Investigation into the sustainable use of mine waste to treat or prevent acid mine drainage

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Dissertation accepted in fulfilment of the requirements for the degree *Master of Science in Engineering Science with Chemical Engineering* at the North-West University

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SOLEMN DECLARATION

I, **Naythan van Wyk**, hereby declare that the dissertation entitled, “***Investigation into the sustainable use of mine waste to treat and or prevent acid mine drainage”,*** which I hereby submit, in fulfilment of the requirements for the award of the degree of Master of Engineering (Chemical Engineering) at the North-West University, is my own individual work and has not been previously submitted to any other institution.

Signed at Potchefstroom, South Africa.

29th November 2022

Date

29th November 2022

Date

OUTPUTS FROM THE STUDY

Publications

1) **van Wyk, N**., Eloka-Eboka, A. C., & Fosso-Kankeu, E. (2022). The potential of using alkaline gold mine tailing as a cover material to mitigate AMD formation from acidic gold mine tailing pile at Sabie-Pilgrim's Rest Goldfields, South Africa. *Environmental Science Pollution Research* (ESPR), 1-13. – ***Q1 Journal:*** https://doi.org/10.1007/s11356-022-22106-9

International conferences (presentation and articles)

1) **van Wyk, N**., E Fosso, E., B. Waanders, F., Le Roux, M. and Quentin, Q., (2020). Investigation in the Use of Low Sulphide Coal Tailings in Covers with Capillary Barrier Effects to Prevent Acid Mine Drainage. In: *18th JOHANNESBURG Int'l Conference on Science, Engineering, Technology & Waste Management (SETWM-20)*. [online] Johannesburg, pp.39-44. Available: http://www.eares.org/siteadmin/upload/7435EAP1120227.pdf

2) **van Wyk, N.,** Fosso-Kankeu, E., & Eloka-Eboka, A. (2022). Potential of Alkaline Gold Mine Tailings to Treat and Prevent AMD Formation: A Case of an Acidic Gold Mine of Sabie-Pilgrim's Rest Goldfields in South Africa. Proceedings of the 33rd JOHANNESBURG Int'l Conference on "Chemical, Biological & Environmental Engineering" (JCBEE-22) Mar. 17-18, 2022, Johannesburg, South Africa. Available: https://bit.ly/3TVwOu8

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Abstract

Mine waste rock or tailings generate acid when sulphide minerals such as Pyrite (FeS_2) oxidise in the presents of oxygen and water. The acid not neutralised by acid neutralising minerals such as calcite is leached into nearby water bodies such as lakes, rivers and underground water reservoirs and is referred to as Acid Mine Drainage (AMD). AMD is usually highly acidic, containing elevated concentrations of toxic dissolved metals. AMD is the second most significant threat to sustainable life after global warming. The primary aim of this study is to determine the feasibility of using alkaline gold mine tailings as a pH neutralising cover to mitigate AMD generated by gold mine tailings that have become acidic located in the Sabie-Pilgrim's Rest Goldfields, Mpumalanga province, South Africa. The study assessed the acid generating and acid neutralising capabilities of the alkaline (AN), acidic (AG) gold mine tailings and blends (MIX25 and MIX50) using Acid-Base Accounting (ABA), Net Acid Generation (NAG), Acid Buffering Characteristic Curve (ABCC) and leach column test procedures. The results found that the acidic gold mine tailings have become acidic and would continue to produce an acidic effluent. The alkaline gold mine tailing has a high acid neutralising capacity due to the high dolomite content. Results found that blends MIX50 and MIX25 consisting of a 1:1 and 1:3 weight ratio of alkaline and acidic gold mine tailings contained sufficient acid neutralising capacity (due to high Dolomite content) to neutralise acid generated by the acidic gold mine tailing portion of the blend. The leach column tests found that during the first few weeks of the experiment, the columns containing the alkaline gold mine tailing (top layer) used as a pH or acid neutralising cover material could not neutralise the acid generated by the acidic gold mine tailings (bottom layer). However, after prolonged exposure, the alkaline gold mine tailings effectively neutralise the acid generated by the acid-generating gold mine tailings, producing an alkaline effluent.

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RESEARCH ARTICLE

The potential of using alkaline gold mine tailing as a cover material to mitigate AMD formation from acidic gold mine tailing pile at Sabie-Pilgrim's Rest Goldfields, South Africa

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Abstract
Acid mine drainage (AMD) caused by the oxidation of sulphide minerals found in mine waste is a global environmental concern, especially in water-restricted countries with heavy mining industries. Implementing AMD treatment and prevention programs can be extremely expensive, hence the need to identify environmentally sustainable treatment and preventative techniques to mitigate the potential of AMD formation. Soil covers and blends have been identified as an attractive approach. However, prior studies on the characteristics of the soils concerned and the acid-neutralisation rate should be carried out before considering the implementation of a soil cover or blending system to mitigate AMD formation. This study evaluated the acid generation capabilities of acidic gold mine tailings (AG), alkaline gold mine tailings (AN) and blends (MIX25, MIX50). Acid–base accounting (ABA), net acid generation (NAG) and acid-buffering characteristic curve (ABCC) test methods were used to evaluate the acid-generating and acid-neutralising capabilities of AG, AN, MIX25 and MIX50 samples. Leach column tests were conducted using alkaline gold mine tailings (AN) as the top pH neutralising cover (COV25) to determine the potential of the alkaline gold mine tailing to serve as a pH neutralising cover material to prevent and treat AMD generated by the acidic gold mine tailings. The ABA, NAG and ABCC results showed that AN has a high acid-neutralising capacity while AG has the potential to generate acid. The results further indicated that the AN to AG blend ratio of 1:3 by weight (MIX25) would neutralise the acid generated by AG. Leach column experiment (COV25) found that using AN as a pH neutralising cover would be a feasible option.

Keywords Alkaline · Acidic · Gold mine tailings · AMD · Cover material · pH · Environment · Mining

Introduction

Acid mine drainage (AMD) is generated when sulphide minerals such as pyrite (FeS_2) and pyrrhotite ($Fe_{(1-x)}S$) found in mine wastes are oxidised by water and oxygen supplied by the surrounding environment. AMD pollutes vast quantities of underground and surface water resources and is considered to be the second-largest threat to sustainable life after global warming (Dold 2010; Koch et al. 2017; Madzivire et al. 2014; Smart et al. 2002). It is important to note that when the mine waste becomes acidic ($pH < 4$), ferric iron (Fe^{3+}) becomes the primary oxidiser. The quaintly of acid generated per mole of sulphide minerals when oxidised by ferric iron compared to oxidation of sulphide minerals via oxygen can be up to fourfold larger, and the rate of oxidation can be up to two magnitudes higher. When oxidised by oxygen, sulphide minerals that do not generate acid become acid-generating minerals when oxidised by ferric iron. It is thus of the utmost importance that the pH of mine waste is maintained above a pH of 4 to reduce the quantity and rate of acid generation (Appelo and Postma 2005; Chandra and Gerson 2010; Dold 2017; Moses et al. 1987).

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There are many conventional AMD treatment and prevention techniques such as passivation, backfilling, desalination, permeable reactive barriers, lime neutralisation, waste-heap covers, adsorption, in situ biological remediation, constructed wetlands, sulfidogenic bioreactors, backfilling, reverse osmosis, filtration, ion exchange and electrodialysis which have been developed over the years (Moodley et al. 2018; Saha and Sinha 2018). The implementation of traditional AMD treatment and prevention techniques is limited due to the constant depletion of natural resources, poor performances, high cost of construction and implementation, design inaccuracies, generation of additional wastes, difficulty in understanding the functionality and the use of hazardous chemicals (Moodley et al. 2018; Saha and Sinha 2018).

In the past few years, there has been an increase in research on the use of industrial waste or by-products to treat and prevent AMD. Waste materials and by-products from the paper mill, wine, seafood and steel mill industries have shown the ability to reduce and eliminate some of the limitations associated with conventional AMD treatment and prevention techniques (Moodley et al. 2018). There is a need to conduct more research on the use of industrial wastes and by-products to develop environmentally sustainable AMD prevention and treatment techniques. Prevention and treatment are the two primary strategies for AMD remediation. Prevention involves inhibiting AMD generation at the source by minimising the contact between sulphide ore, oxygen, water and bacteria (Aubertin et al. 2016). This method is used as a permanent solution as it stops AMD generation entirely and does not require any further treatment, such as secondary mineral removal or sludge disposal (Moodley et al. 2018).

