile)
2. Concentrating the agricultural limestone in the top half of the profile (that is localised within the first 5 cm of the soil profile)

For this study, an average of 900 mm of rainfall was used to represent a year of irrigation. A 3-year irrigation period was simulated by applying 2700 L.m⁻² of AMD to the surface of the columns during this experiment. Soil with a loamy sand texture was used in the experiment because of its drainage capability and potential irrigability. Table 5.1 shows the chemical properties of the soil used in this study.

The AMD solution used in the experiment was the same as that used in the previous chapters of the study. It had a pH of approximately 2, contained 7 mM of sulphuric acid to provide its acid signature and 5 mM of each metal cation. Table 5.2 provides a summary of the chemical composition of the AMD solution.

In chapter four, it was determined that calcitic and dolomitic limestone with the finest particle size (< 0.25 mm) was the most reactive size fraction, with the greatest neutralizing potential of the various particle size fractions of the limestone used in this study. This led to its use in this experiment as it is the most appropriate size fraction to use for neutralization of the synthetic AMD solution in this study. However, it is expected that even finer particle size fractions would be better.

Table 5.1: The chemical properties of the loamy sand used in the soil column experiment.

Soil chemical properties		
pH _(water)	6.65	
Electrical conductivity - EC _s (mS.m ⁻¹)	73.8	
Cation exchange capacity - CEC (cmol _c .kg ⁻¹)	19	
Extractable acidity - EA (cmol _c .kg ⁻¹ H ⁺)	0.17	
Element	Available concentration (mg.kg ⁻¹)	Total concentration (mg.kg ⁻¹)
Ca	2375	2960
Mg	265	524
Na	195	227
K	74	467
P	448	990
Al	320	7840
Fe	125	13211
Mn	61	137
S	194	386

Note: EC_s is the conductivity of a 1:5 soil-water mixture. The available concentrations were determined using the Mehlich 3 (M3) extraction and the total concentrations were determined by HNO₃ microwavable digestion.

Table 5.2: Summary of the chemical composition of the synthetic AMD solution used in the column experiment.

pH of the synthetic AMD	Initial acidity of the solution (mmol/L H ⁺)	Metal cation in solution	Concentration of metal in solution (mg/L)	Sulphate concentration in solution (mg/L)
2	14.8	Fe	279	3074
		Al	135	
		Mn	275	

Note: The AMD solution was also used in the previous experiments of the study.

5.2.2 Soil Column Size, Components and Set-Up

It was challenging to use 2700 L.m⁻² as the total volume of AMD to be applied to the soil columns in a laboratory setting with the available equipment within the timeframe practical for experimentation. Thus, columns having a significantly small surface area were used to reduce the total volume of AMD to a volume that is appropriate and practical for laboratory work. Therefore, columns were made specifically for this experiment.

These columns had a surface area of 9.62 x 10⁻⁴ m² and were constructed with commercially available Marley PVC pipe with a diameter of 0.035 m and a length of 0.1 m. This brought the total volume of AMD to be applied to each column according to the 3-year irrigation period to 2.6 L which was more appropriate to the timeframe allocated for experimentation as well as laboratory work.

A PVC endcap with a single drainage outlet with a diameter of 0.005 m was fitted onto the bottom of each column to allow drainage to exit the soil columns. A 20 µm nylon filter was embedded into each endcap to aid in preventing solids from passing through the columns. Glass honey jars were placed beneath each column to be used as collection vessels for the leachate exiting from the soil columns.

5.2.3 Determining the Quantity of Agricultural Limestone to be Applied to the Columns for Neutralization of the AMD.

The agricultural limestone used in this experiment was the same which was used in chapter four of this study. The quantity of each type of limestone appropriate to neutralize the acidity introduced by the AMD was determined according to the total volume of AMD (2.6 L) used during the experiment. This approach considers the potential acid generating contributions of each metal that is present in 1 litre of the AMD solution as well as its initial acidity (as determined from Chapter 3 of this study). The table below provides the acidic contributions of the AMD solution used.

Table 5.3: Quantification of the acidity present in the synthetic AMD solution.

Acidic potential from	mM H ⁺ .L ⁻¹
Initial acidity	14.8
Fe	12.8
Al	16.8
Mn	14.8
Total acidity	59.2

Note: These values were derived from the findings of Chapter 3

From Table 5.3 it is observed that adding 2.6 litres of AMD can potentially introduce a total of 154 mmol of acidity (as H⁺) to each of the soil columns. From this quantification, the theoretical amount of each type of limestone needed can be determined because an equivalent quantity of alkalinity (154 mmol of CO₃²⁻) is required to neutralize the acidity as per an acid-base accounting principle which was used in Chapter 4 of this study.

The required amount of alkalinity per limestone type can be converted to a theoretical amount of calcitic and dolomitic limestone which contains the necessary amount of alkalinity to neutralize the total acidity introduced to the soil columns by adding AMD to it. As explained in the previous chapter, the mass of each type of limestone was determined by multiplying the total alkalinity required per limestone by the molar mass of analytical grade calcite (100.09 g.mol⁻¹) and dolomite (184.41 g.mol⁻¹) respectively.

Table 5.4: The amount of calcitic and dolomitic limestone appropriate to neutralize the total acidity introduced by applying 2.6 L of AMD to the soil columns.

Limestone type	Amount required for neutralization (g)
Calcite	15.4
Dolomite	14.2

5.2.4 Packing Procedure for the Columns

Each of the soil columns was packed to a depth of 0.06 m, which left 0.04 m to accommodate the volume of AMD which was added to percolate through the soil columns. The average mass of loamy sand required to fill the columns to this depth was 0.078 kg. Triplicate columns were used in the experiment.

Control columns without any agricultural limestone were also used in the experiment. The control columns were packed by loading two separate increments of 0.039 kg of soil. After the first increment was loaded into the column, it was lightly tapped to compact the soil and the surface was then lightly scratched before the addition of the second increment. Scratching the surface immediately after compaction and before the addition of the next increment enhanced layer and hydraulic conductivity of the soil (Sukati, 2012; Dlamini, 2020).

The columns with calcitic and dolomitic limestone contained at certain placement positions in the soil profile were packed as follows:

1. The columns with limestone incorporated into the “root zone” of the soil profile. The required amount of calcite or dolomite (see Table 5.4) was added to the total mass of soil (0.078 kg), which was mixed to incorporate the limestone into the soil before being packed into columns as explained in the packing procedure of the control columns.
2. The columns with the localised limestone within the top half of the soil profile. The first increment of soil was packed into the columns as described by the packing procedure for the control columns above. Then the required amount of calcite or dolomite was mixed into the final increment of soil before being packed into the columns.

5.2.5 Adding the AMD to the Soil Columns.

For this study, it was decided that the pore volume (PV) of the soil be determined to guide the addition of AMD to the soil columns. This was determined according to the following equation:

$$PV = \left(1 - \frac{\rho_b}{\rho_s}\right) \times V_{\text{total}} \quad (26)$$

Where, ρ_b is the dry bulk density of the soil (1.35 g.cm^{-3}), ρ_s is the particle density (2.65 g.cm^{-3}) and V_{total} is the total volume of the soil column (57.73 cm^3). It was established that one pore volume equates to 28.5 ml from this equation. This was rounded off to 30 ml for the purposes of this experiment. The total volume of AMD to be applied to each soil column is 2.6 L. Therefore, a total of 87 pore volumes of AMD had to be applied to each soil column during a 9 week period.

However, the approach in this experiment was to apply more than one pore volume to each of the soil columns per addition, so that the effect of a 3-year irrigation period with AMD on the soil profiles could be simulated within the time frame practical for laboratory work. This resulted in the extreme leaching of the soil profile.

The columns, therefore, received 150 ml of AMD per addition, after an equilibration period of at least 3 days between the additions. The abovementioned volume was applied to the soil columns during each addition by dividing it into three 50 ml aliquots. This was achieved using 50 ml syringes to administer the solution to the columns.

During the equilibration period, leachate from the columns was collected in glass honey jars for analysis. Only leachates collected at the beginning, middle and end of the experiment were kept for chemical analysis by ICP-OES due to the associated analytical costs and financial limitations.

5.2.6 Analytical Procedures

Analysis of the leachates from the soil columns:

1. pH throughout the experiment
2. Metal concentrations of the leachates collected at the beginning, middle and end of the experiment

This was done to assess the influence of the placement positions of agricultural limestone in the soil profile on neutralizing AMD. See Appendix A5 Table A5.1 and A5.2 for the pH and metal concentration data of the leachates from the various soil column treatments.

The analysis of the soil from the columns:

After the experiment was concluded, bulk soil samples from each of the columns were removed and placed into glass beakers. The soil samples were oven dried at 30°C for a 24-hour period. Thereafter, the soil samples were physically milled in the glass beakers using a pestle. The following chemical parameters were analysed:

1. Soil pH
2. Electrical conductivity
3. Macronutrient status of the soil according to the Mehlich 3 (M3) extraction
4. Total trace element concentrations of the soil according to a nitric acid microwave digestion

It is noted that during the preparation of the soil samples that milling could have possibly exposed the surface of the limestone which may have been armoured during the experiment. This could result in soil pH levels that are high. The first two soil chemical properties were mainly used as indicators of a favourable rooting environment for crop growth after neutralizing AMD in the strategically limed soil profile. The last two properties were assessed to determine the status of primary and secondary nutrients as well as the feasibility of sequestering elements within the profile after neutralizing AMD in the limed soil columns. See Appendix A6 for the soil chemical data after the soil column experiment was concluded.

5.3 Results and Discussion

5.3.1 Assessing the Influence of the Placement Position of Agricultural Limestone on Neutralizing AMD in a Soil Profile.

Figure 5.1 shows the effect of neutralizing AMD applied to loamy sand columns without agricultural limestone, referred to as control columns, during a simulated 3-year irrigation period. The “first year” of the irrigation period ended when a cumulative volume of 0.87 L of AMD was added to the soil columns.

The “second year” ended when a cumulative volume of 1.7 L was added, and the “final year” of the irrigation period ended when a cumulative volume of 2.6 L of AMD was added. Due to time limitations associated with this experiment, a higher leaching fraction and much lower resident time are expected in contrast to a field-based experiment. At the beginning of the irrigation period, the pH of the AMD leachate was 5.55 and was partially neutralised. However, as more AMD was added to the columns the pH of the leachate decreased to 3, which occurred before the “first year” of the irrigation period ended. As the end of the first year of the irrigation period neared, a steady decrease in the pH of the leachate followed. Thereafter the leachate had a pH which corresponded to the initial pH of the AMD ($\text{pH} = 2$) for the rest of the irrigation period.

This implies that before the first year of the irrigation period ended, the soil profile was severely acidified and was unable to neutralize the AMD passing through it. Thus, the soils’ inherent acid buffering capacity was eradicated. Partially neutralizing the percolate at the beginning of the irrigation period facilitated an increase in the pH of the AMD to 5.5.

This could be a result of exchange reactions occurring on negatively charged surfaces on soil colloids (clay complexes). These reactions are attributed to the presence of variable-charge minerals, which act as a sink for acid-forming cations like H^+ and Al^{3+} ions (Dvorackova et al, 2022).

Cations in the soil solution exchange with those that are attached to the surfaces of the clay complexes. This results in an increase in the concentration of the acid-forming cations and an increase in the concentration of alkali and alkali earth metals including Ca, Mg, K and Na ions in the soil solution, which would be lost from the soil profile through the leachate from the control columns.

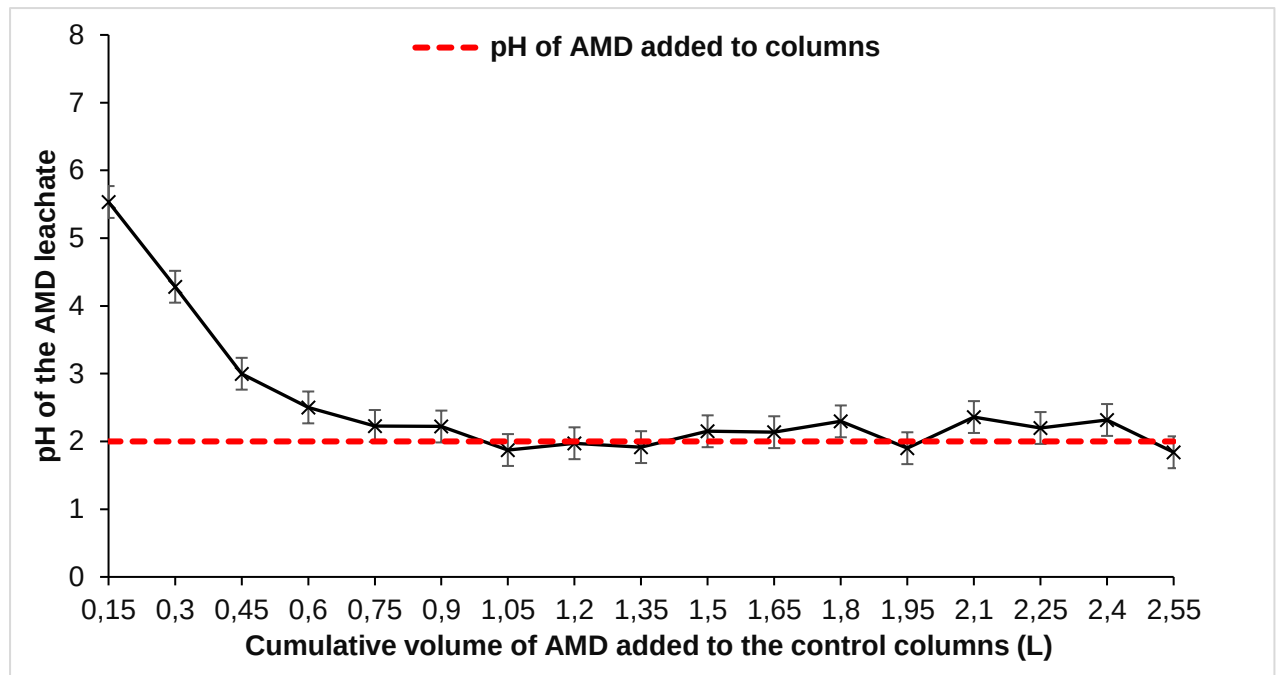


Figure 5.1: The effect of neutralizing AMD that was applied to loamy sand columns which did not contain any agricultural limestone during a “three-year” irrigation period.

This acidification impacting the profile has negative consequences for the nutrient status of the soil. The influence of soil acidification is not only limited to the removal of plant nutrients but also to increasing the mobility and solubility of metals within the soil (Sintorini et al, 2021).

Figure 5.2 shows the metal concentrations present in the leachates collected at the start, middle and end of the experiment from the control columns. In the beginning of the experiment, no Al was detected in the leachate from the control columns. This shows that the soil was able to sequester Al applied through the AMD and supports the theory that exchange reactions facilitated the partial neutralization of the leachate.

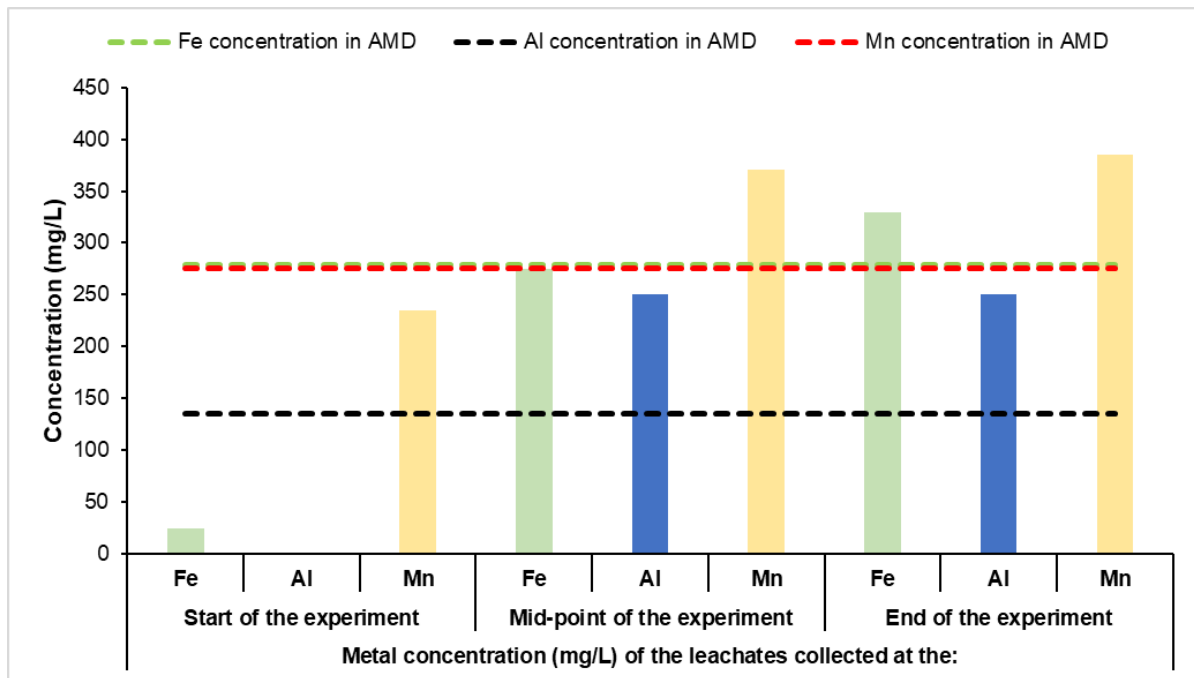


Figure 5.2: The concentrations of Fe, Al and Mn in the leachate from the loamy sand columns that did not contain any agricultural limestone, which was collected at the beginning, middle and end of the “three-year” irrigation period.