Adding an alkaline material to acid-generating tailings is one of the most commonly used AMD treatment techniques. The neutralising material neutralises acid generated by the acid-generating waste and increases the pH of the tailings resulting in the removal of metal/metalloids through precipitation. This is novel in itself; however, using alkaline materials such as lime, limestone and slag can produce large quantities of secondary sludge (Wingenfelder et al. 2005). Neutralising materials such as paper mill by-products, steel mill by-products and phosphate waste rock have gained popularity in AMD remediation. These materials can be used as preventative measures. Some of these by-products include fly ash, mesa lime, green liquor dregs and wood ash, basic oxygen furnace slag and argon oxygen decarburisation sag (Moodley et al. 2018). The use of waste materials or by-products in the prevention and treatment resonates strangely with sustainability, especially if the AMD source is considered acid-generating for the foreseeable future. The use of these materials may benefit multiple industries simultaneously. The cost of transportation should be kept in mind when considering a waste material to prevent or treat AMD at a mining or storage site to ensure that it will be economically viable (Moodley et al. 2018).

The acid-generating and acid-buffering capabilities of mine waste or tailings are evaluated to develop and implement effective AMD treatment and prevention strategies. The methods used to assess the acid-generating and acid-buffering capabilities of mine waste or tailings are either static or kinetic tests, depending on the procedure and time frame. Static tests such as acid–base accounting (ABA), net acid generation (NAG) and acid-buffering characteristic curve (ABCC) are conducted in a relatively short time frame and at a low cost. Kinetic tests such as leach columns or humidity cells are usually conducted over 4 to 12 months and are extremely expensive. Kinetic tests attempt to mimic the natural conditions that the mine waste rock or tailings are or would be exposed to at the disposal site. Results obtained from leach columns and humidity cells are extremely reliable and allow parameters such as oxidation kinetics, sulphide reactivity, rate of acid generation, metal solubility, dissolution rates, cetera to be studied (Smart et al. 2002; Lapakko 2002; Stewart et al. 2006; Oh et al. 2017). The acid-generating capabilities of tailings can be classified as potential acid-forming (PAF), non-acid forming (NAF) or uncertain (UC) using the ABA or NAG results and their respective classification criteria. It is best practice to use ABA results in conjunction with NAG results to eliminate some of the limitations found in both the ABA and NAG test procedures (Oh et al. 2017; Smart et al. 2002).

Mining of gold has been carried out in Sabie-Pilgrim's Rest Goldfields since the eighteenth century, leaving behind several dumps of tailings. Preliminary studies conducted by Rudzani (2018) and Rudzani et al. (2019) on the gold mine tailings in Sabie-Pilgrim's Rest Goldfields area have shown that various tailing dumps facilities may generate leachates with a pH varying between the acidic and alkaline ranges. Hence, the assumption is that alkaline gold mine tailings could be used as a pH neutralising cover to treat and prevent AMD generated by the acidic gold mine tailings. Therefore, the objectives of this study consist of assessing the acid-generating and acid-neutralising capabilities of the alkaline and acidic gold mine tailing dumps and determining the potential and sustainable use of alkaline tailing dump as pH neutralising cover material to treat and prevent AMD formation generated by acidic gold mine tailing using the Sabie Rest Goldfields as a case study.

Material and methods

Study area description

The acidic gold mine tailings (AG) and the alkaline gold mine tailings (AN) are located in Sabie in the Mpumalanga province of South Africa and are located approximately 3.8 km from each other, as seen in Fig. 1. Sabie has an average yearly rainfall of 1195 mm, with the highest average relative humidity of 80% in January and a lowest average relative humidity of 58% in August (CLIMATE SABIE, SOUTH AFRICA 2022). The high average yearly rainfall and the high humidity during the summer months provide optimal conditions for sulphide oxidation and dissolution of minerals.

The alkaline and acidic gold mine tailings consist of fines and thus have a large surface area to react with water and oxygen supplied by the surrounding environment, further enhancing the conditions for sulphide oxidation and dissolution of minerals. There are currently no tailings impoundments operations, emphasising the need to research sustainable use of mine waste to treat and prevent acid generation.

There is no plant growth on the surface of the acid-generating tailings pile, as depicted in Fig. 2, providing an initial

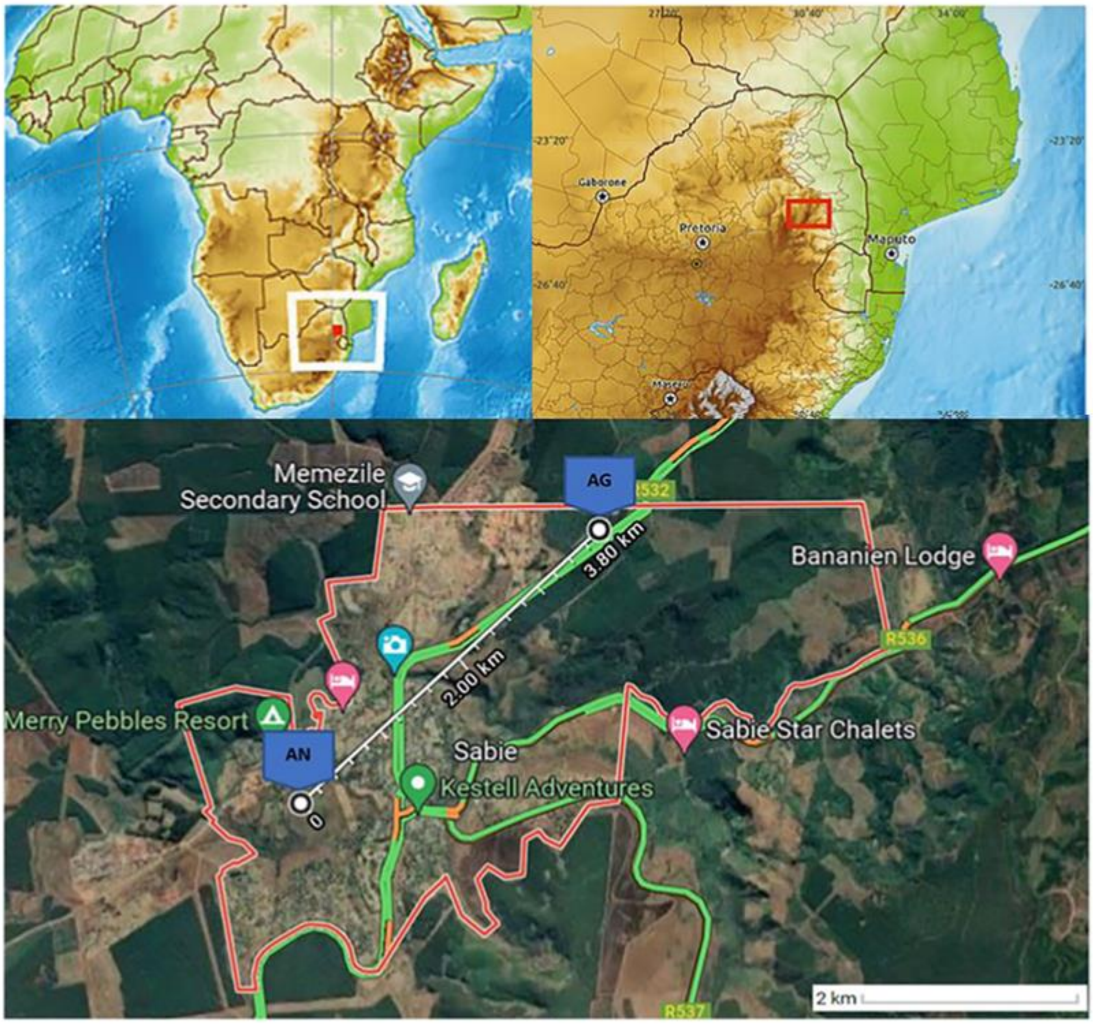

Fig. 1 Location of the study area

Fig. 2 Acidic gold mine tailings (AG)

indication that the tailings had become acidic or toxic. The absence of plant growth allows for erosion resulting in water and oxygen penetration into the acid-generating mine tailings, increasing the rate and extent of acid generation.

A substantial amount of grass-like plant growths was observed on the surface of the alkaline gold mine tailings (Fig. 3), limiting erosion of the tailings pile and penetration of water and oxygen into the alkaline mine tailings pile.