At the middle and end of the experiment, the Al concentrations in the leachate from the control columns were higher than that present in the AMD applied to these columns. As AMD was added to these columns, the soil profile became acidified with most exchange sites being occupied by aluminium ions. This implies that Al^{3+} would easily leach from the soil columns. Furthermore, Al can be solubilised and mobilised through the weathering (dissolution) of clay minerals under the acidic condition developed in the control columns, which contributes to its loss from the soil profile and its increased presence in the leachate.

Iron was detected in the leachate collected at the start of the experiment. Its presence could be responsible for restraining the increase in the pH of the leached AMD to 5.5. In Chapter 3, the buffering influence of iron, aluminium, and manganese on the potential of hydrated lime to neutralize AMD was assessed. It was shown that the presence of ferrous iron (Fe^{2+}) in solution can buffer neutralization and was referred to as the Ferrous iron buffer.

The buffering is caused by the first hydrolysis of Fe which occurred between a pH of 5 and 5.75. As a result of its hydrolysis, additional acidity is generated, which may be responsible for confining the pH of the AMD leachate to 5.5 at the start of the irrigation period.

At the middle and end of the experiment, the Fe concentration in the leachate from the control columns had increased and were higher than the Fe concentration in the AMD added to these columns. This implies that as the irrigation period continued, the longer interaction between the soil and AMD enabled the release of increasing concentrations of metals (like Fe) from the soil columns.

Claudio et al (2017) explain that the oxidation state and subsequent mobility of iron in the soil environment are influenced by oxidation-reduction reactions and soil pH. In soils under acidic and waterlogged conditions, there is a tendency for the concentration of ferrous iron (Fe^{2+}) in solution to increase. This is caused by the reduction of Fe^{3+} in the soil environment to Fe^{2+} .

Iron minerals present in the soil can act as electron acceptors in abiotic and biotic processes. This facilitates anaerobic respiration, which results in the release of Fe^{2+} in solution by the reductive dissolution of many Fe^{3+} oxides in the soil like goethite, hematite, and magnetite (Claudio et al, 2017). Thus, the increasing Fe concentration in the leachate from the control soil columns is likely to be caused by the acidic and waterlogged conditions, which occurred in these columns as the experiment continued.

A significant Mn concentration was detected in the leachate from the control columns throughout the experiment (Figure 5.2). As the experiment progressed, the Mn concentration in the leachate increased beyond its concentration in the AMD that was added to these columns which implies that Mn was mobilised from the soil.

The increasing concentration of Mn in the leachate collected during the experiment could be a result of the reduction from insoluble oxidised forms, namely Mn oxides, which readily occurs when an aerated soil is waterlogged (Sparrow and Uren, 2014). This results in the mobilization of manganous ions (Mn^{2+}) in the soil solution and is described as one of the first measurable effects of reduced conditions influenced by waterlogging (Turner and Patrick, 1968).

The continued increase in the Mn concentration in the leachate is also a result of an acidic environment that developed as AMD was continuously leached through the control columns (Porter et al, 2004), which enabled the mobilisation of Mn in the soil environment.

The results indicate that the control columns were able to partially neutralize the added AMD initially and obtain a pH of 5.5. As the experiment continued, these columns were severely acidified. This shows that the inherent acid buffering capacity of the soil is temporary, insufficient, and quickly eliminated when neutralizing AMD in the soil profile. Therefore, to assist in the neutralization of AMD and reduce the effects of acidification on influencing the soil profile, an alkaline substance is needed.

Figure 5.3 shows the influence of strategically placing dolomitic limestone in the soil profile by localising it within the top half of the profile and mixing it throughout the profile on neutralizing AMD during a “3-year” irrigation period. These soil columns were indeed able to neutralize the AMD. This occurred during the first two additions of the AMD to the soil columns and resulted in a pH of greater than seven for each.

It was also noted that, as the experiment continued, neutralization was partially achieved and towards the end of the first year of the irrigation period, the pH of the leachate from these columns decreased to 5. Neutralizing the AMD at the beginning of the experiment was caused by the dissolution of the dolomite in the soil columns upon contact with the AMD. As a result, carbonate ions were solubilised and released, which created an alkaline condition.

These ions reacted with the leaching AMD, thus decreasing its acidic concentration, and enabling neutralization. This resulted in a decrease in the solubility of metals present in the AMD and lead to their precipitation and sequestration in the soil columns. Therefore, there was an insignificant concentration of metal ions (particularly Fe and Al) present in the leachate collected at the beginning of the experiment.

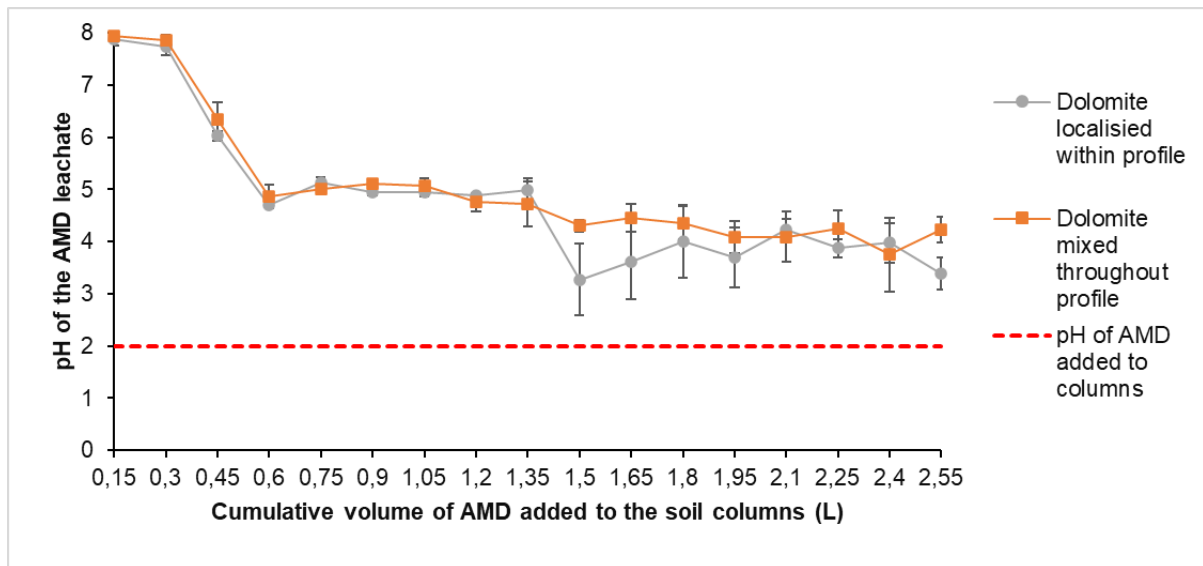


Figure 5.3: The effect of localising dolomitic limestone within the top half of the profile and mixing it throughout the soil profile on neutralizing AMD, which was applied over a “three-year” irrigation period.

Figure 5.4 shows that at the start of the experiment, the leachate from the soil columns which had dolomite localised within the top half of the profile and mixed throughout the profile did not contain Fe and Al. The absence of Fe in the leachate supports the theory that neutralization of the AMD had reduced its solubility and facilitated Fe precipitation, which results in the formation of amorphous Fe compounds in the soil columns (Santomartino and Webb, 2007; Dvorackova et al, 2022).

The absence of Al in the leachate collected at the start of the experiment could be attributed to a combination of the following: exchange reactions occurring on negatively charged surfaces on soil colloids (clay complexes) as well as the precipitation of Al as oxyhydroxide or hydroxysulphate phases caused by a decrease in its solubility facilitated by neutralizing the AMD.

The Mn concentration detected in the leachate collected at the beginning of the experiment from the control columns (Figure 5.2) was greater than that of the leachate from the columns which had dolomite strategically placed within the profile (Figure 5.4). It was mentioned that the Mn concentration in the leachate from the control columns is a result of the reduction from insoluble oxidised forms namely Mn oxides, which occurs when an aerated soil is waterlogged.

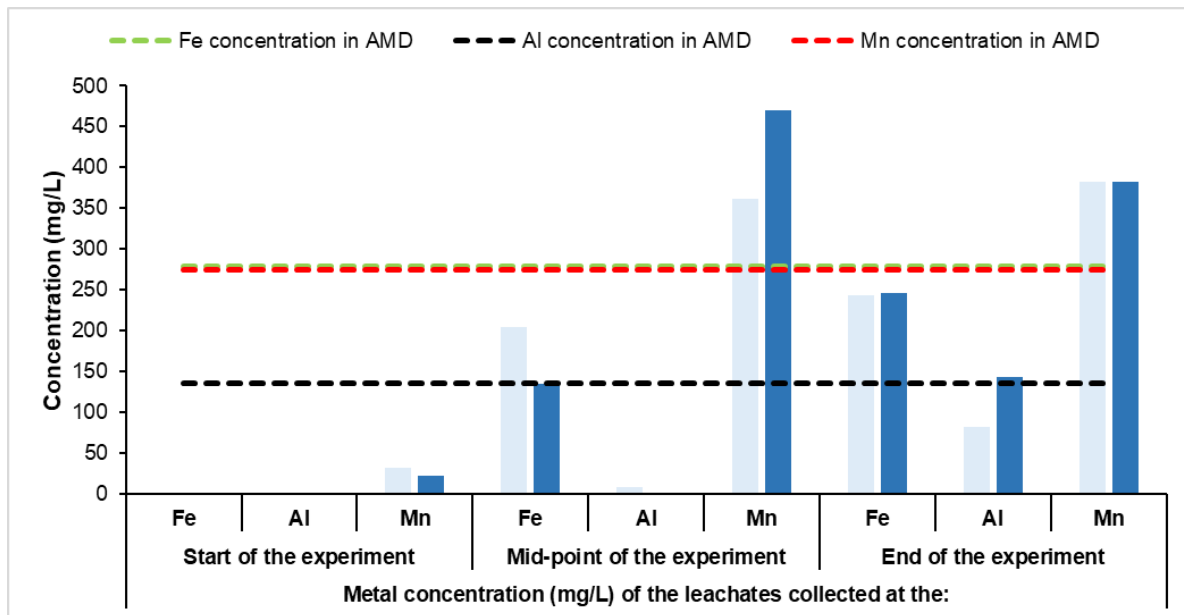


Figure 5.4: The concentrations of metal cations (Fe, Al, and Mn) present in the leachate from the soil columns, which had dolomite localised within (light blue bars) and mixed throughout the profile (dark blue bars) collected at the beginning, middle and end of the “three-year” irrigation period.

However, the presence of dolomite in the soil columns is a source of carbonate, which can remove and sequester soluble Mn (Silva et al, 2010). The removal can occur through the formation of a metal carbonate species as well as Mn oxyhydroxides (MnOOH) (Silva et al, 2010). In the case of dolomite, calcium, magnesium, and carbonate ions are released, which could lead to the formation of kutnohorite ($\text{CaMn}(\text{CO}_3)_2$) as a potential carbonate mineral.

Another metal carbonate that could have formed is rhodochrosite (MnCO_3) (Silva et al, 2010). The formation of either of these metal carbonate species as well as Mn oxyhydroxides could have contributed to the much lower Mn concentration detected in the leachate collected at the beginning of the experiment from the soil columns that had dolomite strategically placed within the profile.

Figure 5.3 shows that as the experiment continued, the neutralization capacity of the dolomitic limestone, which was localised within and mixed throughout the profile, diminished, leading to a decrease in the pH of the leachate from these columns. This was largely due to the consumption of dolomite within the soil columns.

However, the formation of amorphous Fe compounds, precipitation of Al as oxyhydroxide or hydroxysulphate minerals and the precipitation of the Mn-carbonate species and Mn oxyhydroxides in the soil columns can also contribute to the decreased neutralization capability of the dolomitic limestone.

The precipitation of these minerals in areas within the soil columns where dolomitic limestone was present may have led to an armouring influence as described in Chapter 4 of this study. Armouring of the surfaces of the residual dolomitic limestone in these areas may have reduced its capacity to dissolve and maintain its neutralization potential as the experiment continued.

At the start of the second year of the irrigation period, the leachate from the columns, which had dolomite strategically placed within the profile, had a pH of 5 and remained constant for some time (see Figure 5.3). The decrease in the pH of the leachate to 5 and its stabilization at this level is due to the presence of ferrous iron in the leachate, which causes a buffering influence.

Figure 5.4 shows that the leachate collected at the middle of the experiment from these columns had Fe and Mn, with the Mn concentration being the largest. Depletion of dolomite within the columns and its inability to react with AMD in areas where it may have been armoured prevented its dissolution. This reduced the potential for neutralization of the AMD and created zones in the soil columns that could be prone to the effect of acidification. A contributory factor is the unsuitable condition created by the potential waterlogging of the soil columns. It is suggested that, towards the end, these combined influences contributed to the reductive dissolution of Fe³⁺ oxides and the reduction of Mn oxides in the soil thereby leading to the Fe and Mn concentrations detected in the leachate as the experiment progressed.

As the end of the second year of the irrigation period neared, the pH of the leachate from the columns with dolomite strategically placed within the profile decreased to 4 and remained at this level for the rest of the experiment. Therefore, attempting to neutralize all the incoming acidity failed. This is attributed to the presence of Al in the leachate, which had increased as the experiment continued.

The presence of this metal can cause a buffering influence on neutralization as explained in Chapter 3. This is caused by its hydrolysis, which produces additional acidity that is likely responsible for confining the pH of the AMD leachate to 4 from the end of the second year of the irrigation period to the end of the experiment.

Figure 5.4 shows that at the end of the column experiment, Al was detected in the leachate of the columns which had dolomite localised within the profile (143 mg.L^{-1}) and mixed throughout the profile (81 mg.L^{-1}). There is a substantial difference between the Al concentration in the leachate from the columns with dolomite localised within the top half of the profile and that with dolomite mixed throughout the profile. The former placement position had the higher concentration attributed to less dolomite in contact with the soil.

This implies that the capacity of dolomite to facilitate the sequestration of Al introduced to the soil columns during the continuous addition of AMD decreased and could be due to the armouring of the dolomite. This can restrict its capability to dissolve, neutralize and remove metal ions from the AMD as the experiment continued. More likely is the lessened contact time with the AMD, associated with the localised placement method. This can result in minor increases in pH, which is not appropriate for the removal of Al from the AMD as the experiment continued.

Figure 5.3 also confirms that the soil columns with dolomite localised within the profile showed the greatest decrease in the pH of the AMD to 3 as the end of the second year of the irrigation period neared. Thereafter, the pH of the leachate from these columns varied between 3 and 4 for the rest of the experiment. The fluctuation in the pH was caused by the increasing presence of Fe and Al in the leachate from these columns as seen in Figure 5.4.

Figure 5.3 also shows that the neutralization curve of the localised dolomite placement position is below the curve of the mixed dolomite placement position for most of the experiment. This suggests that localising dolomite within the top half of the soil profile has a lower potential to neutralize the AMD most likely due to the lessened contact time with the AMD as compared to mixing it throughout the soil profile.

Figure 5.5 shows the influence of strategically placed calcitic limestone by localising it within the top half of the soil profile and mixing it throughout the profile on neutralizing AMD during a “3-year” irrigation period. These soil columns neutralized the AMD for the first three additions of the solution to the columns. Furthermore, the extent of neutralization was indeed longer when calcite was used in the soil profile compared to dolomite despite the placement position.

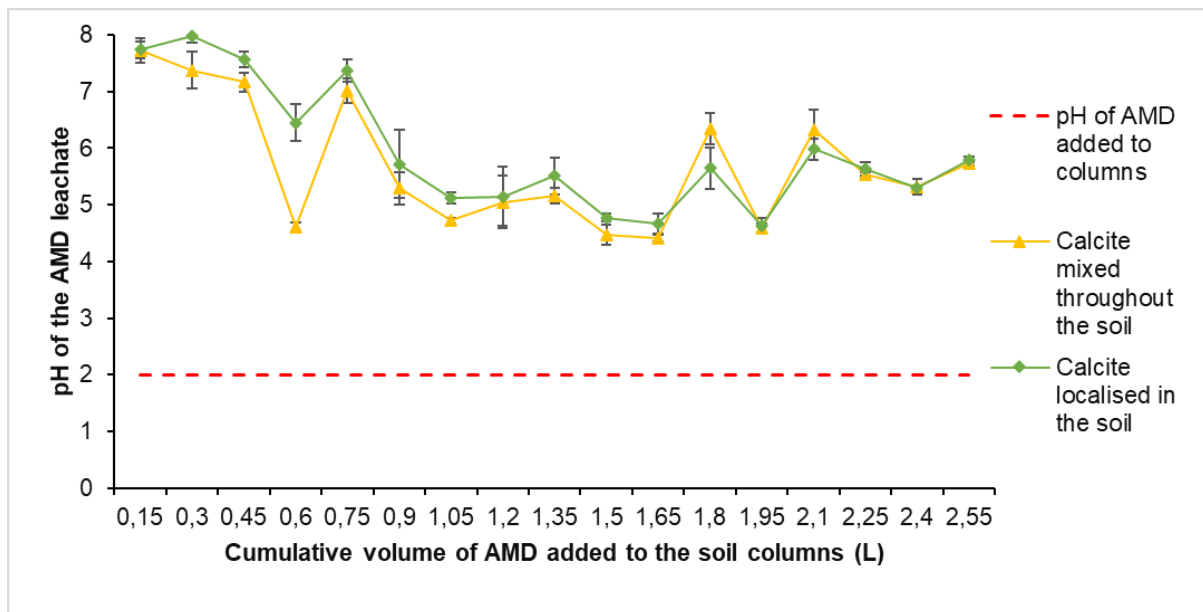


Figure 5.5: The effect of localising calcitic limestone within and mixing it throughout the profile on neutralizing AMD, which was applied over a “three-year” irrigation period.

Achieving neutralization of the AMD contributes to a decrease in the solubility of the metals present within it. Thus, their presence in the leachate, which was collected at the start of the experiment, is negligible (particularly Fe and Al ions). This is due to their precipitation and consequent sequestration within the soil columns.

As the end of the “first year” of the irrigation period neared, the neutralizing ability of both calcite placement positions in the soil profile had decreased. This led to a decrease in the pH of the leachate to 5.7 for the localised and 5.3 for the mixed placement position. The decrease in the pH of the leachate is likely to be caused by a reduced amount of calcite to sustain neutralization as well as the effect of the precipitation of metals within the soil columns.

This study has shown that as the metals precipitate, hydrolysis reactions occur which produce additional acidity that requires alkalinity to neutralize this influence. This contributes to the consumption of calcite. However, the precipitation of the metals in areas in the soil columns where calcitic limestone is predominant can also contribute to an armouring effect.

This can reduce the potential of the calcite in these areas to dissolve, participate in and maintain neutralization of the AMD as the experiment continued. Therefore, it is suggested that the presence of metal ions in the leachate increased as the experiment progressed, and the pH of the AMD decreased.

The pH of the leachate from the columns with calcite localised within the top half of the profile and mixed throughout the soil profile fluctuated between 5.5 and 6 for most of the experiment. Consequently, the concentration of metals present in the leachate would also vary. These columns were able to partially neutralize the leaching AMD and maintained a pH above 5 for most of the three-year irrigation period.

In contrast, the soil columns which had dolomitic limestone strategically placed within the profile maintained a pH below 5 for most of the experiment (Figure 5.3). This implies that the soil columns containing dolomitic limestone would have a yield more soluble metals compared with soil columns containing calcitic limestone. This is likely to be attributed to a decreased neutralization potential of the dolomitic limestone as the AMD leached through the soil columns.

Figure 5.6 below shows the concentrations of the metals present in the leachate from the soil columns which had calcite localised within the top half of the soil profile and mixed throughout the profile that was collected at the beginning, middle and end of the three-year irrigation period. At the start of the experiment, the leachate from these columns did not contain Fe and Al. This was also observed when dolomite was placed in the same positions in the soil columns (Figure 5.4).

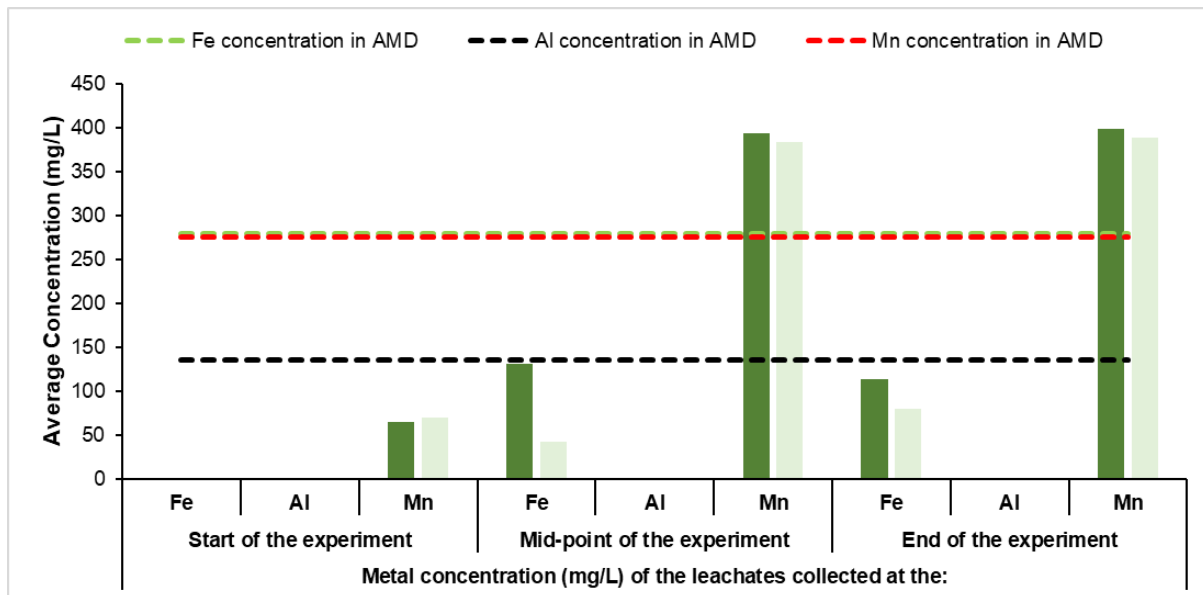


Figure 5.6: The concentrations of metal cations (Fe, Al, and Mn) present in the leachate from the soil columns with calcite localised (light green bars) within and mixed throughout (dark green bars) the soil profile that was collected at the beginning, middle and end of the “three-year” irrigation period.

The very low concentrations of these metals in the leachate supports that neutralizing the AMD during the initial stages of the experiment significantly reduced their solubility and enabled precipitation reactions to occur, which resulted in their sequestration in the soil columns.

It is also noted that Al was not present in the leachate from the columns with calcite throughout the experiment. It is proposed that calcitic limestone, which was able to maintain a pH above 5 for the AMD for most of the experiment, has a better ability to assist in the sequestration of Al within the soil profile compared to dolomite.

A Mn concentration was detected in the leachates collected at the beginning of the experiment from the soil columns that had calcite localised within (69 mg.L^{-1}) and mixed throughout the profile (64 mg.L^{-1}). These concentrations are lower than the Mn concentration present in the AMD which was added to the soil columns. This shows that some of the Mn was sequestered in the soil columns.

However, these concentrations are slightly higher than those present in the leachate from the columns which contained dolomite at the same placement positions within the soil profile. As the experiment continued, the Mn concentration present in the leachate from the soil columns that contained calcite increased like the concentrations noted when dolomite was used in the columns. This shows that dolomite initially has a greater propensity to sequester manganese relative to calcite.

The increasing Mn concentration in the leachates from the soil columns with calcite localised within and mixed throughout the profile could be caused by:

- the depletion of calcite within the columns to maintain an appropriate pH level, which validates the sequestration of Mn within the soil profile.
- The inability of calcite to react with the soil-AMD solution in areas where it may have been armoured, which prevents its dissolution and reduces the chance for neutralization.

Armouring of residual calcite in these areas can create zones prone to the effect of soil acidification in the soil columns and contributes to the mobilization of Mn ions. Furthermore, the reduced conditions created by potential waterlogging of the soil columns can contribute to the reduction of Mn oxides in the soil thereby increasing Mn concentrations in the leachate as the experiment progressed.

At the middle and end of the experiment, Fe concentration was detected in the leachates from the soil columns with calcite localised within and mixed throughout the profile. However, these concentrations are significantly lower than those present in the leachate from the columns with dolomite placed at the same positions within the soil profile at the same stage of the experiment (Figure 5.4).

This shows that calcitic limestone has a greater potential to assist in the sequestration of Fe within the soil profile compared to dolomite because calcitic limestone could maintain a higher pH for the AMD for most of the experiment. Fe presence in the leachate is likely to be due to the gradual depletion of calcite within the columns as well as its inability to react with the AMD in areas where it may have been armoured.

This can reduce the potential for neutralization and attaining an ideal pH level that renders this metal insoluble through its sequestration within the profile. Thus, there are zones or areas within the soil profile that could have been disposed to the effect of soil acidification.

Coupled with this, is the reduced conditions created by the potential waterlogging of the soil columns. These conditions are likely to have contributed to the reductive dissolution of Fe^{3+} oxides in the soil, which contributes to the Fe concentrations detected in the leachate as the experiment progressed.

Figure 5.5 shows that the neutralization curve of the mixed calcite placement position, was slightly below the curve of the localised calcite placement position for most of the experiment. This suggests that mixing calcite throughout the soil profile has a slightly lower potential to neutralize the AMD, most likely due to the lessened spatial contact with the AMD as compared to localising within the top half of the soil profile which facilitated spatial contact with AMD.

Figure 5.6 is in support of this proposition by demonstrating that the metal concentrations that were present in the leachates collected from the columns that had calcite mixed throughout the soil profile were on average higher than the metal concentrations in the leachates collected from the columns that had calcite localised within the soil profile.

5.3.2 Conclusion

The findings of the column experiment reveal that agricultural limestone in the soil profile can neutralize AMD as anticipated. However, this only occurred in the initial phase of the “three-year” irrigation period. As the irrigation period continued the neutralizing capacity of both types of agricultural limestone decreased and is most likely to be caused by their consumption as AMD was added and the potential armouring of the limestone in certain zones in the soil profile. This led to decreasing pH values of the AMD as more was added to the strategically limed soil columns. Therefore, both types of agricultural limestone have a partial capacity to sustain neutralization of the AMD.

The findings of the soil experiment also show that the placement position of the agricultural limestone in a soil profile which was used for this study namely localising the limestone within the top half of the profile and mixing it throughout the profile does not influence the neutralization of AMD.

Therefore, the hypothesis which states that localising agricultural limestone within the top half of the soil profile improves spatial contact with AMD and the potential for neutralization compared to incorporating the limestone throughout the soil profile which reduces spatial contact with AMD and the potential for neutralization is rejected.

The neutralization curves for each of the strategic placement positions of dolomitic and calcitic limestone within the soil profile show that localising dolomite in the top half of the soil profile has a lower potential to neutralize AMD compared to mixing it throughout the profile. However, localising calcite in the top half of the soil profile has a greater potential to neutralize AMD compared to mixing it throughout the profile.

The calcitic limestone also demonstrated a greater ability to neutralize the AMD for a longer duration in comparison to dolomitic limestone irrespective of the placement position. Furthermore, the use of calcitic limestone in the soil profile resulted in the highest pH of the AMD (pH >5) for most of the experiment.

The leachates from the columns with dolomitic limestone strategically placed within the soil profile had on average, higher Fe and Al concentrations at the middle and end of the experiment, whereas the leachates from the columns with calcitic limestone strategically placed within the soil profile did not contain Al during the experiment and had lower Fe concentrations at the middle and end of the experiment.

The lower neutralization potential of localising dolomitic limestone within the top half of the profile in comparison to mixing it throughout the profile is most likely due to its slower dissolution efficiency and the lessened temporal contact with AMD. The higher neutralization potential of localising calcitic limestone within the top half of the profile in comparison to mixing it throughout the profile is most likely due to its quicker dissolution efficiency and increased spatial contact time with AMD.

Therefore, it is suggested that the placement of agricultural limestone in a soil profile to neutralize AMD be guided by the dissolution efficiency of the liming material. It is recommended that liming material with a slow dissolution efficiency be mixed throughout the soil profile. This method is likely to increase the temporal contact between the liming material with AMD which can contribute to the progressive neutralization of the soil solution.

The next section will discuss whether a favourable rooting environment is supported for crop growth after neutralizing AMD in the strategically limed soil columns by evaluating certain soil chemical properties.

5.3.3 Neutralizing AMD in the Strategically Limed Soil Columns to Support a Favourable Rooting Environment for Crop Growth

Upon completion of the soil column experiment, bulk soil samples from each column were removed and prepared for analyses of the pH and electrical conductivity, of the soil samples. These chemical properties were used as indicators to determine whether neutralizing AMD in the strategically limed soil profile can support a favourable rooting environment for crop growth.

It is acknowledged that during the preparation of the soil samples that milling the samples exposed surfaces of the limestone which may have been armoured during the experiment. This will likely result in pH levels that are high and/or close to the initial pH of the soil (6.65) before experimentation. To address the contradiction in the soil pH assessment (due to the influence of the exposed residual and/or unreacted limestone in the soil) it is suggested that the pH of the leachate from the soil columns at the end of the experiment be considered as an indication of the pH status of the soil after termination of the column experiment.

5.3.4 Soil pH Assessment

Soil pH is considered a master variable as it influences the mobility, solubility, and adsorption to colloids of many pollutants in soil. It is a critical factor in predicting the likelihood that a given pollutant will contaminate groundwater, surface water, and food chains (Weil and Brady, 2016). Soil pH also regulates plant nutrient availability by controlling the chemical forms of the different nutrients and influencing their chemical reactions (Oshunsanya, 2018). Thus, to determine if a favourable rooting environment for crop growth is supported after neutralizing AMD in the strategically limed soil columns, the soil pH would need to be within a range which supports crop growth.

Table 5.5 and 5.6 show the pH of the loamy sand columns with dolomitic and calcitic limestone that was localised within and mixed throughout the soil profile as well as the pH of the leachate at the end of the experiment. The pH of the control columns, namely those which did not contain agricultural limestone, is also provided.

Table 5.5: The pH of the loamy sand with dolomitic limestone that was localised within and mixed throughout the soil profile.

Soil liming option	Soil pH before experiment	Soil pH after experiment	Leachate pH at the end of the experiment
Dolomite localised in the soil profile	6.65	6.38	3.39
Dolomite mixed throughout the soil profile		6.57	4.22
No dolomite in the soil profile		2.81	1.84

Note: the soil pH was assessed using the methodology of a 1:2.5 soil to water ratio suspension on a mass basis.

Both tables show that the control columns had a soil pH of 2.81 and a leachate pH of 1.84 after the conclusion of the experiment. This implies that the control columns were severely acidified, and the corresponding soil pH is characteristic of an acid sulphate soil (Weil and Brady, 2016), which occurs when soils are contaminated by and exposed to mining activities.

The influence of neutralizing AMD through a soil profile that does not contain agricultural limestone largely acidifies it as previously shown. This is contributed to by the exogenous input of the AMD, which depletes the soils' inherent ability to maintain its pH level. This is commonly referred to as buffering and soil properties such as the cation exchange capacity (CEC), soil organic matter (SOM), and clay content play important roles in mitigating the effects of acid inputs (Wei et al, 2019).

During the experiment, the soil acidified because of exchange reactions, which displaced non-acid or base ions held onto colloidal complexes with acid cations (H^+ and Al^{3+}) from the AMD. The non-acid ions, which include Ca^{2+} , Mg^{2+} , Na^+ and K^+ , were lost through the leachate along with anions (mainly sulphate) and metals. Eventually, the exchange complex as well as the soil solution becomes increasingly saturated by acid cations and results in an acid soil (Weil and Brady, 2016).

Leaching AMD through the control columns severely degrades the soil as it creates an extremely acidic rooting environment that is devoid of essential plant nutrients. The resultant soil pH of the control columns is below the threshold range in which plants can grow (that is a soil pH range of 5 to 8) and which is optimal for nutrient availability (that is a soil pH range of 6.5 to 7.5) (Miller, 2016). Instead, the rooting environment will be subjected to several toxicities such as Al, Mn, and Fe as well as nutrient deficiencies. This will negatively influence the growth of all organisms that live in the soil, including plants, animals, and microbes (Weil and Brady, 2016).

Table 5.5 shows that after neutralizing AMD during the three-year irrigation period, the soil columns with dolomitic limestone localised within the soil profile had a pH of 6.38. This pH value is likely to be that of the exposed residual and/or unreacted limestone and not the pH of the soil after the experiment ended. The pH of the leachate from these columns at the end of the experiment was 3.39 (see Figure 5.3). This pH value is likely to provide an indication of the pH status of the soil with dolomitic limestone localised within the profile.

Correspondingly, the soil columns which had dolomite mixed throughout the soil profile had a pH of 6.57 which is likely the pH of the exposed residual limestone in the profile and not the pH of the soil after the experiment ended. The pH of the leachate from these columns at the end of the experiment was 4.22 (see Figure 5.3). This value is likely to indicate the pH status of the soil with dolomitic limestone mixed throughout the profile.

This implies that the soil columns with dolomitic limestone that was localised within and mixed throughout the profile were acidified during the experiment. The acidification could be attributed to the armouring of the dolomite within the soil columns. This restricts the dolomite from dissolving and facilitating neutralization of the AMD, which can contribute to the acidification of the soil.

The pH of the leachate at the end of the experiment of the soil columns with dolomitic limestone localised within and mixed throughout the profile suggest that the pH status of the soil is likely to be below the threshold range in which plants can grow and which is optimal for nutrient availability. Thus, an unfavourable rooting environment for crop growth is likely to be realised after neutralizing AMD in soil columns with dolomitic limestone irrespective of its placement position within the soil profile.

After neutralizing AMD during the three-year irrigation period, the soil columns with calcitic limestone localised within the soil profile had a pH of 6.83 (Table 5.6). This pH is likely to be that of the exposed residual and/or unreacted limestone in the profile and not the pH status of the soil after the experiment ended. The pH of the leachate from these columns at the end of the experiment was 5.80 (see Figure 5.5). This pH value could be considered as an indication of the pH status of the soil with calcitic limestone localised within the profile.

Correspondingly, the soil columns which had calcite mixed throughout the soil profile had a pH of 6.70 which is likely the pH of the exposed and/or unreacted residual limestone in the profile and not the pH of the soil after the experiment ended. The pH of the leachate from these columns at the end of the experiment was 5.73 (see Figure 5.5). This pH value could be regarded as an indication of the pH status of the soil with calcitic limestone mixed throughout the profile.