Sample collection and preparation

Samples were collected during the dry season, winter in South Africa (July). Three samples were collected from an acid-generating (AG) gold mine tailings pile located in the Sabie area of Mpumalanga province in South Africa. Samples were collected from the base of the tailings pile, top of the tailings pile and 30 cm under the top layer of the tailings pile, following standard practice. Three samples were collected from an alkaline (AN) gold mine tailings pile located in the Sabie area in Mpumalanga, South Africa. Samples were collected from the base of the tailings pile, top of the tailings pile and 30 cm under the top layer of the tailings pile.

Twelve kilograms of each gold mine tailings sample was collected and dried. The samples were sieved using a 200 mesh to obtain samples with a particle size distribution smaller than 75 µm to conduct the static and kinetic tests (Smart et al. 2002; Stewart et al. 2006). The samples were then stored in airtight containers to limit the degree of pre-oxidation as proposed by ASTM D5744-18. Sample mixtures were prepared to determine whether or not AN would possess sufficient readily available acid-buffering

Fig. 3 Alkaline gold mine tailings

capabilities to neutralise any acid generated by the AG portion of the sample. Two mixtures were prepared by mixing AN and AG with a weight ratio of 1:3 (MIX25) and 1:1 (MIX50). MIX25 and MIX50 were subjected to the same static tests (ABA, NAG and ABCC) used to evaluate AG and AN's acid-generating capabilities.

Paste pH

The paste pH was prepared by mixing 25 g of sample with 50 mL of deionised water (conductivity of 0.05 µS/cm). The pH of the paste-like slurry was measured after 4 h had elapsed according to the method adopted by Smart et al. (2002).

Acid-neutralising capacity (ANC)

The ANC method considered in this study is a modified version of the standard ANC method initially developed by Sobek (1978). The modified ANC test method procedure was obtained from Smart et al. (2002) and Stewart et al. (2006). A fizz rating was allocated to each sample by observing the reaction between the sample and two drops of 8% hydrochloric acid (HCl). Two grams of each sample was digested using a predetermined volume and concentration of hydrochloric acid, based on the fizz rating allocated to each sample, followed by the addition of 20 ml of deionised water. Exactly 4, 20 and 40 mL of 0.5 M HCl were used to digest AG, MIX25 and MIX50, respectively, while 60 mL of 1 M HCl was used to digest AN. The samples were continuously mixed and heated at a temperature of 85 °C for 2 h, followed by the addition of deionised water to obtain a solution volume of 125 mL. The samples were allowed to cool down to room temperature and then titrated to a pH of 8.3 using sodium hydroxide. During titration, two drops of 30% hydrogen peroxide (H_2O_2) were added at a pH of 5 to promote the precipitation of $Fe(OH)_3$ and the oxidation of Fe^{2+}.

A blank was prepared for each sample, and the ANC experiment was repeated in triplicates for each sample to ensure accurate results and repeatability.

The acid-neutralising capability (ANC) was calculated using Eq. (1).

$$\mathrm{ANC}\ (\mathrm{kg\ H_2SO_4/ton}) = \frac{\left(\mathrm{V_{HCl}} - \lceil \mathrm{V_{NaOH}} \times \frac{\mathrm{V_{HCl,\ Blank}}}{\mathrm{V_{NaOH,\ Blank}}} \rceil\right) \times \mathrm{M_{HCl}}}{\mathrm{m}} \times \mathrm{C} \tag{1}$$

where:

V_{HCl}	*volume HCl acid used (mL)*
$V_{HCl\ Blank}$	*volume acid added to the blank (mL)*
V_{NaOH}	*volumeNaOH used (mL)*
$V_{NaOH\ Blank}$	*volume NaOH added to blank (mL)*
M_{HCl}	*molarity of HCl acid used (M)*
m	*sample weight (g)*
C	*ANC constant with a value of 49*

Maximum potential acidity (MPA)

The maximum potential acidity (MPA) was calculated by multiplying the total sulphur content by a factor of 30.6, as indicated in Eq. (2).

$$MPA\ (\mathrm{kgH_2SO_4/tonne}) = (S\%) \times 30.6 \tag{2}$$

Net acid production potential (NAPP) and ANC to MPA ratio (RANC$_{/MPA}$)

The net acid production potential (NAPP) and the ANC to MPA ratio ($R_{\mathrm{ANC/MPA}}$) were calculated using Eqs. (3) and (4), respectively as

$$NAPP = MPA - ANC \tag{3}$$

$$R_{\mathrm{ANC/MPA}} = \frac{ANC}{MPA} \tag{4}$$

Net acid generation (NAG) test

The single addition NAG test was conducted using the procedure described by Smart et al. (2002) and Stewart et al. (2006); 2.5 g of each sample was accurately weighed into a 250-mL Erlenmeyer flask, followed by adding 250 mL of 15% H_2O_2 to each sample. The pH of the H_2O_2 solution was adjusted to a pH of 4.5 using sodium hydroxide before adding it to the samples. Erlenmeyer flasks were covered with a watch glass, placed in a fume hood and left overnight. The sample was then gently heated at a temperature of 40 °C for 2 h to remove excess H_2O_2 and encourage the release of inherent acid-neutralising capacity. The sample solutions were continuously stirred during heating using a magnetic stirrer. The solutions were then allowed to cool down to room temperature. The pH of the solutions was measured and referred to as the NAGpH. The solutions were then titrated to a pH of 4.5 and 7 using a 0.1 M NaOH solution. The volume and concentration of NaOH were used to calculate the NAG value using Eq. (5).

$$NAG\ (\mathrm{kgH_2SO_4/tonne}) = (49 \times V \times M)/w \tag{5}$$

where:

V volume of NaOH used during the titration (mL)

M concentration of NaOH used during the titration (mol/L)

W weight of the sample (g)

Acid-buffering characteristic curve (ABCC)

The acid-buffering characteristic curve (ABCC) test was conducted following the test procedure described in Smart et al. (2002) and Stewart et al. (2006). Two grams of each sample was accurately weighed into a 250-mL Erlenmeyer flask, followed by adding 100 mL of deionised water to the sample. The samples were continually stirred using a magnetic mixer. One hour of premixing was allowed to occur; after which, 0.3 mL of 0.1 M, 0.4 mL of 0.1 M and 0.4 mL of 0.5 M HCl were incrementally added to MIX25, MIX50 and AN, respectively. Thirty to forty-five minutes were allowed to elapse after each addition, after which pH was measured and recorded. The pH was plotted against the calculated kg H_2SO_4/t. Equation (6) converted the accumulative HCl to kg H_2SO_4/t equivalent.

$$H_2SO_4\ \text{added}\ (\mathrm{kg/t}) = (V \times C \times 49)/W \tag{6}$$

where:

V *accumulative HCl volume (mL)*

C *HCl concentration (M)*

W *sample weight*

The net acid production potential (NAPP) and the net acid generation pH (NAGpH) are usually used in conjunction to classify a sample's acid generating potential as PAF, NAF or UC to a higher degree of confidence. The classification criteria used to classify sample acid generation capabilities using the NAPP and NAGpH are summarised in Table 1 (Oh et al. 2017; Smart et al. 2002).

Table 1 NAPP and NAGpH classification criteria

Classification	Test criteria
NAF	NAPP $\le$ 0 and NAGpH $\ge$ 4.4
PAF	NAPP > 0 and NAGpH < 4.4
UC	(NAPP $\le$ 0 and NAGpH < 4.5) or if (NAPP > 0 and NAGpH $\ge$ 4.5)

Mineralogical investigation and calculations

The different crystalline phases present in the AG and AN samples were identified and quantified using X-ray diffraction (XRD), a non-destructive analytical technique. The samples were then analysed using PANalytical X'Pert Pro multipurpose diffractometer with X'Celerator detector and fixed slits with Fe-filtered Co-Kα radiation. PANalytical Highscore$^+$program, ICDD PDF 4 + and PAN ICSD database were used to identify the crystalline mineral phases present in the samples. The relative phase amount or quantity (wt %) was quantified using the Rietveld method. The acid neutralisation capabilities of AN based on the carbonate minerals ($ANC_{min,c}$) were calculated using Eq. (7) as adopted from Karlsson et al. (2018).

$$ANC_{min,c} = 83.3 \times \left[\frac{MW_c}{MW_{c,min}}\right] \times wt\%_{c,min} \times CF \tag{7}$$

where:

- *$ANC_{min,c}$ is the ANC contribution of carbonate minerals to the total ANC_{min}.*
- *MW_c is the carbon molar weight of carbon present in the mineral in the form of a carbonate.*
- *$MW_{c,min}$ is the molar weight of and carbonate mineral, respectively (g/mol).*
- *$wt\%_{c,min}$ is the weight percentage of carbonate mineral in the sample.*
- *CF is a conversion factor with a value of 0.98 to convert the unit of ANC_{min} from kg $CaCO_3$/t to kg H_2SO_4/t.*

Leach column tests

Leach columns with a diameter of 20.3 cm and a height of 10.2 cm were designed and constructed for this study in accordance with the design parameters found in ASTM D5744-18 option B. Option B of the ASTM D5744-18 does not include the introduction of dry or wet air into the leach column cells. The leach column cells were stored in a controlled environment with a constant temperature and humidity as stipulated in D5744-18.