Table 5.6: The pH of the loamy sand with calcitic limestone that was localised within and mixed throughout the soil profile.

Soil liming option	Soil pH before experiment	Soil pH after experiment	Leachate pH at the end of the experiment
Calcite localised in the soil profile	6.65	6.83	5.80
Calcite mixed throughout the soil profile		6.70	5.73
No calcite in the soil profile		2.81	1.84

Note: the soil pH was assessed using the methodology of a 1:2.5 soil to water ratio suspension on a mass basis.

The pH of the leachate at the end of the experiment of the soil columns with calcitic limestone that was localised within and mixed throughout the profile shows that the soil profiles were also acidified during the experiment. However, it is noted that the extent of the acidification is lower than when dolomite was present in the soil columns. The acidification is also likely to be attributed to the armouring of the calcite within the soil columns which restricts its dissolution and the neutralization of the AMD.

Although the calcite may have been armoured during the soil column experiment, it has a quicker dissolution efficiency in comparison to the dolomitic limestone, with the potential to raise pH. This can increase the pH-dependant charges on soil colloids, which assists in the retention of non-acid cations in the soil environment and minimises their leaching loss (Weil and Brady, 2016). This could result in a greater proportion of base ions on the exchange complex and surrounding soil solution as opposed to acid ions. Thus, the extent of acidification of the soil columns with calcite would be lower in comparison to that of the columns with dolomite.

The pH of the leachate at the end of the experiment of the soil columns with calcitic limestone localised within and mixed throughout the profile suggest that the pH status of the soil will at least be within the threshold range in which plants can grow and which is sub-optimal for nutrient availability. Thus, a favourable rooting environment for crop growth could potentially be realised after neutralizing AMD in soil columns with calcitic limestone irrespective of its placement position within the soil profile.

Summary

When agricultural limestone is absent in the soil profile, the effect of neutralizing AMD through the profile mostly acidifies it. This creates an extremely acidic rooting environment that cannot support crop growth because the rooting environment is likely to be subjected to several toxicities and nutrient deficiencies.

Liming the soil profile by localising agricultural limestone within the top half of the profile or by mixing it throughout the profile can potentially support a rooting environment in which crops can grow after neutralizing AMD in the soil profile.

When dolomitic limestone was used the soil profile was exposed to acidification and its extent is likely to result in conditions that negatively influence the availability of essential plant nutrients as well as a rooting environment in which crops may not be able to grow. However, when calcitic limestone was used the soil profile was acidified but to a lesser extent than when dolomitic limestone was used. This can potentially contribute towards a rooting environment in which crops can grow.

Thus, localising the agricultural limestone within the top half of the profile as well as mixing it throughout the soil profile does not influence the neutralization of AMD to support a favourable rooting environment for crop growth. However, it is suggested that the type of agricultural limestone used in the soil profile, which can influence neutralization of AMD, is an important factor to consider in the development of soil liming strategies for irrigation with AMD.

The electrical conductivity of the soil profile, commonly referred to as EC, was the next chemical parameter evaluated to determine if the rooting environment can support crop growth after neutralizing AMD in the strategically limed soil columns.

5.3.5 Soil Salinity Assessment

Electrical conductivity is defined as a measure of the total concentration of soluble salts in the soil solution (Weil and Brady, 2016). It is commonly used as an indicator to evaluate soil salinity (EC_e) and the degradation of soils (Kargas et al, 2022). This is because it is one of the most detrimental environmental factors which restrict the productivity of agricultural crops (Sonmez et al, 2008).

Various methods can be used to measure soil salinity. However, it is conventionally estimated according to the electrical conductivity of a saturated soil paste extract, commonly referred to as EC_e (He et al, 2012; Weil and Brady, 2016; Kargas et al, 2022). This method is challenging for various reasons. The preparation of the soil-saturated paste is a laborious and time-consuming process (Kargas et al, 2022) and determining the appropriate water saturation point when preparing a saturated paste extract is difficult (He et al, 2012). As a result, the laboratory work for the measurement of EC_e can be very difficult, expensive, and intensive (Sonmez et al, 2008).

The Soil Laboratory at the Department of Plant and Soil Sciences, University of Pretoria does not offer this method of analysing soil salinity. Thus, an alternative method practical for laboratory work and analysis was used to measure soil salinity in this study in the Soil Laboratory at the Department of Plant and Soil Sciences, University of Pretoria. One of the most widely used methods is to measure the conductivity of a soil-water mixture itself, referred to as EC_s (Weil and Brady, 2016). However, this measurement cannot be used to assess soil salinity. It needs to be converted to a soil salinity measurement, namely an EC_e reading.

To achieve this, a regression equation derived from an experimental soil salinity study conducted by Sonmez et al (2008) for loamy textured soil was used to estimate the saturated paste electrical conductivity (EC_e) from the measured conductivity of a 1:5 soil to water extract ratio (EC_s). The equation which was used is:

$$EC_e \text{ (mS.m}^{-1}\text{)} = 7.58(EC_s \text{ mS.m}^{-1}\text{)} + 0.06 \quad (r^2 = 0.99)$$

There are several classification systems for salt affected soils available in literature and common systems include the US Salinity Laboratory Staff (1954) and the Irrigation Water Management: Training Manual No. 1 - Introduction to Irrigation (FAO, 1985). Typically, saline soils are characterised by a high concentration of soluble salts, high soil EC_e values ($EC_e > 400 \text{ mS.m}^{-1}$) and a pH less than 8.5 (Ronquest, 2019).

Sodic soils can be saline or non-saline and are characterised by the composition of soluble salts with higher proportion of Na, relative to Ca and Mg on the exchange complex (Kargas et al, 2022; Weil and Brady, 2016). It is also mentioned that at least 15% of the exchange complex should comprise of Na^+ ions ($ESP > 15$) for soil to be characterised as sodic (Ronquest, 2019).

Crop growth, development and yield are affected by soil salinity because of salt stress, which restricts physiological and metabolic processes in crop development (Ronquest, 2019). This reduces the growth and yield potential of a crop (Maas and Hoffman 1977). A common symptom of salinity stress is the general stunting in crop growth and as the salt concentration increases above a certain threshold, both the growth rate and plant size decreases (Maas and Grattan 1999).

Different crops are more sensitive to salinity stress than others and each has its own threshold. Mass and Hoffman (1977) explain that the threshold is a range of salinity values whereby the growth and development of a crop will be negatively influenced if it is exceeded. It is also explained as the maximum allowable soil saturation electrical conductivity (EC_e) value before a reduction in yield occurs.

Ronquest (2019) has categorised soil salinity thresholds (EC_e) and sensitivity rankings according to literature from Mass and Grattan (1999). These thresholds (Table 5.7) will be used as a reference in this study to assess if the rooting environment can support crop growth after neutralizing AMD in the strategically limed soil columns.

Table 5.7: Soil salinity thresholds (EC_e) and sensitivity rankings from Ronquest (2019).

Sensitivity Ranking	EC_e Threshold Range ($mS.m^{-1}$)
Sensitive	0 - 150
Moderately Sensitive	150 - 300
Moderately Tolerant	300 – 600
Tolerant	600 – 1000
Unsuitable	>1000

The initial EC_e of the loamy sand used in this study was estimated at $566 mS.m^{-1}$ and was classified as saline. It is thought that its saline character was caused by soluble salt formed from the natural weathering of primary minerals in rocks and parent materials (Weil and Brady, 2016) that are found in the area from which the soil was obtained. Based on the estimated EC_e of the loamy sand, it falls within the moderately tolerant sensitivity ranking as per Table 5.7.

The figure below shows the estimated EC_e of the loamy sand columns with dolomitic and calcitic limestone localised within the top half of the profile and mixed throughout the soil profile after neutralizing AMD during the three-year irrigation period.

The control columns displayed a 40% increase in the EC_e relative to the soils initial EC_e during the “three-year” irrigation period. Based on the resultant EC_e ($793 mS.m^{-1}$), the soil is classed as saline and falls within the tolerant sensitivity ranking (Table 5.7).

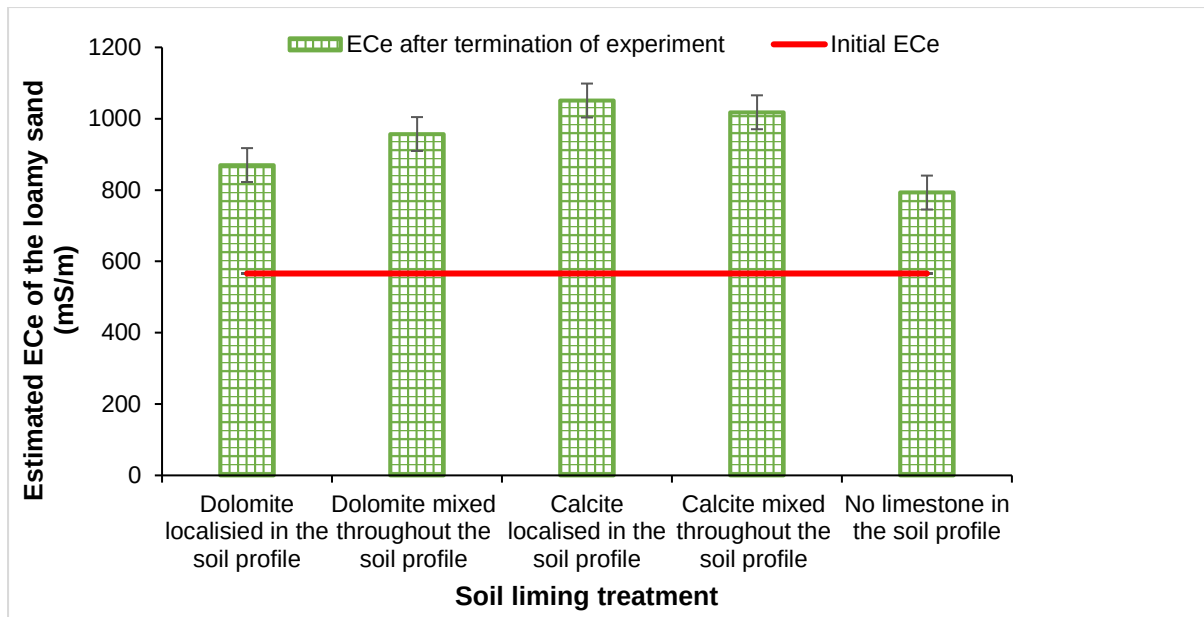


Figure 5.7: Estimated EC_e of the loamy sand columns after neutralizing AMD during a “three-year” irrigation period.

The soil columns with dolomitic limestone localised within the top half of the profile and mixed throughout the profile also showed an increase in the EC_e after the experiment ended. During the “three-year” irrigation period, the electrical conductivity increased by 54% relative to the soils initial EC_e, for the localised dolomite placement position and 69% for the mixed dolomite placement position.

This indicates that the mixed placement position resulted in a highly saline soil environment. This could be due to an increase in the temporal contact between the dolomitic limestone with the percolating AMD, which progressively leads to the generation of soluble salts in the profile during neutralization. The resultant EC_e values of the soil from the columns with dolomitic limestone localised within the top half of the profile (870 mS.m⁻¹) and mixed throughout the profile (957 mS.m⁻¹) indicate that the soil is saline and falls within the tolerant sensitivity ranking (Table 5.7).

Similarly, the soil columns with calcitic limestone localised within and mixed throughout the profile exhibited an increase in the EC_e at the conclusion of the experiment. These columns also showed the highest resultant EC_e values for the soil treatments used in this study. During the “three-year” irrigation period, the soil electrical conductivity increased by a factor of 86% relative to the soils initial EC_e, for the localised calcite placement position and 80% for the mixed calcite placement position.

This implies that the localised placement position results in a slightly higher saline environment. This could be caused due to the increase in the spatial contact between the calcitic limestone and AMD, which allows for the generation of a higher soluble salt concentration to occur within the soil profile. The resultant EC_e values of the soil from the columns with calcitic limestone localised within (1051mS.m^{-1}) and mixed throughout the profile (1018mS.m^{-1}) shows that the soil is saline and falls within the unsuitable sensitivity ranking (Table 5.7).

During the experiment, the control columns were predisposed to intense acidification. As the experiment continued, the soil-solution essentially comprised of an increasing mixture of metals, anions (particularly sulphate due to its significance in the AMD) and base cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+). The presence of sulphate ions together with the abovementioned base cations in the soil-solution can lead to a concentrated or saturated condition, which enables the precipitation of various salts in the soil column.

The precipitation of sodium sulphate is likely to contribute to the increased salinity of the soil (Weil and Brady, 2016) which leads to a saline rooting environment after neutralizing AMD in the control columns. It is also possible that the precipitation of salts that are primarily sulphates of calcium (gypsum) occurred in the control columns. However, these precipitates are unlikely to contribute to salinization of the soil profile. The precipitation of gypsum within the soil profile will effectively lower soil salinity (Ronquest, 2019).

The soil columns with agricultural limestone had higher resultant EC_e values compared to the control columns. In addition, the columns with calcitic limestone had higher resultant EC_e values than the columns with dolomitic limestone after the “three-year” irrigation period. Therefore, the calcitic limestone used for this study has the potential to generate higher soluble salt concentrations within the soil profile relative to the dolomitic limestone. This is attributed to a larger calcium content and Ca:Mg ratio associated with the calcitic rather than the dolomitic limestone used for this study.

When the agricultural limestone reacts with the AMD, it dissolves thereby releasing calcium and magnesium ions into the soil solution. Exchange sites on colloidal surfaces have an affinity for these cations which enables their retention in place of other ions like Na. The latter ion is displaced from the exchange sites and its availability in the soil solution increases.

The presence of sulphate ions from the AMD coupled with available Na^+ ions in the soil solution can lead to a concentrated condition that facilitates the precipitation of sodium sulphate. This can contribute to the saline conditions of the soil columns which were treated with the calcitic and dolomitic limestone.

Summary

Using calcitic or dolomitic limestone to neutralize AMD in strategically limed soil profiles can increase its EC because of the precipitation of sulphate salts like sodium sulphate within the profile. The resultant increase has the potential to render the soil profile saline.

The calcitic limestone used in this study contributed to higher estimated EC_e values in comparison to dolomitic limestone, despite its placement position within the soil profile. This led to a highly saline soil condition as well as an unsuitable rooting environment to support crop growth.

This concern highlights the need to constantly monitor sulphate concentrations in the irrigation water and in the soil moisture, especially if long term irrigation is intended. It is, therefore, necessary to incorporate a leaching fraction as part of the soil liming strategy and the irrigation management plan to remove salts from the root zone. This would enable measures to be developed to mitigate excessive salt accumulations and influence the root zone and crop growth potential when neutralizing AMD in strategically limed soils.

5.3.6 The Availability of Macronutrients and the feasibility of Sequestering Metals in the Profile After Neutralizing AMD in the Limed Soil Columns.

After the soil column experiment had ended, bulk soil samples from each column were removed and prepared for chemical analyses. The macronutrient status and total trace element concentrations in the soil profiles were determined according to the Mehlich-3 extraction and nitric acid digestion respectively. This was done to show the availability and feasibility of sequestering elements within the profile after neutralizing AMD in the soil columns.

Macronutrient Status Assessment

Plants, like all other living organisms, require food for their growth, development, and survival, which comes from the atmosphere, water, and soil minerals. Each type of plant has an optimum and a minimum nutrient requirement level for its growth. This challenges the establishment of a general threshold range to support plant growth. However, most plants show deficiency symptoms below the minimum nutrient level, which negatively influences its growth, but excessive nutrient uptake can also cause poor growth because of toxicity symptoms.

These nutrients comprise several components such as proteins, nucleic acids and chlorophyll and are important for processes such as energy transfer and the functioning of enzymes in plant species. Plants require mostly primary macronutrients in large quantities and secondary macronutrients in lesser quantities.

The Mehlich 3 (M3) extraction was used to determine the status of the primary (P and K) and secondary (Ca, Mg and S) nutrients of the soil columns after the soil column experiment ended. The N status could not be determined using the M3 extraction. However, it is recommended that future work and studies in this area consider its determination.

Table 5.8 shows the status of the primary nutrient elements in the soil before and after neutralizing AMD in the strategically limed columns as well as the percentage change in the status of each. A negative percentage implies a decrease in the status of a specific nutrient element pre-experimentation in relation to its initial availability in the soil.

The control columns with no agricultural limestone in the soil profile had the lowest potassium status (6 mg.kg^{-1}) at the end of the experiment with the greatest percent change, that is a 91% decrease from the soil's initial potassium status. The extent of this decrease shows that the soil is significantly depleted of potassium as a primary nutrient.

The decrease in the potassium status of the control columns is attributed to the effect of soil acidification on the profile where potassium ions were removed from the exchange complex, which was leached from the soil as AMD was continuously added during the experiment.

The soil columns with calcite localised within the top-half of the profile and mixed throughout the profile had potassium statuses of 18 and 19 mg.kg⁻¹ respectively when the experiment was concluded. Each of the columns experienced a 76 (localised) and 75% (mixed) decrease from the soil's initial potassium status. Similarly, the columns with dolomite localised within and mixed throughout the profile had potassium statuses of 17 and 19 mg.kg⁻¹ respectively with a concomitant 77 and 74% decrease in the soil's initial potassium status after the experiment ended.

Table 5.8: The final and percentage change of Mehlich extractable phosphorus (P) and potassium (K) as primary nutrient elements after neutralizing AMD in the strategically limed columns.