Ten leach columns were designed and constructed specifically for the leach column test. One leach column cell was used as a blank with no sample being loaded into the cell. Three columns were loaded with 1 kg of AG sample (AG1, AG2 and AG3), three columns were loaded with 1 kg of AN

(AN1, AN2 and AN3) and the remaining three columns were loaded with 0.75 kg AG as the bottom layer and 0.25 kg AN as the top layer (COV251, COV252 and COV253).

Following the D5744-18 option B leach column procedure, the leach columns were leached weekly. The first week of leaching consisted of leaching the cells with 1000 mL of deionised water. The leach columns were leached with 750 mL of deionised water from week 2 onwards. The leach columns were flooded with deionised water for a period of 1 h. The lid of the columns remained connected to prevent external airborne contamination and to limit the effect of evaporation. The drainage process was initiated by opening the drainage valve allowing the leachate to drain dropwise into the collection vessel. The collection vessels were then set aside for leachate analysis. The analysis was reported accordingly.

Leachate acidity

The acidity of the leachates was determined by titrating the leachate sample with a sample volume of 50 mL with 0.02 N sodium hydroxide (NaOH) to a pH of 3.7 and 8.3 in accordance with the test procedure found in Baird et al. (2017). The volume (*V*) and normality (*N*) of NaOH used during titration, sample volume (S_v) and a conversion factor of 50,000 were used to calculate the acidity of the leachates as in Eq. (8).

$$Acidity, as \frac{mg\ CaCO_3}{L} = \frac{V \times N \times 50,000}{S_V} \tag{8}$$

Leachate alkalinity

The alkalinity of leachates was determined by titrating the leachate sample with a sample volume of 50 mL with 0.02 N sulphuric acid (H_2SO_4) to a pH of 8.3 and 4.5 in accordance with the test procedure by Baird et al. (2017). The volume (*V*) and normality (*N*) of H_2SO_4 used during titration, sample volume (S_v) and a conversion factor of 50,000 were used to calculate the alkalinity of the leachates as presented by Eq. (9)

$$\text{Alkalinity, as} \frac{mg\ CaCO_3}{L} = \frac{V \times N \times 50,000}{S_V} \tag{9}$$

Results and discussion

Samples collected from the base of the tailings pile, top of the tailings pile and 30 cm under the top layer of the tailings pile of AG and AN were subject to ABA, NAG and ABCC tests and yielded similar results. This study includes the ABA, NAG and ABCC analysis of the samples collected from the base of the tailings. Additionally, the samples collected from the base of AG and AN were used in the leach column tests.

Acid–base accounting (ABA)

Acid–base accounting (ABA) findings are presented in Table 2, wherein it showed that AG had a paste pH of 2.5 as presented, confirming that AG tailings have become highly acidic. A low paste pH of 2.5 suggests that AG tailings could contain up to 30 kg H_2SO_4 per ton of material of stored acidity in the form of acidic sulphate salts, which will be released immediately when exposed to water, according to Weber et al. (2006). As seen in Table 2, AG has an ANC of 0 kg H_2SO_4/t and MPA of 13 kg H_2SO_4/t. An ANC of 0 kg H_2SO_4/t of AG corresponds with the tailing becoming extremely acidic as AG does not have any acid-neutralising capabilities to buffer its pH to near-neutral conditions.

AG tailing pile thus has a NAPP of 13 kg H_2SO_4/t, suggesting that AG may generate up to 13 kg of sulphuric acid per ton of material. However, under these acidic conditions, ferric iron will be the primary oxidiser of sulphide minerals, which means the true maximum potential acidity may be greater than the calculated MPA. AN has a relatively high paste pH of 7.7, as seen in Table 2, providing an initial indication that AN may contain highly reactive acid-neutralising minerals such as carbonates and that AN may be non-acid forming. As further seen in Table 2, AN has an ANC of 184 kg H_2SO_4/t, which is substantially higher than its MPA of 2 kg H_2SO_4/t. Thus, AN has a NAPP of – 182 kg H_2SO_4/t, indicating that AN will be able to neutralise any acid generated by its sulphur minerals.

MIX25 and MIX50 have a paste pH of 5.1 and 6.1, respectively, which is substantially high than the paste pH of AG. This suggests that ANC of the AN portion of MIX25 and MIX50 may be readily available to neutralise

Table 2 Acid–base accounting (ABA) analysis of the study

Sample	Paste pH	ANC (kg H_2SO_4/t)	S_{Total}	MPA (kg H_2SO_4/t)	NAPP (kg H_2SO_4/t)	$R_{ANC/MPA}$
AG	2.5	0	0.43	13	13	0
MIX25	5.1	56	0.34	10	– 46	5
MIX50	6.1	96	0.25	8	– 89	13
AN	7.7	184	0.07	2	– 182	86

acid generated by the AG portion of MIX25 and MIX50 as a paste pH test evaluates the readily available acidity/alkalinity of a sample. MIX25 and MIX50 have ANC values of 56 and 96 kg H_2SO_4/t, respectively, which is relatively high compared to their corresponding MPA values of 8 and 10 kg H_2SO_4/t. MIX25 and MIX50 have NAPP values of − 46 and − 89 kg H_2SO_4/t, respectively, indicating that MIX25 and MIX50 contain sufficient quantities of acid-neutralising minerals to neutralise acid generated by the AG portion of MIX25 and MIX50 blends.

The ABA provides minimal information on the reactivity of the acid-neutralising minerals. When the goal is to use AN as a cover or as a mixture to mitigate the acid generated by AG, it cannot be assumed that AN will have sufficient readily available acid-neutralising capabilities to neutralise acid generated by AG, creating the need to conduct ABCC tests. The ABA results are confirmed by the results obtained in a study conducted by Lusunzi (2018).

Acid-buffering characteristic curve (ABCC)

AG does not have an ABCC as it has no acid-neutralising capabilities. The ABCC curves of MIX25, MIX50 and AN are illustrated in Fig. 4. As seen in Fig. 4, MIX25, MIX50 and AN have the ability to neutralise 53, 87 and 170 kg H_2SO_4/t, respectively, before the pH of the solution drops below a pH of 2.5, which corresponds closely to the ANC results determined using the ABA method as indicated earlier in Table 2.

The rate and quantity of acid generated increase dramatically when the pH of mine tailings drops below a pH of 4 due to the oxidation of sulphide minerals via ferric iron. Thus, the effective or readily available acid-neutralising capacities refers to the quantity of acid neutralised before the pH of the solution drops to a value of 4. MIX25, MIX50 and AN neutralised 35, 77 and 155 kg H_2SO_4/t, respectively, before the pH of the solution drops to a pH of 4 (Fig. 4). Thus, a large portion of the ANC determined using the ABA method is readily available for acid neutralisation.

A comparison of the ANC of each sample using the ABCC and the ABA method is presented in Table 3. As seen in Table 3, a substantially large portion of the ANC measured using the ABA method is readily available for acid neutralisation. A high concentration of highly reactive carbonate minerals such as calcite or dolomite will most likely be the cause of the high availability of acid neutralisation. It can be concluded that the ANC of MIX25, MIX50 and AN are not overestimated and will be readily available for acid neutralisation.

Net acid generation (NAG)

Net acid generation analysis is presented in Table 4. Therein, AG, MIX25, MIX50 and AN have NAGpH values of 2.7, 4.9, 5, 5.9 and NAG values of 6.9, 0, 0, 0 kg H_2SO_4/t, respectively. The NAG outcome thus indicates AN, MIX25 and MIX50 are NAF as they have NAG values of 0 and NAGpH value > 4.5. AG is considered to be PAF as it has NAG values > 0 and NAGpH value < 4.5 and could release up to 6.9 kg of sulphuric acid per ton of material.