Soil Column	Phosphorous (P) Status			Potassium (K) Status		
	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Change (%)	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Change (%)
Control		155	-65		6	-91
Calcite localised		5	-99		18	-76
Calcite mixed throughout	448	7	-98	74	19	-75
Dolomite Localised		17	-96		17	-77
Dolomite mixed throughout		26	-94		19	-74

When compared to the control columns, the columns with calcitic and dolomitic limestone localised within and mixed throughout the soil profile had higher final potassium statuses and lower decreases from the soil's initial potassium status. This shows that liming the soil columns to neutralize AMD during the experiment assists in sustaining a portion of the soil's potassium status despite the placement position of the agricultural limestone.

The decrease in the potassium status of the soil columns with agricultural limestone is attributed to its replacement by calcium ions on exchange sites. This is due to the affinity of Ca for the exchange sites because of its smaller ionic radius and higher charge compared to K, which facilitates its adsorption on exchange sites through outer-sphere complexes.

As the AMD reacted with the limestone in the soil columns, calcium solubilised due to the dissolution of limestone. Its increasing presence in the soil solution makes it available to replace potassium ions held on the exchange complex. This facilitates its removal from the soil profile by leaching, which resulted in the decrease in the soil's potassium status. It is also possible that the CEC decreased because of the precipitation of Al, Fe and Mn oxides on soil mineral surfaces which would facilitate the removal of potassium ions on the exchange complex.

To compensate for this loss, an appropriate K fertilizer management strategy should be incorporated into the liming strategy to supply adequate quantities of potassium for crop growth when irrigating with AMD. However, it should be noted that this may also increase the salinity of the system.

Table 5.8 also shows that the control columns had the highest final phosphorus status (155 mg.kg^{-1}) and the lowest percent change with a 65% decrease from the soil's initial phosphorus status.

However, the soil columns with calcite localised within and mixed throughout the profile had significantly lower phosphorus statuses of 5 and 7 mg.kg^{-1} respectively and the highest percent change, that is a 99 and 98% decrease from the soil's initial phosphorus status respectively. The columns with dolomite localised within and mixed throughout the profile had slightly higher phosphorus statuses of 17 and 26 mg.kg^{-1} respectively. However, these columns also displayed significant percent changes with a 96 and 94% decrease from the soil's initial phosphorus status respectively.

The decrease in the P status of the control columns is attributed to its acidification and the possible waterlogging of these soil columns during the experiment with subsequent reduced conditions. It is established that soil pH and redox potential are primary factors that control the solubility and fate of phosphorus in the soil environment (Zhang et al, 2021).

Acidification can promote the dissolution and reduction of Fe-Mn oxyhydroxides in soil. This decreases the amount of soil reducible Mn under anoxic conditions. This Mn mobilization shortens the period that redox is poised at Mn reduction, thereby increasing the speed at which the Fe reduction process occurs (Zhang et al, 2021). As a result, P mobilisation is enhanced due to Fe reduction, which facilitates its removal from the soil through leaching (Zhang et al, 2021).

The substantial decrease in the phosphorus status of the columns with agricultural limestone is diagnostic of its fixation in the soil profile as opposed to its removal by leaching. Phosphorus is highly reactive in the presence of lime in the soil environment. This enables a series of reactions to occur, which progressively reduces the solubility of P in the soil solution (Leytem and Mikkelsen, 2005) - commonly referred to as fixation.

The fixation of phosphorus (and potentially molybdenum) in these columns is driven by its reaction with calcium and the agricultural limestone in the soil profile, which allows for the development of relatively strong calcium phosphate bonds at the surface of the limestone. This can lead to the formation of poorly soluble calcium phosphate minerals (Hopkins and Ellsworth, 2005), which results in the interlocking or fixing of P and reduces its solubility and availability.

A consequence of neutralizing AMD in the strategically limed soil columns is the precipitation of Fe, Al, and Mn hydroxides within the soil profile as well as on the surfaces of the agricultural limestone. These mineral precipitates can contribute to the fixation of P as they serve as strong sorption sites for phosphorus (Leytem and Mikkelsen, 2005). P fixation through the presence of the abovementioned metal hydroxides involves a series of chemical reactions that results in the interlocking of P. This could be due to reactions with the surfaces of these minerals, which enable the formation of inner-sphere complexes.

This involves replacing a hydroxyl group (OH^-) on the surface structure of the metal hydroxide with a phosphate ion resulting in its fixation (Mahdi et al, 2012). Alternatively, the phosphate ion may further penetrate the metal hydroxide surface, by forming a stable binuclear bridge (Mahdi et al, 2012).

This shows that neutralizing AMD in the strategically limed soil columns has an influence on fixing phosphorus thus influencing the supply of this primary nutrient to crops. An appropriate P fertilizer management strategy should be part of the liming strategy to improve its status to support crop growth when irrigating with AMD on limed soil.

The following management strategies could be considered to achieve this (Hopkins and Ellsworth, 2005). These include the application of:

- relatively high P fertilizer rates,
- concentrated P fertilizer bands,
- complexed P fertilizer,
- slow-release fertilizer P,
- cation complexing P fertilizer, and
- in-season P fertilizer usage.

Calcium, magnesium, and sulphur are collectively referred to as secondary nutrients. They are referred to as secondary nutrients because plants require them in smaller quantities compared to the primary nutrients. However, they are also considered essential plant nutrients due to their roles in plant growth and production. Table 5.9 shows the secondary nutrient element status of the soil, after neutralizing AMD in the strategically limed columns as well as the percentage change in the status of each nutrient element.

The control columns showed the lowest resultant Ca and Mg status of 7 and 5 mg.kg⁻¹ respectively with the greatest percent change (-100 and -98%), which signifies their complete depletion in the soil. The significant decreases in the calcium and magnesium status are attributed to the effect of acidification on the soil profile, which displaced these ions from exchange sites. Consequently, they were removed from the soil through leaching during the experiment.

The control columns displayed an increase in the resultant sulphur availability as well as an increased percent change. Several mechanisms can retain sulphates in acid soils. One such mechanism could be the precipitation of calcium sulphate compounds like gypsum in the soil profile, due to a concentrated soil solution containing sulphate and calcium ions.

However, the most common SO₄ retention mechanism is a result of variable charge of Fe and Al oxides. With decreasing pH, surface charge becomes positive, which facilitates a higher amount of SO₄ being sorbed (Dubikova et al, 2002). Another potential mechanism of SO₄ retention in acid soils is the precipitation of basaluminite or alunite and their Fe analogues (Dubikova et al, 2002).

Table 5.9: The final and percentage change in the status of Mehlich extractable Calcium (Ca), Magnesium (Mg) and Sulphur (S) as secondary nutrient elements after neutralizing AMD in the strategically limed columns.

Soil Column	Calcium (Ca) Status			Magnesium (Mg) Status			Sulphur (S) Status		
	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Change (%)	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Change (%)	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Change (%)
Control		7	-100		5	-98		632	227
Calcite localised		3307	39		65	-76		1629	741
Calcite mixed throughout	2375	3265	37	265	68	-74	194	1522	686
Dolomite Localised		4744	100		2477	834		1230	535
Dolomite mixed throughout		5878	147		2983	1024		1227	534

The soil columns with dolomitic limestone localised within the top-half of the profile and mixed throughout the soil profile showed increases in the status of each secondary nutrient. These columns also had the highest Ca and Mg status and percent change after the experiment ended. This was unexpected because the calcitic limestone used in the experiment had a greater calcium content as well as Ca:Mg ratio associated with it. Thus, it was thought that the soil columns treated with calcite would have resulted in the highest Ca status after the experiment ended.

The significant increases in the status and percent change of Ca and Mg, suggests that a portion of the dolomite, which was initially added to these columns, was unable to react with the AMD during the experiment. This is likely to be attributed to the effect of armouring of the surfaces of the dolomitic limestone by metal precipitates. In section 5.3.1 of this chapter, it was shown that the dolomitic limestone could have been more influenced by armouring in comparison to calcitic limestone. As a result, its dissolution potential was limited during the experiment, which resulted in a residual portion of dolomite in the soil profile that dissolved during the M3 extraction. This could have contributed to the significant increases in the resultant Ca and Mg statuses in the soil.

The columns which contained dolomitic limestone also revealed an increase in the S status as well as an increased percent change. This shows an enrichment of the soil profile with this nutrient element. The increased S status was caused by a saturated soil solution, with respect to calcium and sulphate ions, which could lead to the precipitation of a calcium sulphate salt (Potgieter-Vermaak et al, 2006) like gypsum in the soil profile.

The soil columns with calcitic limestone localised within and mixed throughout the soil profile only showed an increase in the status and percent change of Ca and S. The status of Mg decreased in these columns. The decrease is attributed to the replacement of Mg by Ca ions on exchange sites. This is due to the affinity of Ca for exchange sites, which facilitates its adsorption on these sites through outer-sphere complexes and contributes to its increase.

As the AMD reacted with the calcitic limestone in the soil columns, calcium was mobilized through its dissolution. Its increasing presence in the soil solution disposes it to replace Mg ions held on the exchange complex. This facilitates its removal from the soil profile by leaching, which resulted in the decrease in the magnesium status.

These columns also had the highest sulphur status after the experiment ended. This shows that using calcitic limestone to neutralize the AMD has the potential to facilitate the sequestration of a larger amount of sulphur (as SO_4^{2-}) in comparison with dolomitic limestone. Thus, a greater quantity of sulphate salts can precipitate in the soil profile.

Trace Element Accumulation Assessment

The total trace element (Fe, Al, and Mn) concentrations were determined using a nitric acid microwavable digestion to assess the degree of accumulation of these elements in the strategically limed soil profiles after the experiment ended to demonstrate the feasibility of sequestering these elements within the profile.

The table below provides the total concentrations of Fe, Al, and Mn initially present in the soil as well as their concentrations after neutralizing AMD in the strategically limed columns and the control columns. The percentage change in the total concentrations of each metal is also provided. A positive percentage change shows an enrichment in the concentration of the trace element in relation to its initial concentration in the soil.

As previously indicated, the control columns were influenced the most by soil acidification during the experiment. This is demonstrated by the 27% decrease in the Al concentration of the control columns after the experiment ended. The decrease implies that aluminium was released from the soil profile through leaching during the simulated “three-year” irrigation period. Its loss is attributed to the weathering of Al bearing minerals in the soil profile.

Table 5.10: The final and percentage change in the total concentrations of Fe, Al, and Mn as trace elements after neutralizing AMD in the strategically limed columns.

Soil Column	Iron (Fe) Concentration			Aluminium (Al) Concentration			Manganese (Mn) Concentration		
	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Change (%)	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Change (%)	Initial Concentration (mg/kg)	Final Concentration (mg/kg)	Percent Change (%)
Control		15938	21		5723	-27		195	42
Calcite localised in the soil profile		18633	41		8703	11		1407	926
Calcite mixed throughout the soil profile		17963	36		9614	23		1268	824
Dolomite localised in the soil profile	13211	18372	39	7840	10028	28	137	549	300
Dolomite mixed throughout the soil profile		17786	35		12003	53		656	378

The increase in the solubility and mobility of Al was influenced by the acidity and constituents capable of releasing this metal in the solid fraction of the soil (Kryzevicius et al, 2019). As AMD was added to the control columns, acidic conditions (pH <4.5) developed, which facilitated the weathering of aluminosilicate (clay) minerals as well as Al-hydroxide dissolution. This contributes to the solubilisation and increased mobility of Al, thus leading to its loss from the soil profile (Sutela & Vehanen, 2017) and decreased concentration after the experiment was completed. This can have negative consequences on plant life, receiving groundwater sources and the aquatic environment (Vazquez, 2010).

The total iron and manganese concentrations of the control columns increased by 21 and 42 % respectively after the experiment ended. These increases present an accumulation of the abovementioned trace elements within the soil profile, which is likely due to the formation of minerals in the acidified soil columns and the retention of these metals because of sorption mechanisms.

The increased total Fe concentration of the control columns is probably caused by the formation of Jarosite ($\text{KFe}_3(\text{SO}_4)_2(\text{OH})_6$) which is a common mineral occurring in acid sulphate soils and soils that have been acidified with AMD (Dubikova et al, 2002; Frempong and Yanful, 2005). Its formation within the soil profile can act as a potential contributor to the accumulation of iron in the profile.

Additionally, the presence of iron oxyhydroxides in the soil like ferrihydrite and the formation of amorphous Fe-oxyhydroxides as AMD leached through the control columns can act as sinks for the adsorption of metals like iron and manganese due to their greater specific surface area and variable charge (Dubikova et al, 2002), which could also contribute to the accumulation of Fe in the control columns.

The increased manganese concentration of the control soil columns could have been caused by the oxidation of Mn^{2+} to Mn^{3+} during the initial phase of the experiment. It is understood that Mn (III) is extremely reactive and cannot persist for long without being oxidised to Mn (IV) or reduced to Mn (II). However, under acidic conditions it can persist for longer periods (Mudaly, 2015). Mn^{3+} is also one of the most powerful oxidizing agents in soil (second only to the hydroxyl free radical) as well as one of the most powerful reducing agents (Mudaly, 2015).

Thus, its presence in the soil environment can assist with the oxidation of Mn^{2+} from the exogenous input of the AMD to the control soil columns during the experiment. This can enable the formation of MnOOH , which is a stable mineral under acidic conditions (Mudaly, 2015) and could contribute to the accumulation of Mn in the control columns.

The total iron concentrations of the soil columns treated with calcite and dolomite localised within the top-half of the profile (17963 & 17786 mg.kg^{-1}) and mixed throughout the profile (18633 & 18372 mg.kg^{-1}) are very similar. Each of these columns displayed an increase in the total Fe concentration after the experiment ended and had much higher concentrations in relation to the control columns.

On average, the soil columns that were treated with calcitic limestone show a slightly higher total Fe concentration in comparison to columns treated with dolomitic limestone. This implies that using calcitic limestone to neutralize the AMD has the potential to facilitate the accumulation of a larger amount of iron in comparison to dolomitic limestone. This suggests that Fe has a greater affinity to being sequestered in a calcitic environment, which is likely caused by the higher pH levels afforded.

The increased total iron concentrations within the strategically limed soil columns are a result of raising the pH of the AMD to a level which is appropriate for the oxidation of Fe^{2+} to Fe^{3+} . This stimulates the precipitation of Fe(III) minerals within the limed soil columns. It is advocated that the most likely Ferric mineral to precipitate in these columns would be schwertmannite, in conjunction to amorphous Fe-oxyhydroxide minerals. The formation of these minerals contributes to the accumulation of Fe in the strategically limed soil columns as well as provides surfaces for the adsorption of Fe from the leaching AMD solution.

The soil columns treated with calcite and dolomite localised within and mixed throughout the profile also revealed an increase in the total Al concentration after the experiment ended and had much higher concentrations in relation to the control columns. However, on average, the soil columns that were treated with dolomitic limestone showed higher total Al concentrations in comparison to columns treated with calcitic limestone placed at the same locations within the soil profile.

The increase in the total aluminium concentrations within the strategically limed soil columns is a result of increasing the pH of the leaching AMD, to a level which is appropriate for the precipitation of Al minerals within the soil profiles. It is suggested that the most likely aluminium mineral to precipitate in these columns would be hydrobasaluminite. Through the formation of this mineral, an accumulation of Al in the strategically limed soil columns is feasible.

The difference between the total Al concentrations in the soil columns that were treated with calcite and dolomite could be attributed to the neutralization efficiencies of each type of limestone. It was observed that when dolomitic limestone was used to neutralize the leaching AMD, the soil profile was slightly acidified. This may have led to acidified zones within the soil profile, which facilitates the solubilisation and mobilization of Al from soil components within these columns.

As a result, there is an increased presence of Al in the soil solution, which can precipitate within the profile especially in areas where residual dolomite is present or through adsorption onto the surfaces of Al minerals. Alternatively, the dolomitic limestone could be more influenced by Al during the neutralization of the leaching AMD through the armouring of its surfaces. This could result in the surfaces of residual dolomite within the soil profile being coated by Al precipitates and could contribute to the higher total Al concentrations detected in these soil columns in comparison to the calcite containing soil columns.

The soil columns treated with calcite and dolomite localised within and mixed throughout the profile exhibited significant increases in the total Mn concentration after the experiment ended. On average, the soil columns that were treated with calcitic limestone showed higher total Mn concentrations in comparison to columns treated with dolomitic limestone placed at the same locations within the soil profile.

Using calcitic limestone to neutralize AMD has the potential to facilitate the accumulation of a larger amount of manganese in comparison to dolomitic limestone. This suggests that, like Fe, Mn has a greater affinity to being sequestered in a calcitic environment, which is caused by its greater neutralizing potential as well as the higher pH levels afforded when it is used.

The increased Mn concentrations are attributed to the formation of Mn carbonate minerals and Mn oxyhydroxides, which have precipitated within the soil profile. In addition, the formation of Mn oxyhydroxides and Fe-oxyhydroxides in the soil profile provides an overall greater surface area for Mn^{2+} to be adsorbed to, which could contribute to the significance in the percentage change in the total concentration of Mn present in the limed soil profiles.

Summary

Neutralizing AMD in the strategically limed soil columns has an influence on the status of the primary nutrient elements. Thus, it is recommended that an appropriate fertilizer management plan is integrated with the soil liming strategy. This would provide mitigation measures to manage primary nutrient deficiencies on influencing crop growth when neutralizing AMD in strategically limed soils.

The secondary nutrient status and availability of the soil is not as significantly impacted when neutralizing AMD in the strategically limed soil columns because the agricultural limestone serves as sources of Ca and Mg and the AMD as a source of S, which contributes to their status in the soil profile.

The accumulation of the trace elements Fe, Al and Mn in the strategically limed soil profiles shows that their sequestration within the profile is feasible. It is proposed that preconditioning soil with alkaline materials is an alternative mine water treatment strategy. However, it is recommended for future work that an investigation into the bioavailability of the accumulated trace elements be conducted.

5.3.7 Conclusion

The soil column experiment shows that localising agricultural limestone within the top half of the profile as well as mixing it throughout the soil profile can neutralize AMD. However, this only occurred in the initial phase of the “three-year” irrigation period and as the experiment continued the neutralizing capacity of the agricultural limestone decreased. Therefore, the ability of either calcitic or dolomitic limestone to sustain neutralization is partial.

The neutralization curves for each of the placement positions of agricultural limestone within the soil profile show that localising dolomite in the top half of the soil profile has a lower potential to neutralize AMD compared to mixing it throughout the profile. However, in the case of calcite, localising it in the top half of the soil profile has a greater potential to neutralize AMD compared to mixing it throughout the profile.

This implies that the placement position of agricultural limestone within a soil profile, namely localising it within the top half of the profile and mixing it throughout the profile does not have an influence on the neutralization of AMD. Furthermore, the hypothesis which states that localising agricultural limestone within the top half of the soil profile improves the spatial contact with AMD and the potential for neutralization compared to incorporating the limestone throughout the soil profile which reduces the spatial contact with AMD and the potential for neutralization is rejected.

The lower neutralization potential of localising dolomitic limestone within the top half of the profile in comparison to mixing it throughout the profile is likely due to its slower dissolution efficacy. The higher neutralization potential of localising calcitic limestone within the top half of the profile in comparison to mixing it throughout the profile is most likely due to an increased spatial contact with AMD coupled with a higher dissolution efficacy.

This shows that the placement of agricultural limestone in a soil profile to neutralize AMD be guided by the dissolution efficacy of the liming material. It is recommended that liming materials with a slow dissolution efficacy be mixed throughout the soil profile. This method is likely to increase the temporal contact between the liming material and AMD which contributes to a longer period to facilitate neutralization of the soil solution.

When agricultural limestone is absent in the soil profile, the effect of neutralizing AMD through the profile mostly acidifies it. This creates an extremely acidic rooting environment that cannot support all crop growth because the rooting environment is likely to be subjected to several toxicities and nutrient deficiencies.

When dolomitic limestone was used the soil profile was likely exposed to acidification and its extent could result in conditions that negatively influence the availability of essential plant nutrients and led to a rooting environment in which crops may not be able to grow. However, when calcitic limestone was used the soil profile was also acidified but to a lesser extent than when dolomitic limestone was used. This can potentially contribute towards a rooting environment in which crops can grow.

Thus, localising the agricultural limestone within the top half of the profile as well as mixing it throughout the soil profile does not influence the neutralization of AMD to support a favourable rooting environment for crop growth. However, it is suggested that the type of agricultural limestone used in the soil profile, which can influence neutralization of AMD, is an important factor to consider in the development of soil liming strategies for irrigation with AMD.

A consequence of neutralizing AMD in a strategically limed soil profile is an increase in soil EC because of the generation of high levels of soluble salts within the profile. This leads to saline conditions as well as a potentially unsuitable rooting environment to support crop growth. Using calcitic limestone resulted in the highest soil EC after the experiment ended which implies that it facilitated the generation of a higher soluble salt concentration relative to dolomitic limestone. Furthermore, the high EC of the soil which had calcite makes it unsuitable for crop growth.

It is therefore supported that the placement position of agricultural limestone within the soil profile does not influence the neutralization of AMD to support a favourable rooting environment for crop growth. It is suggested that the type of agricultural limestone used in the soil profile is an important factor to consider as it can influence the neutralization of AMD.

Neutralizing AMD in the strategically limed soil columns decreases the status of phosphorus and potassium in the soil. This can lead to a primary nutrient deficiency and a potentially unsuitable rooting environment to support crop growth.

Thus, it is recommended that an appropriate fertilizer management plan form part of the development of soil liming strategies for irrigation with AMD. The secondary nutrient status and availability of the soil is not as impacted when neutralizing AMD in the strategically limed soil columns.

The accumulation of the trace elements Fe, Al and Mn in the strategically limed soil profiles shows that their sequestration within the profile is indeed feasible. This supports the disposition that preconditioning soil with alkaline materials can be considered an alternative mine water treatment strategy. However, it is recommended for future work that an investigation into the bioavailability of the accumulated trace elements be conducted.

It is acknowledged that this study was conducted in a laboratory setting which is a controlled environment. Future work can consider expanding on this field of research by conducting trials or experiments guided by the findings of this study, under actual field conditions. This is suggested because under field conditions, soil profiles are likely to be susceptible to intense wetting and drying cycles which can influence a variety of soil physical and chemical properties.

Under field conditions, there is a possibility of excessive salt accumulation in the soil which could lead to saline conditions. Soil sealing or crusting of the surface could also occur due to the formation of various precipitates. The accumulation of precipitates in the sub-soil could also reduce soil redox potential and negatively influence soil biodiversity and similarly influence crop production.

Soil physical properties could be altered by changes in pore geometry, porosity, bulk density, aggregation, and structure formation. Another possible implication on soil chemical properties could be soil mineralogy changes potentially through destabilization of clay minerals.

CHAPTER 6: SYNTHESIS

6.1 Summary and Conclusion

The first hypothesis for this study states that iron is expected to have the most significant buffering influence on the neutralising potential of hydrated lime compared to aluminium and manganese as its oxidation and hydrolysis is strongly acidifying. This hypothesis is accepted based on the findings of the first experiment detailed in chapter three. The objective of this experiment was to determine the additional acidity generated by the hydrolysis of iron, aluminium, and manganese and how this buffers the neutralising potential of hydrated lime.

It was demonstrated that Fe has the potential to buffer the neutralisation potential of hydrated lime because of two acid generating influences, namely the ferric and ferrous iron buffers. The titration experiment showed that each of them influenced the neutralization potential of hydrated lime below the neutral condition. The ferric iron buffer is attributed to the oxidation of Fe^{2+} to Fe^{3+} , followed by the hydrolysis and precipitation of Fe^{3+} , which occurs between a pH of 2 and 3.49. Thereafter, the influence of the ferrous iron buffer occurs due to the hydrolysis and precipitation of residual Fe^{2+} , which occurs between a pH of about 5 and 5.75.

The second hypothesis for this study states that iron will limit the potential of larger particle sizes of agricultural limestone to neutralise AMD to a greater extent than aluminium and manganese as these larger particles are likely to be armoured by iron precipitates.

This hypothesis is rejected based on the findings of the second experiment elaborated upon in chapter four. The objective of this experiment was to determine the effect that these metals have on the potential of varying particle size fractions of calcite and dolomite to dissolve and enable neutralization.

The findings were that the dissolution of the larger particle size fractions of calcite and dolomite is specifically influenced by Al precipitates and then by Fe precipitates during the neutralization of AMD. The former precipitate has a more prominent influence on restricting the potential of larger particle size fractions of calcite and dolomite to neutralize AMD.

The latter precipitate further contributes to the armouring of the particles and a restriction in the dissolution of the medium and coarse agricultural limestone particle size fractions. Manganese did not restrict the dissolution of the varying particle size fractions of calcite and dolomite used.

The third hypothesis for this study states that localising agricultural limestone within the top half of the soil profile improves the spatial contact with AMD and the potential for neutralization compared to incorporating limestone throughout the soil profile which reduces the spatial contact with AMD and the potential for neutralization.

This hypothesis is rejected based on the findings of the final experiment of the study described in chapter five. The objective of this experiment was to determine the potential of the placement position of agricultural limestone in a soil profile to neutralize AMD to support a favourable rooting environment for crop growth.

It was found that the placement position of the agricultural limestone within a soil profile does not have an influence on the neutralization of AMD to support a favourable rooting environment for crop growth. However, it is suggested that the type of agricultural limestone used in the soil profile, which can influence neutralization of AMD, is an important factor to consider. Therefore, it is recommended that liming materials with a slow dissolution efficacy be mixed throughout the soil profile. This is likely to increase the temporal contact between the liming material and AMD which contributes to a longer period to facilitate neutralization of the soil solution.

6.2 The Development of Soil Liming Strategies for Irrigation with AMD

The principal aim of this study was to develop soil liming strategies for irrigation with AMD. The outcome of the abovementioned experiments was used as a guideline for the development of soil liming strategies for irrigation with AMD. It is therefore recommended as follows:

- A. Calculate the total amount of acidity that Fe, Al, and Mn could generate as a neutral condition of the AMD is reached.
- B. Utilise the appropriate size fraction of liming materials typically used in agricultural applications, which is calcite and dolomite.
- C. Consider the influence of the dissolution efficacy of the agricultural limestone within a soil profile on neutralizing AMD.

- D. Implement a monitoring program to track sulphate concentrations in the irrigation water as well as the soil moisture.
- E. Incorporate an appropriate fertilizer management plan to address primary nutrient deficiency.

A strategy to lime soil for irrigation with mine impacted water must acknowledge that Fe, Al, and Mn can generate additional acidity during the neutralization of AMD. The acid generating potential of the abovementioned metals are attributed to their oxidation, hydrolysis, and consequent precipitation.

These processes exert buffering influences on the potential of alkaline materials to increase the pH of AMD. The risk of ignoring the acidic contributions of these metals in a liming strategy can lead to an inadequate amount of alkalinity (liming material) that is required to neutralize AMD being applied to soil.

Therefore, the basis for the development of a soil liming strategy for irrigation with AMD is to calculate the total amount of acidity that each of these metals could generate as a neutral condition is achieved. This approach provides a guideline using an acid-base accounting principle to determine the corresponding quantity of net alkalinity to neutralize the quantified acidity of the irrigation.

The next step in the development of a soil liming strategy for irrigation with AMD is to utilise the appropriate size fraction of liming materials typically used in agricultural applications, namely calcite and dolomite. Neutralizing mine impacted water (AMD) is dependent on the particle size fraction of the liming material used.

Using an inappropriate size fraction will influence its neutralizing potential. This is caused by the presence of metals in the AMD, which precipitate as minerals as its pH increases. These precipitates can armour the surfaces of the agricultural limestone, prevent their dissolution and limit neutralization.

Decreasing the particle size fraction of calcite and dolomite increases their reactivity by increasing the surface area available for neutralization. Calcite and dolomite with a particle size of less than 0.25 mm is an appropriate size fraction applicable to neutralization of AMD for use as irrigation. However, it is anticipated that finer fractions are likely to be better.

Having established the appropriate particle size to use, it is then necessary to consider the dissolution efficacy of the agricultural limestone in relation to its placement position within a soil profile on neutralizing AMD.

This includes incorporating the agricultural limestone within the root zone of the profile. - that is mixing it throughout the soil profile or concentrating it in the top half of the profile - that is localising it within the soil profile.

The spatial placement of the liming material in the soil profile does not influence neutralization of AMD. However, the dissolution efficacy of the liming material is suggested to guide its placement. In the instance of slowly dissolving material, it is suggested that it be mixed throughout the profile to extend the temporal contact with AMD to facilitate neutralization.

The fourth step in the development of a soil liming strategy for irrigation with AMD is to implement a monitoring program to track sulphate concentrations in the irrigation water as well as the soil moisture. Furthermore, a leaching fraction needs to be incorporated into the strategy to lessen the influence of salt accumulations and salinity in the root zone.

The final step in the development of a soil liming strategy for irrigation with AMD is to incorporate an appropriate fertilizer management plan to address primary nutrient deficiency consequences of the previous steps on the root zone.

6.3 Recommendation for Future Research

Spectrophotometric methods of iron and manganese analysis have potential for further study regarding the neutralization of AMD in an aqueous setting. This could determine a quantification of the extent to which these metals had oxidised, and their concentrations sequestered in solution.

The precipitates or floc of the metals which formed during the titration experiment could potentially generate further acidity overtime. Therefore, it is recommended that future work considers this potential because of the relatively short reaction time allowed for the titration experiments in this study.

Neutralizing AMD with limestone removes acidity which enables metal precipitation reactions. Treating AMD in this manner will cause the precipitation of aluminium and ferric hydroxides around limestone grains, which armour their surfaces. Therefore, to improve the efficacy of calculation of the total amount of liming material needed for neutralization, it is recommended that future research focusses on quantifying the extent of the coating of the surfaces of the liming material.

The accumulation of Fe, Al, and Mn in the strategically limed soil profiles may lead to excessive concentrations within the profile, which can be toxic to crops and thus influence their growth. Thus, there is the potential for future investigation into the bioavailability of the metal accumulations in the limed soil profiles.

There is potential for future investigation into considering the effect of various soil textures in the development of soil liming strategies for irrigation with acid mine drainage. It is presumed that soil texture will influence the degree of neutralization of acid mine drainage used for irrigation because of drainage capability. This could further contribute to the development of the liming strategies by facilitating irrigation management practises in relation to allowing sufficient residence time between irrigation and liming material to facilitate the in-situ neutralization of the water.

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APPENDIX A1

This calculation was used to determine the required amount of salt(s) to produce each AMD solution:

Required amount of salt (mg.L^{-1}) = Concentration of metal cation in AMD solution (mg.L^{-1}) $\times \frac{\text{molar mass of the salt (g.mol}^{-1}\text{)}}{\text{molar mass of the metal cation in AMD treatment (g.mol}^{-1}\text{)}} \times \text{stoichiometric salt : metal cation ratio.}$

The inputs for the calculation are provided in the table below.

Table A1.1: Inputs for determining the required amount of salt(s) to synthesize the various AMD solutions.

Metal	Mass concentration of metal cation in AMD solution (mg.L^{-1})	molar mass of salt (g.mol^{-1})	molar mass of metal cation in AMD solution (g.mol^{-1})	stoichiometric salt : metal cation ratio.
Fe	280	278.03	55.845	1
Al	135	666.44	26.9815	0.5
Mn	275	223.07	54.9380	1

The following salts were used to synthesis the various AMD solution:

- $\text{AMDFe} = \text{FeSO}_4 \cdot 7\text{H}_2\text{O}$
- $\text{AMDAI} = \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$
- $\text{AMDMn} = \text{MnSO}_4 \cdot 7\text{H}_2\text{O}$
- $\text{AMDFe+Al+Mn} = \text{FeSO}_4 \cdot 7\text{H}_2\text{O} + \text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O} + \text{MnSO}_4 \cdot 7\text{H}_2\text{O}$

A summary of the outputs from the above calculation is provided in the table below.

The amounts provided were for the synthesis of 20 litres of solution.

AMD solution	Sulphate-salt(s) used	Mass of salts(s) required (g)
AMD-Fe	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	27.803
AMD-Al	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	33.322
AMD-Mn	$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$	22.307
AMD-Fe-Al-Mn	$\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$	27.803
	$\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$	33.322
	$\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$	22.307

APPENDIX A2

Table A2.1: Titration data for the control solution

Volume of titrant used (ml)	pH of solution		
	Rep 1	Rep 2	Rep 3
0	2	2	2
8	2.26	2.16	2.2
16	2.51	2.32	2.46
24	2.9	2.7	2.93
32	3.4	3.44	3.47
36	6.6	6.67	6.73
37	7.04	7.26	7.15
40	10.33	10.36	10.42

Table A2.2: Titration data for the AMD-Fe solution

Vol of titrant used (ml)	pH of solution		
	Rep 1	Rep 2	Rep 3
0	2	2	2
6	2.09	2.12	2.11
12	2.21	2.21	2.21
18	2.38	2.38	2.38
24	2.73	2.66	2.61
30	2.9	2.89	2.9
36	3.11	3.09	3.07
42	3.63	3.49	3.38
43	3.75	3.66	3.49
44	3.92	3.83	3.57
45	4.44	4.09	3.75
46	4.76	4.35	4.01
47	4.81	4.7	4.16
48	5.22	5.03	4.53
54	5.58	5.47	5.3
60	5.81	5.82	5.64
61	5.95	5.9	5.82
62	5.99	5.82	5.83
63	6.08	5.94	5.86
64	6.49	6.4	6.25
65	6.64	6.58	6.41
66	6.83	6.92	6.83
72	10.49	10.35	9.97

Table A2.3: Titration data for the AMD-Mn solution

Vol of titrant used (ml)	pH of solution		
	Rep 1	Rep 2	Rep 3
0	2	2	2
6	2.1	2.07	2.08
12	2.2	2.19	2.2
18	2.34	2.38	2.38
24	2.55	2.55	2.55
30	2.81	2.8	2.81
31	3.01	2.99	2.94
32	3.05	3.02	3.01
33	3.18	3.09	3.09
34	3.26	3.22	3.18
35	3.39	3.34	3.26
36	3.46	3.43	3.4
39	5.67	5.33	4.76
42	6.6	6.75	6.84
45	6.67	6.85	6.93
48	6.93	7.02	7.1
51	7.02	7.19	7.24
54	7.19	7.27	7.35
57	7.3	7.35	7.38
60	7.43	7.45	7.52
63	7.52	7.55	7.58
68	7.61	7.57	7.52
74	7.7	7.76	7.88
80	8.9	8.97	8.28
86	10.51	10.43	9.21
92	11.02	11.03	10.47
98	11.26	11.21	10.89
104	11.35	11.36	11.04
110	11.5	11.45	11.28
116	11.53	11.51	11.36
122	11.74	11.6	11.47

Table A2.3: Titration data for the AMD-AI solution

Vol of titrant used (ml)	pH of solution		
	Rep 1	Rep 2	Rep 3
0	2	2	2
6	2.2	2.21	2.22
12	2.33	2.34	2.34
18	2.49	2.51	2.48
24	2.68	2.68	2.73
30	3.01	3.01	3.01
36	3.75	3.75	3.7
38	4.13	4.18	4.09
40	4.18	4.26	4.18
42	4.26	4.26	4.28
44	4.26	4.28	4.26
46	4.28	4.31	4.34
48	4.43	4.43	4.35
54	4.41	4.43	4.4
60	4.6	4.44	4.41
66	4.73	4.6	4.6
72	5.45	5.37	5.21
78	6.74	6.88	6.91
84	8.55	8.63	8.71
90	9.15	9.24	9.15
96	9.36	9.4	9.4
102	10.52	10.66	10.68

Table A2.4: Titration data for the AMD-Fe-Al-Mn solution

Vol of titrant used (ml)	pH of solution		
	Rep 1	Rep 2	Rep 3
0	2	2	2
6	2.13	2.22	2.18
12	2.3	2.3	2.3
18	2.56	2.48	2.46
24	2.82	2.74	2.7
30	3.17	3.11	3
36	3.9	3.84	3.84
42	4.27	4.27	4.29
48	4.28	4.37	4.27
54	4.48	4.49	4.4
60	4.62	4.44	4.48
66	4.74	4.7	4.7
72	5.29	5.22	5.27
78	5.68	5.8	5.72
84	5.81	5.98	5.89
90	6.27	6.2	6.12
96	6.48	6.57	6.57
102	6.91	6.91	6.91
108	7	7	7.01
118	7.6	7.6	7.6
128	8.1	8	8.1
138	9.24	9.12	9.16
148	10.62	10.48	10.41
154	10.85	10.84	10.72
160	11.09	10.9	10.97

APPENDIX A3

Table A3.1: The metal concentrations in the AMD solutions which contain single metals after a neutral and alkaline pH was reached.