Table 3 ANC comparison

Sample	ANC (ABA) (kg H_2SO_4/t)	ANC ($ABCC_{pH=2.5}$) (kg H_2SO_4/t)	ANC ($ABCC_{pH=4}$) (kg H_2SO_4/t)
MIX25	56	53	35
MIX50	96	87	77
AN	184	170	155

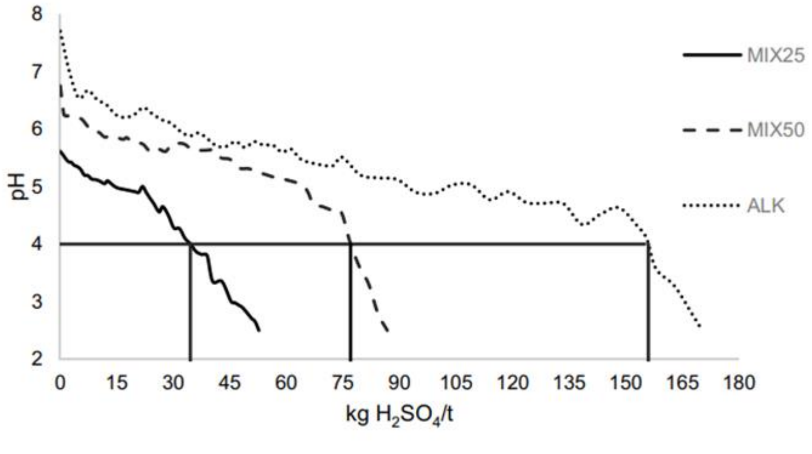

Fig. 4 ABCC of MIX25, MIX50 and AN

Table 4 NAG results

Sample	NAGpH	NAG (kg H_2SO_4/t)
AG	2.7	6.9
MIX25	4.9	0
MIX50	5	0
AN	5.9	0

Final classification

Using the NAPP, NAGpH and the classification criteria summarised in Table 1, the acid-generating capabilities of AG, MIX25, MIX50 and AN can be classified as PAF, NAF, NAF and NAF, respectively, to a high degree of confidence as presented in Table 5.

When considering the ABA, NAG and ABCC results, MIX25 and MIX50 both seem to be suitable options to treat and prevent further acid generation caused by the acid-generating gold mine tailings (AG). However, MIX25 (25 wt% AN to 75 wt% AG ratio) would be the more economically feasible option compared to using MIX50 (50 wt% AN to 50 wt% AG ratio) as a reduced quantity of AN tailing will require transporting. Using alkaline tailing as a pH neutralising cover compared to mixing the alkaline gold mine tailings pile and acidic gold mine tailings pile may reduce the efficiency of the acid-buffering capabilities of the alkaline tailings. However, it would reduce the construction cost by eliminating the high cost of mixing these two tailing piles.

Mineralogy

Table 6 summarises the minerals found in the AG and AN samples using XRD analysis. As seen in Table 6, AN has a relatively high dolomite content of 22.4%, a highly reactive acid-neutralising carbonate mineral confirming the availability of the ANC of AN, MIX25 and MIX50 evaluated by the ABCC test. Additionally, the acid-neutralising mineral muscovite was found in both AN and AG. However, muscovite is a slow-weathering acid-neutralising mineral, and its contribution to acid neutralisation is considered to be negligible and will thus not be considered in further calculations (Karlsson et al. 2018). No highly reactive carbonate minerals or fast weathering acid-neutralising minerals were found in the AG sample, confirming that AG has no acid-neutralising capabilities based on the mineralogical investigation. The mineralogy is confirmed by a study conducted by Rudzani et al. (2019).

Table 5 Final classification

Sample	NAPP (kg H_2SO_4/t)	NAGpH	Classification
AG	13	2.7	PAF
MIX25	−46	4.9	NAF
MIX50	−89	5	NAF
AN	−182	5.9	NAF

Table 6 XRD analysis

Mineral	Molecular formula	AN (wt %)	AG (wt %)
Quartz	SiO_2	65.4	86.9
Dolomite	$MgCa(CO_3)_2$	22.4	0.0
Muscovite	$(KF)_2\,(Al_2O_3)_3\,(SiO_2)_6$	6.2	10.2
Goethite	FeO_2H	4.6	2.7
Hematite	Fe_2O_3	0.7	0.1
Gypsum	$CaSO_4{\cdot}2H_2O$	0.6	0.0

Mineralogical acid-neutralising capabilities (ANC_{min})

The mineralogical acid-neutralising (ANC_{min}) potential of AN was calculated using Eq. (7), and the weight percentage of dolomite present in the AN sample (Table 6). The molecular weight (MW_c) of carbon was multiplied by 2 as there are two carbon atoms in the dolomite molecule, as seen in Table 6. Using Eq. (7), the ANC_{min} was calculated to be 238 kg H_2SO_4/t and will thus neutralise 238 kg of sulphuric acid per ton of material before its acid-neutralising capabilities are depleted. The calculated ANC_{min} of 238 kg H_2SO_4/t is extremely close to the acid ANC determined using the modified ABA method, which had a value of 184 kg H_2SO_4/t (Table 2). The mineralogical investigation confirmed that AN has a high acid-neutralising capacity, due to the high dolomite content. It was concluded that most of the ANC of AN would be readily available for acid neutralisation, confirming the ABCC results of AN, MIX25 and MIX50.

Leach column tests

Leach column pH test

The leach column pH test outcomes are presented in Fig. 5. As seen in Fig. 5, AG samples (AG1, AG2 and AG3) maintained a low leachate pH ranging from 2.2 at the start of the leaching test to 3.1 at the end of the leachate test, confirming the static test results of AG. The initial low pH values of 2.2 and 2.6 for weeks 1 and 2 indicate a sizeable initial release of stored acidity. It was concluded that the AG tailings have become acidic with a high stored acidity content and will continue to generate an acidic effluent for the foreseeable future.

Three columns were loaded with AN samples, namely columns AN1, AN2 and AN3. The occurrence of channelling in column AN2 compromised the results of AN2 and

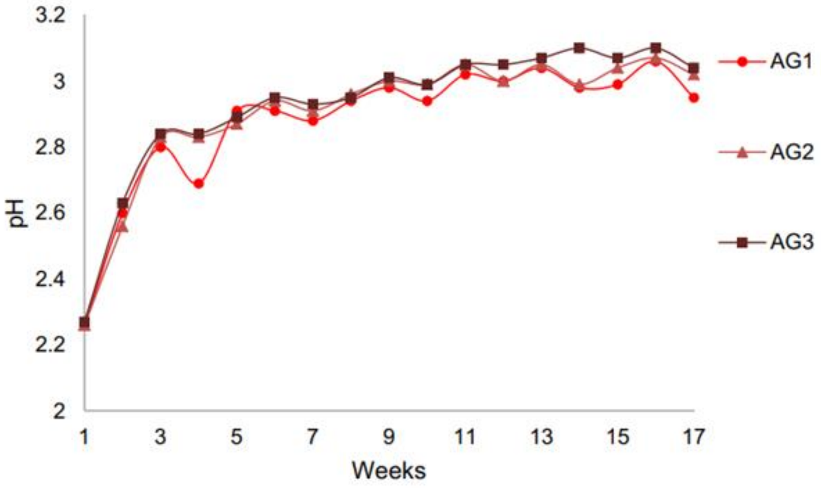

Fig. 5 Leachate pH of GA1, AG2 and AG3

rendered it unusable for this study. Thus, only the leach column results of AN1 and AN3 are reported in this study. As seen in Fig. 6, the leachate pH of AN1 and AN3 remained alkaline throughout the experiment, gradually increasing to a pH of 8.2 towards the end. The slight increase of the leachate pH from 7.5 (Week1) to a pH of 8.2 (Week17) may indicate an increasing dissolution rate of dolomite in AN as time progressed.

As seen in Fig. 6, the leach columns that used AN as a pH neutralising cover with an AN to AG weight ratio of 1:3 pH (COV251, COV252 and COV253) showed a low initial leachate pH of 2.5. The initial low pH conditions correspond to the immediate initial release of storage acidity of the AG bottom layer of the column, corresponding to the initial low pH condition of the AG leachates (Fig. 5). Thus, the acid-neutralising minerals in the top acid-neutralising AN cover were not able to dissolve to any extent sufficiently to neutralise the stored acidity of the bottom AG layer of the columns.