Solution	Final metal concentration in solution (mg/L) after reaching a neutral pH condition	Final metal concentration in solution (mg/L) after reaching a alkaline pH condition
AMD-Fe Rep1	0.223	0.921
AMD-Fe Rep2	0.764	0.955
AMD-Fe Rep3	0.268	0.703
AMD-Al Rep1	0.492	0.173
AMD-Al Rep2	0.436	0.184
AMD-Al Rep3	0.429	0.169
AMD-Mn Rep1	164.239	0.001
AMD-Mn Rep2	122.49	0.002
AMD-Mn Rep3	134.549	0.004

Table A3.2: Metal concentrations in the AMD solutions containing all three metals after a neutral and alkaline pH was reached.

Solution	Final metal concentration in solution (mg/L) after reaching a neutral pH condition			Final metal concentration in solution (mg/L) after reaching an alkaline pH condition		
	Fe	Al	Mn	Fe	Al	Mn
AMD-Fe-Al-Mn Rep1	0.000	0.047	133.321	0.015	0.099	0.110
AMD-Fe-Al-Mn Rep2	0.000	0.048	140.905	0.000	0.074	0.081
AMD-Fe-Al-Mn Rep3	0.000	0.066	150.635	0.000	0.059	0.008

APPENDIX A4

Table A4.1: The total Ca and Mg contents of each particle size fraction of calcite and dolomite used in this study determined by a nitric acid microwave digestion.

Elemental content (mg.kg ⁻¹)	Calcite particle size fraction			Dolomite particle size fraction		
	1 – 2 mm	0.25 – 0.50 mm	< 0.25 mm	1 – 2 mm	0.25 – 0.50 mm	< 0.25 mm
Calcium	20583	22083	22333	10667	9750	9000
Magnesium	3917	3667	2750	6500	6417	6250

Table A4.2: Amount of calcium present in the required amount of calcitic limestone used to neutralise 100 ml of each acidic solution.

Solution	Required amount of calcite (g) used for neutralization of each solution	Amount of Ca ²⁺ (mol) present in the required amount of calcite used to neutralize each solution (M _{initial})
Control	0.148	0.00148
AMD-Fe	0.276	0.00276
AMD-Al	0.316	0.00316
AMD-Mn	0.296	0.00296
AMD-Fe-Al-Mn	0.592	0.00592

Table A4.3: The calcium concentration in each solution treated with the various particle size fractions of calcite after 30 days of equilibration (determined by ICP-OES).

Treatment Type	The average equilibrium Ca concentration (mol.L ⁻¹) in each solution treated with the different particle size fractions of calcite after 30-day period (M _{equilibrium})
Control Calcite 1-2 mm	0.00783
Control Calcite 0.25-0.50 mm	0.00923
Control Calcite < 0.25 mm	0.00931
AMD-Fe Calcite 1-2 mm	0.01692
AMD-Fe Calcite 0.25-0.50 mm	0.01801
AMD-Fe Calcite <0.25 mm	0.02425
AMD-Al Calcite 1-2 mm	0.01472
AMD-Al Calcite 0.25-0.50 mm	0.02201
AMD-Al Calcite <0.25 mm	0.02395
AMD-Mn Calcite 1-2 mm	0.01238
AMD-Mn Calcite 0.25-0.50 mm	0.01355
AMD-Mn Calcite <0.25 mm	0.01375
AMD-Fe-Al-Mn Calcite 1-2 mm	0.01816
AMD-Fe-Al-Mn Calcite 0.25-0.50 mm	0.02201
AMD-Fe-Al-Mn Calcite <0.25 mm	0.02940

Note that 100 ml of each acidic solution was used which is equal to the Volume of solution (V) in the equation below.

Example calculation: Control Calcite 1 – 2 mm size fraction

$$\begin{aligned}
 \% \text{ Calcitic Limestone dissolution} &= \frac{M_{\text{Equilibrium}} \cdot V}{M_{\text{Initial}}} \times 100 \\
 &= \frac{0.00783 \times 0.1}{0.00148} \times 100 \\
 &= \underline{53 \%}
 \end{aligned}$$

Table A4.4: Amount of magnesium present in the required amount of dolomitic limestone used to neutralise 100 ml of each acidic solution.

Solution	Required amount (g) of dolomite used for neutralization of each solution	Amount of Mg ²⁺ (mol) present in the required amount of dolomite used to neutralize each solution (M_{initial})
Control	0.136	0.000738
AMD-Fe	0.253	0.001372
AMD-Al	0.29	0.001573
AMD-Mn	0.272	0.001475
AMD-Fe-Al-Mn	0.545	0.002956

Table A4.5: The magnesium concentration in each solution treated with the various particle size fractions of calcite after 30 days of equilibration (Determined by ICP-OES).

Treatment Type	The average equilibrium Mg concentration (mol.L^{-1}) in each solution treated with the different particle size fractions of calcite after 30-day period ($M_{\text{equilibrium}}$)
Control Dolomite1-2 mm	0.00457
Control Dolomite0.25-0.50 mm	0.00490
Control Dolomite< 0.25 mm	0.00543
AMD-Fe Dolomite1-2 mm	0.01123
AMD-Fe Dolomite0.25-0.50 mm	0.01304
AMD-Fe Dolomite<0.25 mm	0.01177
AMD-Al Dolomite1-2 mm	0.01206
AMD-Al Dolomite0.25-0.50 mm	0.01473
AMD-Al Dolomite<0.25 mm	0.01502
AMD-Mn Dolomite1-2 mm	0.00708
AMD-Mn Dolomite0.25-0.50 mm	0.00683
AMD-Mn Dolomite<0.25 mm	0.00720
AMD-Fe-Al-Mn Dolomite1-2 mm	0.01498
AMD-Fe-Al-Mn Dolomite0.25-0.50 mm	0.01670
AMD-Fe-Al-Mn Dolomite<0.25 mm	0.01786

Note that 100 ml of each acidic solution was used which is equal to the Volume of solution (V) in the equation below.

Example calculation: Control Dolomite 1 – 2 mm size fraction

$$\begin{aligned}\% \text{ Dolomitic Limestone dissolution} &= \frac{M_{\text{Equilibrium}} \times V}{M_{\text{Initial}}} \times 100 \\ &= \frac{0.00457 \times 0.1}{0.000738} \times 100 \\ &= \underline{62 \%}\end{aligned}$$

Table A4.6: The calcium concentration in each solution treated with the various particle size fractions of calcite and dolomite determined by ICP-OES.

Treatment	Ca concentration in solution (mg/L)
Control Calcite 1-2 mm R1	317.5
Control Calcite 1-2 mm R2	301.2
Control Calcite 1-2 mm R3	323.3
Control Calcite 0.25-0.50 mm R1	330.2
Control Calcite 0.25-0.50 mm R2	380.5
Control Calcite 0.25-0.50 mm R3	398
Control Calcite < 0.25 mm R1	355.2
Control Calcite < 0.25 mm R2	392.1
Control Calcite < 0.25 mm R3	372.2
Control Dolomite 1-2 mm R1	167.3
Control Dolomite 1-2 mm R2	186.3
Control Dolomite 1-2 mm R3	180.1
Control Dolomite 0.25-0.50 mm R1	199.5
Control Dolomite 0.25-0.50 mm R2	204.1
Control Dolomite 0.25-0.50 mm R3	193.1
Control Dolomite <0.25 mm R1	221.8
Control Dolomite <0.25 mm R2	220.2
Control Dolomite <0.25 mm R3	220

Note R means replicate.

Treatment	Ca concentration in solution (mg/L)
Al Calcite 1-2 mm R2	616.5
Al Calcite 1-2 mm R3	569
Al Calcite 0.25-0.50 mm R1	860.5
Al Calcite 0.25-0.50 mm R2	911
Al Calcite <0.25 mm R1	899
Al Calcite <0.25 mm R2	954.5
Al Calcite <0.25 mm R3	1027.5
Al Dolomite 1-2 mm R1	463.2
Al Dolomite 1-2 mm R2	480.45
Al Dolomite 1-2 mm R3	456.35
Al Dolomite 0.25-0.50 mm R1	556
Al Dolomite 0.25-0.50 mm R2	588.5
Al Dolomite 0.25-0.50 mm R3	531.5
Al Dolomite <0.25 mm R1	568
Al Dolomite <0.25 mm R2	569
Al Dolomite <0.25 mm R3	587

Note R means replicate.

Treatment	Ca concentration in solution (mg/L)
Mn Calcite 1-2 mm R1	494.95
Mn Calcite 1-2 mm R2	496.05
Mn Calcite 1-2 mm R3	497.4
Mn Calcite 0.25-0.50 mm R1	529
Mn Calcite 0.25-0.50 mm R2	547
Mn Calcite 0.25-0.50 mm R3	551.5
Mn Calcite <0.25 mm R1	545
Mn Calcite <0.25 mm R2	548
Mn Calcite <0.25 mm R3	558.5
Mn Dolomite 1-2 mm R1	278
Mn Dolomite 1-2 mm R2	289.9
Mn Dolomite 1-2 mm R3	286.1
Mn Dolomite 0.25-0.50 mm R1	289.4
Mn Dolomite 0.25-0.50 mm R2	289.4
Mn Dolomite 0.25-0.50 mm R3	280.2
Mn Dolomite <0.25 mm R1	288.5
Mn Dolomite <0.25 mm R2	306
Mn Dolomite <0.25 mm R3	302.7

Note R means replicate.

Treatment	Ca concentration in solution (mg/L)
Fe Calcite 1-2 mm R1	682.3
Fe Calcite 1-2 mm R2	686.8
Fe Calcite 1-2 mm R3	665.9
Fe Calcite 0.25-0.50 mm R1	695.7
Fe Calcite 0.25-0.50 mm R2	713.6
Fe Calcite 0.25-0.50 mm R3	757.5
Fe Calcite <0.25 mm R1	947.5
Fe Calcite <0.25 mm R2	989.3
Fe Calcite <0.25 mm R3	980.9
Fe Dolomite 1-2 mm R1	397.5
Fe Dolomite 1-2 mm R2	428.4
Fe Dolomite 1-2 mm R3	491.8
Fe Dolomite 0.25-0.50 mm R1	489.3
Fe Dolomite 0.25-0.50 mm R2	486
Fe Dolomite 0.25-0.50 mm R3	463.85
Fe Dolomite <0.25 mm R1	474.85
Fe Dolomite <0.25 mm R2	419.15
Fe Dolomite <0.25 mm R3	427.75

Note R means replicate.

Treatment	Ca concentration in solution (mg/L)
Fe+Al+Mn Calcite 1-2 mm R1	742.5
Fe+Al+Mn Calcite 1-2 mm R2	732.5
Fe+Al+Mn Calcite 1-2 mm R3	709
Fe+Al+Mn Calcite 0.25-0.50 mm R1	854
Fe+Al+Mn Calcite 0.25-0.50 mm R2	774.5
Fe+Al+Mn Calcite 0.25-0.50 mm R3	1017.5
Fe+Al+Mn Calcite <0.25 mm R1	1186.5
Fe+Al+Mn Calcite <0.25 mm R2	1196
Fe+Al+Mn Calcite <0.25 mm R3	1153
Fe+Al+Mn Dolomite 1-2 mm R1	613.5
Fe+Al+Mn Dolomite 1-2 mm R2	594
Fe+Al+Mn Dolomite 1-2 mm R3	596.5
Fe+Al+Mn Dolomite 0.25-0.50 mm R1	660
Fe+Al+Mn Dolomite 0.25-0.50 mm R2	683
Fe+Al+Mn Dolomite 0.25-0.50 mm R3	737.5
Fe+Al+Mn Dolomite <0.25 mm R1	729
Fe+Al+Mn Dolomite <0.25 mm R2	735.5
Fe+Al+Mn Dolomite <0.25 mm R3	702

Note R means replicate.

Table A4.7: Neutralization data for the control solution treated with the various particle size fractions of calcite and dolomite.

Reaction/equilibration time (hours)	Calcite 1 -2 mm			Calcite 0.25 - 0.50 mm			Calcite < 0.25 mm			Dolomite 1 -2 mm			Dolomite 0.25 - 0.50 mm			Dolomite < 0.25 mm		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
0	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
48	2.44	2.53	2.6	3.84	3.93	3.75	6.03	6.12	6.12	3	2.84	2.93	4.39	4.41	4.74	6.14	6.22	6.22
96	2.81	3.03	3.04	5.33	5.45	5.48	6.29	6.36	6.36	3.54	3.23	3.42	5.89	5.73	5.84	6.38	6.38	6.38
144	3.45	3.98	4.17	6.12	6.25	6.3	6.76	6.79	6.73	4.96	3.75	4.74	6.38	6.29	6.34	6.74	6.71	6.67
192	4.17	5.32	5.58	6.34	6.48	6.5	6.85	6.92	6.9	5.92	5.35	5.92	6.65	6.57	6.57	6.84	6.87	6.87
240	5.69	5.93	6.06	6.7	6.74	6.78	7.09	7.09	7.07	6.23	5.9	6.3	6.76	6.78	6.76	6.97	7.06	7.01
288	5.7	6.16	6.38	6.82	6.91	6.94	7.16	7.16	7.12	6.32	6.08	6.5	6.82	6.83	6.8	7	7.12	7.08
336	6.19	6.45	6.6	6.91	6.99	6.99	7.2	7.26	7.17	6.66	6.47	6.66	7.09	7.07	7.1	7.24	7.34	7.28
384	6.52	6.71	6.86	7.25	7.25	7.35	7.52	7.54	7.52	6.84	6.62	6.86	7.17	7.16	7.22	7.26	7.4	7.33
432	7	6.91	6.97	7.17	7.21	7.26	7.4	7.37	7.35	7.09	6.97	7.08	7.26	7.26	7.34	7.41	7.52	7.5
504	7.35	7.17	7.17	7.33	7.43	7.43	7.6	7.56	7.52	7.24	7.01	7.18	7.29	7.35	7.43	7.54	7.69	7.58
552	6.66	6.97	7.09	7.37	7.43	7.51	7.59	7.61	7.61	7.06	7.08	7.31	7.49	7.49	7.61	7.66	7.69	7.67
648	6.72	7.09	7.26	7.47	7.57	7.64	7.09	7.36	7.45	7.02	7.18	7.3	7.57	7.52	7.6	7.9	7.71	7.99
720	6.74	7	7.18	7.37	7.44	7.53	7.59	7.53	7.55	7.29	7.4	7.5	7.81	7.81	7.9	8.01	8.07	8.01

Table A4.8: Neutralization data for the AMD-Fe solution treated with the various particle size fractions of calcite and dolomite.