After the initial release of stored acidity (Week 1), the pH of the leachates of COV251, COV252 and COV253 increased substantially to neutral conditions (Weeks 2–9) and to alkaline conditions (Weeks 9–17), proving that the acid-neutralising minerals in the top AN cover were able to neutralise the acid generated by the bottom AG layer of the column. In other words, the dramatic increase in leachate pH of COV251, COV252 and COV253 suggests

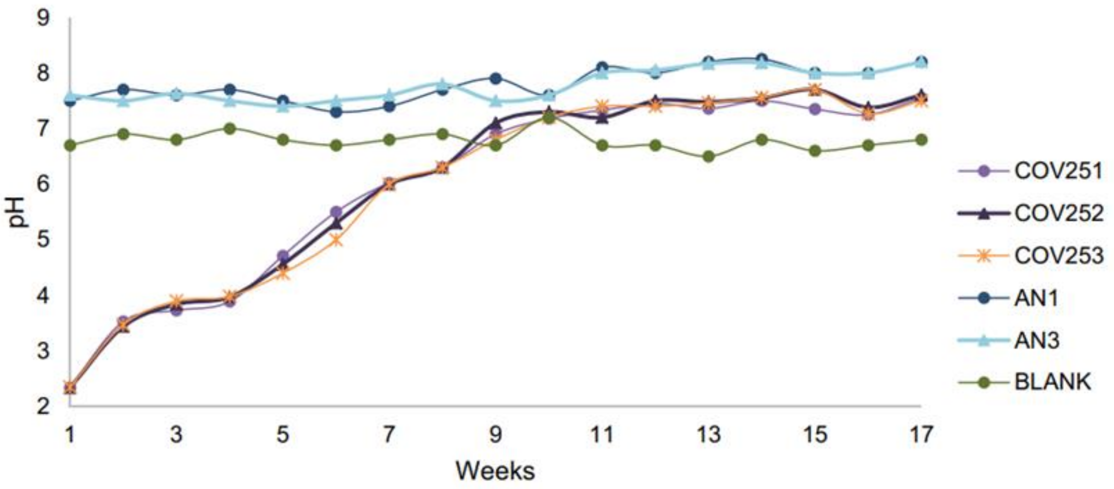

Fig. 6 Leachate pH of AN1, AN3, COV251, COV252, COV253 and BLANK

that the rate of acid neutralisation due to the dissolution of dolomite (AN) is higher than the rate of acid generation (AG).

Leach column acidity results

As seen in Table 7, leach columns AG1, AG2 and AG3 release leachates with extremely high acidity (Weeks 1–2), which corresponds to the release of stored acidity. The acidity released by AG1, AG2 and AG3 decreased substantially after the initial release of acidity in weeks 1 to 2. AG1, AG2 and AG3 continued to release leachates with relatively high acidity from week 3 through to week 17, confirming that AG tailings will generate acidic effluent for the foreseeable future. Additionally, due to the highly acidic conditions of the AG tailings (paste pH of 2.5), ferric iron will be the primary oxidiser of any sulphide minerals, resulting in an increased acid generating potential and rate of acid generation.

The acidity of COV251, COV252 and COV253 during the first week 1 is slightly lower than AG1, AG2 and AG3, indicating that the acid-neutralising minerals in the top AN layer of the column contributed to acid neutralisation to a certain extent. Keeping in mind that the AG columns contained 1 kg of AG sample and the COV25 columns contained 0.75 kg of AG (bottom layer) and 0.25 kg AN (top layer), it can be seen that from week 2 to week 17, AG columns produce four times the acidity compared to the COV25 columns indicating that AN (top layer) does contribute to acid neutralisation. However, the top AN layer of the column was not able to provide the required acid-neutralising capabilities to neutralise the high quantity of acid generated by the bottom AG layer during the first few weeks of the leach column experiment due to the slow dissolution of the acid-neutralising mineral, dolomite, in AN compared to the dissolution of acid-generating salts (stored acidity) in AG. Findings showed a delay in the remediation of acidity using a pH neutralising cover system consisting of AN and AG; however, prolonged exposure will ensure effective prevention of AMD formation over a certain period.

Leach column alkalinity results

Leach column alkalinity results are presented in Table 8. The AG columns constantly produced acidic leachates with pH below 3.2 and thus would have an alkalinity of 0 mg $CaCO_3$/L. The AN leach columns AN1 and AN3 constantly produced alkaline leachates with alkalinity ranging from 60 to 72 $CaCO_3$/L when excluding the first 2 weeks (Table 8). As seen in Table 8, the COV251, COV252 and COV253 leach column produced leachates with no alkalinity for the first 5 weeks of the leach column experiment. However, as the leach column experiment progressed from week 5 to week 17 the COV25 leach columns produced leachates with alkalinity ranging from 28 to 35 mg $CaCO_3$/L, confirming that AN would be able to be neutralise acid generated by the bottom AG layer and can thus be used as a pH neutralising cover material to mitigate AMD formation and further pollution of receiving water.

Table 7 Leach column acidity results

	Acidity (mg $CaCO_3$/L)					
Week	AG1	AG2	AG3	COV251	COV252	COV253
1	7900	8500	7820	6630	6580	6440
2	256	268	220	54	60	68
3	80	88	180	20	24	18
4	84	82	80	24	26	34
5	64	68	64	24	24	24
6	60	62	60	14	14	8
7	62	61	60	22	24	21
8	56	54	52	11	10	10
9	72	60	58	14	12	10
10	64	62	61	9	9	10
11	48	46	44	6	7	6
12	47	47	45	4	4	6
13	46	44	43	6	5	6
14	50	49	47	6	5	5
15	48	45	43	6	6	7
16	52	52	46	9	4	4
17	38	37	35	6	4	4

Table 8 Leach column alkalinity results

	Alkalinity (mg $CaCO_3$/L)				
Week	COV251	COV252	COV253	AN1	AN3
1	0	0	0	24	22
2	0	0	0	44	46
3	0	0	0	64	60
4	0	0	0	64	68
5	0	0	0	68	60
6	5	4	3	64	60
7	5	4	3	66	70
8	16	15	20	67	68
9	28	31	30	68	66
10	30	32	35	69	68
11	33	37	34	70	70
12	33	34	32	66	66
13	31	32	32	67	64
14	31	34	33	70	66
15	32	34	32	72	72
16	32	32	32	72	72
17	32	34	32	72	72

Conclusion

The AG gold mine tailings acid-generating capabilities of the Sabie-Pilgrim's Rest Goldfields are considered PAF using conventional ABA and NAG classification criteria. The low paste pH and the leach column result confirmed that the AG tailing has become acidic. The AG columns continuously produced leachates that were acidic throughout the leach column experiments, indicating that the AG tailings would continue to generate an acidic effluent for the foreseeable future. The AG leach column acidity result confirmed a high stored acidity content, which will be released instantaneously when exposed to water, as observed during the first week of leaching.

The AN gold mine tailings are considered to be non-acid forming using conventional ABA and NAG classification criteria. However, AN tailings may still generate alkaline mine drainage. The ANC results suggest that AN would neutralise up to 184 kg H_2SO_4/t. The ABCC, mineralogy and mineralogical calculations confirmed that AN had high acid-neutralising capabilities which would be readily available for acid neutralisation. The AN leach columns continually produced alkaline leachates with high alkalinity throughout the leach column experiments, confirming that the AN tailings would produce an alkaline effluent due to the dissolution of acid-neutralising mineral dolomite. The results of the COV25 leaching columns showed a delay in the remediation of acidity using AN tailings as a pH neutralising cover; however, prolonged exposure will ensure effective prevention of AMD formation over a certain period. The alkaline gold mine tailings are located less than 5 km from the acid-generating mine tailings, making it an economically attractive option. Therefore, it is recommended that the alkaline gold mine tailings are utilised as a pH neutralising cover material to mitigate AMD formation generated by the acidic gold mine tailings to prevent further pollution of receiving water in the Sabie-Pilgrim's Rest Goldfields area. Researching the use of a multi-layer or blending approach may reduce or completely neutralise the high initial acidity release observed in the first few weeks of the COV25 leach columns test.

Author contribution NvW carried out the study, conducted literature survey, carried out the experiments and analysis and wrote the manuscript. ACE supervised the study, corrected the draft, handled the editorial processing and he is the corresponding author. EFK co-supervised the study and corrected the draft.

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Data availability Data and materials are available.