Reaction/equilibration time (hours)	Calcite 1 -2 mm			Calcite 0.25 - 0.50 mm			Calcite < 0.25 mm			Dolomite 1 -2 mm			Dolomite 0.25 - 0.50 mm			Dolomite < 0.25 mm		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
0	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
48	3.21	3	2.99	5.06	5.04	4.8	5.32	5.41	5.41	5.15	3.66	3.61	5.38	5.41	5.45	5.49	5.5	5.5
96	4.88	3.83	3.94	5.32	5.32	5.19	5.41	5.57	5.54	4.89	4.48	4.34	5.26	5.22	5.26	5.42	5.43	5.41
144	5.23	5.14	5.05	5.17	5.23	5.5	5.94	5.99	5.94	4.91	4.73	4.7	5.55	5.47	5.55	5.63	5.77	5.65
192	5.03	5.06	4.93	5.73	5.75	5.58	6.21	6.21	6.18	4.81	4.67	4.64	5.87	5.8	5.81	6.12	6.16	6.26
240	5.01	4.91	4.98	5.79	5.74	5.63	6.57	6.55	6.55	5.12	4.84	4.6	6.05	6.01	5.92	6.39	6.37	6.44
288	5.49	5.13	5.06	6.11	6.04	5.86	6.71	6.75	6.82	5.38	4.91	4.7	6.32	6.25	6.32	6.56	6.63	6.65
336	5.35	4.98	5.07	6.43	6.27	6.13	6.82	6.9	6.91	5.68	5.09	4.93	6.61	6.66	6.64	6.9	6.89	6.92
384	5.42	5.09	5.18	6.74	6.7	6.62	7.16	7.16	7.24	5.87	5.22	5.04	6.74	6.82	6.8	7	6.98	7.05
432	5.58	5.18	5.2	6.74	6.83	6.74	7.17	7.17	7.17	6.27	5.42	5.21	6.85	7.01	7.08	7.17	7.18	7.26
504	5.88	5.37	5.46	6.83	7	7.04	7.35	7.36	7.41	6.75	5.92	5.67	7.09	7.25	7.35	7.42	7.42	7.44
552	6.07	5.46	5.52	6.96	7.06	7	7.38	7.38	7.45	6.92	6.25	6.02	7.17	7.33	7.41	7.49	7.49	7.49
648	6.49	5.74	5.92	7.02	7.12	7.22	7.46	7.51	7.55	6.9	6.48	6.3	7.18	7.34	7.42	7.46	7.52	7.52
720	6.59	6.02	6.21	7	7.27	7.28	7.48	7.5	7.54	7.02	6.83	6.73	7.55	7.72	7.72	7.76	7.81	7.83

Table A4.9: Neutralization data for the AMD-AI solution treated with the various particle size fractions of calcite and dolomite.

Reaction/equilibration time (hours)	Calcite 1 -2 mm			Calcite 0.25 - 0.50 mm			Calcite < 0.25 mm			Dolomite 1 -2 mm			Dolomite 0.25 - 0.50 mm			Dolomite < 0.25 mm		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
0	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
48	3.06	3.15	3.01	4.18	4.19	4.23	5.02	5.04	5.15	3.66	3.83	3.84	4.48	4.54	4.47	5.01	5.14	4.85
96	3.97	3.92	3.92	4.29	4.27	4.36	5.99	5.96	5.91	4.21	4.33	4.25	4.71	4.72	4.7	5.86	5.83	5.82
144	4.11	4.19	4.08	4.41	4.43	4.54	6.16	6.07	6.31	4.19	4.19	4.18	5.41	5.55	4.76	6.11	6.23	6.12
192	4.16	4.14	4.14	5.1	5	5.69	6.53	6.51	6.65	4.42	4.42	4.43	6.18	6.11	5.67	6.51	6.58	6.55
240	4.27	4.27	4.26	5.81	5.9	6.02	6.65	6.65	6.83	4.35	4.4	4.43	6.28	6.3	6.1	6.61	6.64	6.61
288	4.27	4.26	4.22	6.13	6.31	6.36	6.81	6.8	6.98	4.37	4.45	4.44	6.36	6.5	6.26	6.63	6.65	6.61
336	4.2	4.2	4.2	6.32	6.46	6.52	6.89	6.82	6.99	4.52	4.54	4.6	6.6	6.61	6.56	6.82	6.88	6.86
384	4.3	4.3	4.28	6.6	6.8	6.88	7.14	7.12	7.23	4.58	4.58	4.61	6.61	6.72	6.67	6.84	6.92	6.92
432	4.29	4.26	4.26	6.55	6.72	6.83	7	7	7.12	4.61	4.67	4.69	6.64	6.82	6.84	6.94	7.08	7.09
504	4.37	4.39	4.35	6.92	7.07	7.09	7.26	7.24	7.35	4.75	4.87	4.91	7.03	7.14	7.12	7.17	7.35	7.25
552	4.35	4.34	4.31	6.83	6.93	7	7.17	7.27	7.29	5.06	5.21	5.48	7.05	7.17	7.17	7.17	7.26	7.25
648	4.31	4.35	4.27	7.28	7	7.09	7.26	7.36	7.36	5.36	5.73	6.09	7.09	7.32	7.36	7.41	7.44	7.44
720	4.31	4.37	4.29	6.55	6.86	7	7.24	7.34	7.35	6.09	6.29	6.5	7.2	7.35	7.36	7.39	7.52	7.46

Table A4.10: Neutralization data for the AMD-Mn solution treated with the various particle size fractions of calcite and dolomite.

Reaction/equilibration time (hours)	Calcite 1 -2 mm			Calcite 0.25 - 0.50 mm			Calcite < 0.25 mm			Dolomite 1 -2 mm			Dolomite 0.25 - 0.50 mm			Dolomite < 0.25 mm		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
0	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
48	3.1	3.18	3.38	5.41	5.41	5.41	5.94	5.94	5.98	5.41	5.19	5.33	5.72	5.7	5.74	5.74	5.82	5.74
96	4.01	4.27	4.93	5.92	6	5.94	6.26	6.29	6.3	5.64	5.58	5.63	5.81	5.8	5.82	5.84	5.84	5.89
144	5.68	5.5	5.77	6.26	6.32	6.3	6.51	6.56	6.55	5.89	5.89	5.89	5.99	6.07	6.08	6.08	6.07	6.14
192	6.05	6.01	6.18	6.45	6.47	6.48	6.61	6.63	6.65	6.16	6.21	6.25	6.27	6.29	6.33	6.28	6.23	6.33
240	6.23	6.26	6.38	6.61	6.59	6.61	6.74	6.74	6.82	6.43	6.37	6.27	6.31	6.39	6.36	6.31	6.31	6.35
288	6.53	6.47	6.54	6.7	6.73	6.73	6.9	6.91	6.97	6.21	6.32	6.32	6.26	6.32	6.35	6.25	6.24	6.28
336	6.53	6.48	6.57	6.74	6.76	6.83	6.91	6.98	7	6.26	6.36	6.35	6.3	6.43	6.43	6.43	6.42	6.43
384	6.98	6.87	6.94	7.07	7.09	7.15	7.16	7.16	7.25	6.54	6.56	6.54	6.53	6.57	6.59	6.56	6.55	6.59
432	6.91	6.84	6.91	7.09	7.07	7.1	7.09	7.13	7.17	6.57	6.37	6.64	6.61	6.67	6.67	6.64	6.59	6.62
504	7.01	7	7	7.13	7.11	7.17	7.17	7.24	7.18	6.68	6.77	6.72	6.73	6.76	6.71	6.68	6.66	6.68
552	6.93	7	7.07	7.17	7.15	7.24	7.21	7.24	7.21	6.71	6.87	6.84	6.84	6.85	6.82	6.83	6.79	6.79
648	7.09	7.09	7.17	7.22	7.25	7.29	7.25	7.22	7.18	6.45	6.63	6.69	6.66	6.72	6.74	6.69	6.69	6.69
720	6.64	6.86	7	7.09	7.11	7.18	7.16	7.11	7.1	6.61	6.88	6.94	6.94	6.98	6.96	6.95	6.93	6.94

Table A4.11: Neutralization data for the AMD-Fe-Al-Mn solution treated with the various particle size fractions of calcite and dolomite.

Reaction/equilibration time (hours)	Calcite 1 -2 mm			Calcite 0.25 - 0.50 mm			Calcite < 0.25 mm			Dolomite 1 -2 mm			Dolomite 0.25 - 0.50 mm			Dolomite < 0.25 mm		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
0	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2	2
48	3.93	3.93	3.93	4.37	4.38	4.39	5.43	5.34	5.41	4.46	4.44	4.47	4.62	4.62	4.62	4.75	4.7	4.71
96	4.22	4.2	4.2	4.46	4.45	4.45	5.58	5.62	5.55	4.55	4.48	4.55	4.72	4.71	4.69	4.82	4.75	4.77
144	4.42	4.44	4.44	4.96	5.04	4.96	5.78	5.92	5.8	4.7	4.52	4.61	4.89	4.96	4.9	5.1	5.11	5.04
192	4.32	4.31	4.32	5.35	5.6	5.42	5.85	5.77	5.74	4.63	4.59	4.67	5.05	5.09	5.05	5.17	5.12	5.17
240	4.38	4.36	4.38	5.53	5.57	5.58	5.96	5.78	5.73	4.75	4.61	4.66	5.14	5.16	5.16	5.27	5.3	5.3
288	4.45	4.45	4.45	5.68	5.68	5.68	6.09	6.04	6.05	4.82	4.75	4.75	5.19	5.21	5.35	5.3	5.34	5.32
336	4.48	4.44	4.46	5.72	5.83	5.74	6.24	6.2	6.24	4.98	4.8	4.85	5.31	5.33	5.3	5.39	5.4	5.42
384	4.57	4.51	4.51	5.93	5.96	6	6.5	6.52	6.53	5.27	5.02	5.03	5.43	5.46	5.46	5.54	5.54	5.54
432	4.52	4.5	4.51	5.98	6.04	5.98	6.51	6.53	6.57	5.46	5.1	5.04	5.46	5.5	5.51	5.59	5.59	5.59
504	4.56	4.61	4.61	6.24	6.39	6.33	6.71	6.73	6.74	5.34	5.18	5.18	5.67	5.64	5.67	5.76	5.69	5.79
552	4.53	4.53	4.53	6.31	6.52	6.52	6.76	6.69	6.72	5.34	5.24	5.21	5.69	5.67	5.7	5.78	5.77	5.78
648	4.47	4.49	4.52	6.31	6.54	6.6	6.82	6.74	6.8	5.36	5.31	5.29	5.7	5.67	5.68	5.79	5.79	5.87
720	4.57	4.6	4.6	6.29	6.55	6.64	6.82	6.81	6.8	5.55	5.47	5.38	5.98	5.91	5.95	6.08	6.1	6.15

APPENDIX A5

Cumulative vol of AMD added to column (L)	Control column			Calcite mixed through column			Calcite localised within column			Dolomite mixed throughout column			Dolomite localised within column		
	pH of leachate			pH of leachate			pH of leachate			pH of leachate			pH of leachate		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
0.15	5.59	5.47	5.55	7.52	7.87	7.9	7.61	7.9	7.76	7.97	7.93	7.9	7.75	7.93	7.97
0.3	4.66	4.08	4.29	7.09	7.57	7.71	8.02	7.87	8.1	7.77	7.87	7.96	7.82	7.87	7.56
0.45	3.02	2.96	3.02	7	7.31	7.27	7.51	7.49	7.73	6.75	6.43	6.1	6.1	5.92	6.07
0.6	2.49	2.47	2.55	4.56	4.7	4.59	6.6	6.18	6.81	5.1	4.93	4.67	4.66	4.71	4.74
0.75	2.28	2.2	2.21	6.8	7.13	7.21	7.17	7.48	7.55	5.04	5	5	5.26	5.07	5.09
0.9	2.23	2.21	2.22	5.6	5.43	5.04	6.17	5.33	6.49	5.07	5.17	5.1	4.92	5.02	4.92
1.05	1.87	1.86	1.89	4.77	4.68	4.72	5.03	5.13	5.22	5.12	5.21	4.94	4.98	5	4.85
1.2	1.98	1.96	1.98	5.69	4.8	5.06	5.06	4.94	5.9	4.97	4.72	4.64	4.9	4.89	4.88
1.35	1.92	1.89	1.94	5.07	5.34	5.12	5.42	5.36	5.95	5.15	5.11	4.38	5.24	5.06	4.8
1.5	2.16	2.13	2.16	4.35	4.7	4.44	4.79	4.7	4.85	4.24	4.44	4.25	2.92	4.27	3.47
1.65	2.13	2.16	2.12	4.44	4.46	4.35	4.79	4.48	4.8	4.44	4.8	4.27	3.19	4.37	4.53
1.8	2.33	2.29	2.27	6.6	6.09	6.54	5.36	6.09	5.79	4.37	4.76	4.15	3.61	4.37	4.99
1.95	1.9	1.9	1.9	4.52	4.68	4.57	4.79	4.61	4.52	4.02	4.51	3.93	3.31	4.2	4.38
2.1	2.37	2.35	2.36	6.82	6.17	6.25	5.83	6	6.2	4.43	4.66	3.73	4.04	4.34	4.41
2.25	2.25	2.19	2.16	5.56	5.56	5.5	5.78	5.58	5.58	4.41	4.65	3.98	3.72	4.07	3.9
2.4	2.31	2.34	2.3	5.42	5.42	5.18	5.33	5.23	5.32	4.48	4.61	3.32	3.32	3.98	3.98
2.55	1.84	1.84	1.84	5.75	5.74	5.69	5.83	5.74	5.83	4.02	4.52	4.27	3.05	3.47	3.65

Table A5.1: The leachate pH data for each of the soil column treatments.

Table A5.2: Metal concentrations in the leachates collected at the start, middle and end of the column experiment determined by ICP-OES.

Soil Column Treatments	Metal concentration (mg.L) present in the leachate collected at the:																										
	Start of the experiment									Mid-point of the experiment									End of the experiment								
	Fe			Al			Mn			Fe			Al			Mn			Fe			Al			Mn		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Control columns	16.65	35.89	17.86	0.0606	0.8129	0.0517	231.3	244.6	227.1	266.6	277.3	279.2	251.4	247.4	251.1	364.9	374.4	373.8	325.6	339.7	323.2	294.9	226.4	230.1	381.6	396.4	377.9
Calcite mixed throughout profile	0	0	0	0.026	0	0	58.59	48.25	85.57	99.21	75.13	216.4	0.0115	0	0	385.7	402.7	394.3	102.4	84.64	153.4	0.0547	0	0	394.8	423.1	378.5
Calcite localised within profile	0	0	0	0.0527	0.0014	0.0618	78.07	52.84	75.89	21.91	102.1	3.075	0	0	0.012	373.6	368.3	409.4	70.8	85.9	82.27	0.0492	0.0296	0.0108	389.2	379.9	398
Dolomite mixed throughout profile	0	0	0	0.0017	0.0249	0	30.32	23.61	41.28	188.4	210	214.3	0.4177	0.1294	22.24	356.9	364.8	363.7	196.9	297.6	235.7	152.2	21.84	69.24	383.9	384.9	376.7
Dolomite localised within profile	0	0	0	0.0014	0	0.0482	21.67	24.45	18.65	150.2	148.8	105.5	0.4967	0.2816	3.305	465.7	475.1	470.1	285.3	251	202.6	179.5	100.6	150.3	374.9	384.8	385.5

APPENDIX A6

Table A6.1: The pH and EC of each soil column treatment after the experiment was completed.

Soil Column Treatment	Soil pH after experiment			Soil EC _s (mS/m) after experiment		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Control columns	2.85	2.8	2.77	103.2	108.2	100.2
Calcite mixed throughout profile	6.68	6.71	6.7	133.1	133.5	134.1
Calcite localised within profile	6.84	6.83	6.83	143.9	127.9	141.8
Dolomite mixed throughout profile	6.61	6.6	6.51	130.3	130.3	115.6
Dolomite localised within profile	6.35	6.4	6.38	107.3	122.1	112.4

Table A6.2: The Mehlich extractable macronutrient concentrations of each soil column treatment after the experiment was completed.

Soil Coulmn Treatment	Mehlich Extractable P (mg/kg)			Mehlich Extractable K (mg/kg)			Mehlich Extractable Ca (mg/kg)			Mehlich Extractable Mg (mg/kg)			Mehlich Extractable S (mg/kg)		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Control columns	143.37	156.88	165.82	5.99	7.01	5.99	9.62	6.46	4.01	5.53	4.89	5.34	591.26	656.13	649.67
Calcite mixed throughout profile	8.5	7.18	6.63	18.61	19.41	17.96	3291.74	3365.25	3137.76	66.61	69.29	67.2	1432.65	1547.88	1585.63
Calcite localised within profile	4.66	8.44	2.41	18.1	17.44	18.46	2931.14	3027.5	3962.27	62.91	60.71	70.83	1677.02	1371.06	1839.94
Dolomite mixed throughout profile	26.73	14.47	35.37	19.67	19.42	19.24	6162.6	6646.37	4824.52	3077.48	3450	2421.85	1172.39	1353.18	1156.49
Dolomite localised within profile	21.87	14.35	15.92	17.48	17.91	16.38	4723.19	5247.7	4262.27	2442.72	2748.68	2241.06	1182.32	1285.63	1223.05

Table A6.3: The total metal concentrations determined by nitric acid microwave digestion of each soil column treatment after the experiment was completed.

Soil Coulmn Treatment	Total Fe (mg/kg)			Total Al (mg/kg)			Total Mn (mg/kg)		
	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3	Rep 1	Rep 2	Rep 3
Control columns	17877.39	15052.39	14885.72	6665.9	5202.56	5301.73	192.75	196.83	196.83
Calcite mixed throughout profile	17185.72	17485.72	19219.05	9941.73	8458.4	10441.73	1220.83	1340	1243.33
Calcite localised within profile	20635.72	17777.39	17485.72	10750.06	8766.73	6590.9	1480	1366.67	1374.17
Dolomite mixed throughout profile	18135.72	16935.72	18285.72	12691.73	11825.06	11491.73	620.75	609.42	736.92
Dolomite localised within profile	17960.72	17944.05	19210.72	9958.4	10175.06	9950.06	599.08	511.08	536.83