Declarations

Ethics approval The study has no ethical issues (no human or animal is involved), and so approval is not required.

Consent to participate There is no human or animal involved in the research, so no consent to participate is required.

Consent for publication All authors have consented to the publication of the manuscript.

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List of Abbreviations

ABCC	Acid Buffering Characteristic Curve
AMD	Acid Mine Drainage
ANC	Acid Neutralisation Capacity
ANC_{min}	Acid neutralising capacity based on mineralogy
$ANC_{min,c}$	Acid neutralisation capacity of carbonate minerals
$ANC_{min,nc}$	Acid neutralisation capacity of non-carbonate minerals
ARD	Acid Rock Drainage
CF	Conversion factor to convert kg $CaCO_3$/t to kg H_2SO_4/t
C_{MPA}	Maximum potential acidity constant
RR	Relative reactivity of neutralising minerals.
Eq	Equation
HCl	Hydrochloric acid
MPA	Maximum Potential Acidity
MPA_{min}	Maximum Potential Acidity based on mineralogy
MW_c	Molar weight of carbon
$MW_{c,min}$	Molar weight of carbonate mineral.
$MW_{calcite}$	Molar weight of calcite
$MW_{nc,min}$	Molar weight of non-carbonate neutralising mineral.
NaOH	Sodium hydroxide
NAF	Non-Acid Forming
NAG	Net Acid Generation

NAPP	Net Acid Production Potential
PAF	Potential Acid Former
R	Reaction
S%	Sulphur weight percentage
S_i%	Sulphide weight percentage
UC	Uncertain
W_{CAL}	Weight of column after leaching
W_{CBL}	Weight of column before leaching
W_{RPW}	Retained pore water mass
wt%	Weight percentage
$wt\%_{AG,min}$	Weight percentage of acid-generating mineral.
$wt\%_{c,min}$	Weight percentage of carbonate mineral.
$wt\%_{nc,min}$	Weight percentage of non-carbonate mineral.
$wt\%_{s,min}$	Weight percentage of sulphur in mineral.

CHAPTER 1: INTRODUCTION

1.1 Background of study

During mining processes, vast quantities of ore are excavated and subjected to a beneficiation process, separating the low-grade ore which cannot be processed for financial benefit. The low-grade, known as mine waste rock mine tailings, are most often dumped into the environment in large piles. Mine waste rock or tailings are known to contain an elevated concentration of acid-generating sulphide minerals (Dold, 2010; Koch *et al*., 2017). The production of mine waste has increased drastically with the evolution of metal extraction techniques. This trend will increase in the foreseeable future (Dold, 2017).

Acid mine drainage (AMD) is an acidic effluent released by mine waste caused by the oxidation of acid-generating sulphide minerals within the mine waste rock or tailings. Acid-generating sulphide minerals are commonly found in the form of Pyrite (FeS_2) and pyrrhotite ($Fe_{(1-x)}S$ where $x = 0$ to 0.2). Sulphide minerals react with oxygen and water supplied by the environment, producing acid and facilitating the dissolution of toxic heavy metals (Sobek *et al*., 1978; Smart *et al*., 2002; Dold, 2010).

The AMD effluent is usually highly acidic and contains elevated concentrations of sulphate ions (SO_4^{2-}) and dissolved metals such as iron, lead, nickel, aluminium, manganese, copper, zinc and cadmium. The release of metals is promoted by the acidic conditions caused by acid generated during the sulphide mineral oxidation (Dold, 2010; Simate & Ndlovu, 2014; Li *et al*., 2018).

The acid generated during sulphide mineral oxidation reacts with acid-neutralising minerals within the waste rock or tailings. Acid-neutralising reactions such as the dissolution of aluminosilicate minerals, carbonate minerals and ferric oxyhydroxide contribute the most to acid neutralisation (Blowes *et al*., 2013). AMD occurring at operating and abandoned mines is a widespread environmental concern. AMD is the second largest threat to environmental and sustainable life after global warming (Madzivire *et al*., 2014). South Africa is one of the world's largest coal producers and has been mining coal and precious metals since 1857. South Africa relies mainly on coal as its primary energy source for the generation of electricity and will continue to rely on coal for the foreseeable future (Hancox & Götz, 2014).

AMD accumulation at the Grootvlei mine of Pamodzi Gold in springs reached desperate proportions in 2009. The AMD accumulated to the point where the then general manager of

East Rand operations of Pamodzi Gold found himself in the situation of possibly releasing untreated AMD to prevent the flooding of Grootvlei's underground pumping station. The release of untreated AMD would have had far-reaching environmental consequences (McCarthy 2011).

It is estimated that it will cost the South African government an estimated R145 million to implement an interim solution to remedy the AMD in South Africa's Witwatersrand area, according to former Water Affairs Minister Buyelwa Sonjica. The Minister stated that 70% of mines in South Africa are ownerless, meaning the liability falls upon the state (Mining Weekly 2015). Environmentalists have termed AMD as the most significant threat to South Africa's public health and environment (Morodi & Mpofu, 2017). AMD is a multifactor pollutant that will physically, biologically and chemically affect the environment. AMD causes disrupt the food chain and may destroy ecosystems causing irreversible destruction to aquatic and terrestrial habitats. The impact of AMD on the environment and human health is attributed to its toxic metal content and acidity (Simate & Ndlovu, 2014).

Static and kinetic geochemical tests are used to evaluate mine waste's acid-generating capabilities to determine the probability of AMD generation. Static tests are inexpensive and only require a short time frame to complete. Static tests such as Acid-Base Accounting test (ABA), Net-Acid Generation (NAG) and Acid Buffering Characteristic Curve (ABCC) are preliminary screening tools used to evaluate the acid-generating capabilities of mine waste. ABA and NAG are the two most widely utilised static tests used to assess the acid-generating potential and predict the possible occurrence of AMD (Bouzahzah et al., 2015). Static tests provide information on the balance between the theoretical acid-generating and acid-neutralising components (Smart et al., 2002; Stewart et al., 2006; El Amari & Hibti, 2019).

Kinetic tests attempt to mimic the natural conditions and reactions that would take place at the mining or waste rock disposal site. Kinetic tests such as humidity cells are generally used to determine whether or not the waste rock will generate an acidic effluent and to evaluate the rate of acid-generating reactions (Lapakko, 2003). The results obtained from kinetic tests are known to be highly reliable (Oh et al., 2017). The end goal of conducting static, kinetic tests and other mine waste evaluation methods is to provide reliable and accurate information on the acid-generating capabilities of mine waste to develop suitable treatment or prevention strategies that are environmentally sound (Lapakko, 2003).

1.2 Problem Statement

Substantial research has been conducted on the development of AMD treatment and prevention strategies. Disadvantages associated with using traditional/conventional materials in implementing AMD treatment and prevention techniques are high cost, design inaccuracies, poor performance, depletion of natural resources and the generation of additional wastes. There is a need to conduct more research on the use of industrial wastes or by-products in AMD treatment and prevention techniques to develop economic and environmentally sustainable AMD remediation strategies.

1.3 Research Aim

This study aims to determine the feasibility of using alkaline gold mine tailings as a pH neutralising cover to mitigate AMD generated by gold mine tailings that have become acidic in the Sabie-Pilgrim's Rest Goldfields, Mpumalanga province, South Africa.

1.4 Research Objectives

This study aims to evaluate the acid neutralising, acid generating capabilities of alkaline, acidic gold mine tailings and blends to assess the feasibility of using the alkaline gold mine tailings as an acid neutralising cover to mitigate acid generated by the acidic gold mine tailings. Objectives include to:

1) Evaluate the acid-generating capabilities of alkaline and acidic gold mine tailings using the acid-base accounting (ABA) and net acid generation (NAG) test methods.
2) Investigate the acid-generating capabilities of alkaline and acidic gold mine tailings blends using the acid-base accounting (ABA) and net acid generation (NAG) test methods.
3) Evaluate the acid neutralising capabilities of the alkaline gold mine tailings and blends using ABA test methods.
4) Explore the readily available acid neutralising capabilities of the alkaline gold tailings and blends using the acid buffering characteristic curve (ABCC) test procedure.
5) Conduct a mineralogical investigation using X-ray diffraction (XRD) analysis.
6) Calculate and evaluate ta acid neutralising capabilities of the alkaline gold mine tailings using mineralogical calculations.
7) Conduct leach column tests to demine the feasibility of using alkaline gold mine tailings as a pH neutralising cover to mitigate acid generated by the acidic gold mine tailings.

1.5 Research Motivation

Studies have shown that gold mine tailings located in the Sabie-Pilgrim's Rest Goldfields, Mpumalanga province, South Africa, have become acidic and may be a potential source of AMD. Additionally, studies have found that there are gold mine tailings with inherent acid neutralising capabilities located in close proximity to the gold mine tailings that have become acidic.

There is a need to conduct more research on the use of industrial waste or by-products in AMD treatment and prevention techniques to develop economic and environmentally sustainable AMD remediation strategies. Utilising the gold mine tailing with inherent acid neutralising capabilities as an acid neutralising cover material to mitigate acid generated by the acidic gold mine would provide an economical and environmentally sustainable AMD treatment and prevention strategy.

1.6 Scope of study

The scope of the study is limited to the investigation of the use of gold mine tailings with inherent acid neutralising capabilities as an acid neutralising cover to mitigate acid generated by gold mine tailings that have become acidic.

This study is further limited to the two gold mine tailing piles located in the Sabie-Pilgrim's Rest Goldfields in the Mpumalanga province of South Africa. The acid generating and acid neutralising capabilities of the two gold mine tailing piles and blends was evaluated using the ABA, ABCC, NAG, leach column tests and mineralogical investigation.

This study evaluated the acid generating and acid neutralising capabilities of the alkaline and acidic gold mine tailings using ABA, NAG, ABCC and mineralogy. This study further evaluated the acid generating and acid neutralising capabilities of the alkaline and acidic gold mine tailings in greater depth utilising leach column tests. Additionally, the feasibility of using the alkaline gold mine tailings as an acid neutralising cover will be evaluated by constructing leach columns containing the acidic gold mine tailings as the bottom layer and alkaline gold mine tailings as the top acid neutralising cover layer. A layered approach instead of a blended approach was used in the leach column test as the cost of implementing a layered approach is substantially lower than that of a blended approach.

Leach columns are expensive and time-consuming and thus limit the number of leach columns that can be conducted. Due to the high costs associated with conducting a leach column test and time constraints, ten leach columns were built to evaluate the acid-generating and acid-neutralising capabilities of the gold mine tailings and layer configuration. One leach column was used as a blank; three leach columns contained the alkaline gold mine tailings; three columns contained gold mine tailings that have become acidic, while three columns contained the acidic gold mine tailings as a bottom layer and the alkaline gold mine tailings a top acid neutralising cover layer.

1.7 Overview of Thesis

Chapter one introduces the study topic and defines the aims, objectives, motivation for the research and scope of the study.

Chapter two is the literature study that includes research completed on AMD generation processes and a review of popular AMD treatment and prevention techniques. Chapter two includes research on test procedures that evaluated mine waste's acid generation and acid neutralising capabilities and the correlation between mineral content and acid generating and acid neutralising capabilities.

Chapter three contains the procedures used to evaluate the acid generating and acid neutralising capabilities of the gold mine tailings and includes criteria used to evaluate and interpret the results obtained.

Chapter four summarises the result of the tests used to evaluate the acid generating and acid neutralising capabilities of the gold mine tailings and contains interpretation and discussions on the findings of this study.

Chapter five consists of a conclusion summarising this study's main findings. Additionally, chapter five contains recommendations on research that may be conducted to increase the initial acid neutralising capabilities of the alkaline gold mine tailings.

Chapter six consists of a list of all the academic documents used to complete this study.

Chapter seven is an appendix containing the raw XRD analysis.

CHAPTER 2: LITERATURE REVIEW

2.1 Acid mine drainage

Acid mine drainage is an acidic effluent released by mine waste caused by the oxidation of acid-generating sulphide minerals within the mine waste rock or tailings. Acid-generating sulphide minerals are commonly found in the form of Pyrite (FeS_2) and pyrrhotite ($Fe_{(1-x)}S$ where x = 0 to 0.2). Sulphide minerals react with oxygen and water supplied by the environment, producing acid and facilitating the dissolution of toxic heavy metals (Sobek et al., 1978; Smart et al., 2002; Dold, 2010).

The natural weathering process of a mine waste rock piles or tailing piles is illustrated in Figure 1. The surface of the tailings are exposed to an oxidising environment allowing oxygen and water to penetrate the surface of the mine waste rock pile or tailings pile and transported through diffusion, convection and advection, inducing the primary sulphide minerals in the oxidation zone to undergo oxidation and subsequently generating acid and dissolution of toxic metals (Usher *et al*., 2003, Blowes *et al*., 2013, Koch *et al*., 2017).

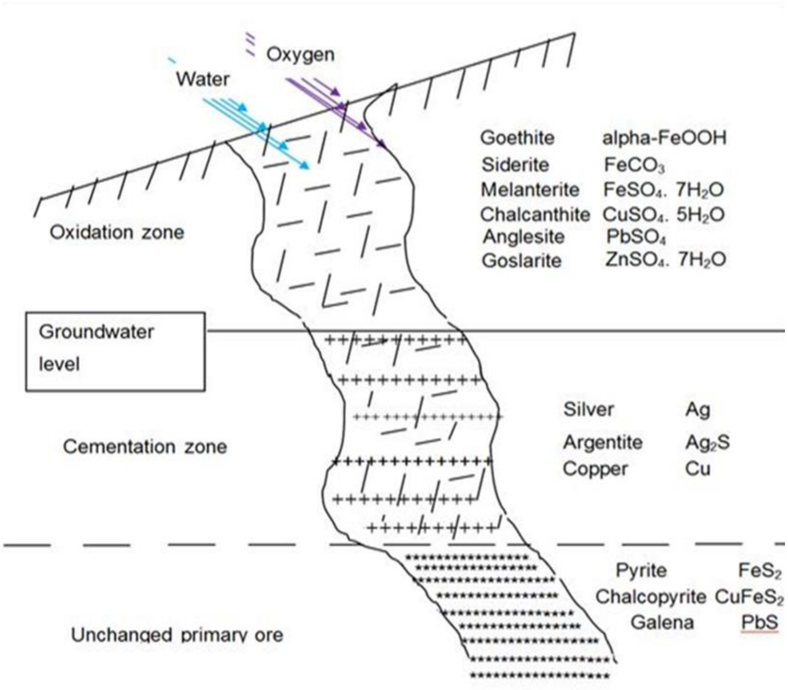

Figure 1: Natural weathering and oxidation processes occurring of waste rock and tailings (Source: Näveke, 1986).

The acidic solution generated in the oxidation zone continues to leach downwards deeper into the mine waste rock pile or tailings pile, further promoting the oxidation of sulphide minerals and the dissolution of hazardous metals. The acidic solution contains high concentrations of sulphates (SO_4^{2-}) and dissolved metals such as arsenic, cadmium, lead, manganese, mercury, zinc, chromium and copper that accumulate in the cementation zone just below the groundwater level, contaminating the underground water (Näveke, 1986; Usher *et al*., 2003).

The possible generation of AMD is one of the most critical environmental concerns related management of a mine and mining waste (Dold 2014, Karlsson *et al*., 2018). One of the most noticeable signs of the release of AMD is the occurrence of yellow boy. Yellow boy is yellow-orange coloured water or stains on the surface of rocks caused by the precipitation of ferric hydroxides ($Fe(OH)_3$) (Usher *et al*., 2003).

2.2 Acid generating minerals

Two acid-generating sulphide minerals, namely Pyrite (FeS_2) and pyrrhotite (Fe_xS), are considered to contribute the most acid generation and release of AMD (Sobek *et al*., 1978; Smart *et al*., 2002; Dold, 2010; Li *et al*., 2018). Table 1 lists the most occurring acid-generating sulphide minerals found in mine waste (Simate & Ndlovu, 2014).

Table 1: Primary sulphide minerals found in waste rock

Metal Sulphide	Chemical formula
Pyrite	FeS_2
Pyrrhotite	$Fe_{1-x}S$
Chalcocite	Cu_2SF
Covelite	CuS
Chalcopyrite	$CuFeS_2$
Molybdenite	MoS_2
Millerite	NiS
Galena	PbS
Sphalerite	ZnS
Aresenopyrite	FeAsS

The quantity of acid generated per mole of sulphide depends on the sulphide mineral crystalline structure. Sulphide minerals with a metal/sulphur ratio smaller than one generate acid when oxidised (pyrite and pyrrhotite). Sulphide minerals with a metal/sulphur ratio equal to one or lower than one does not generate acid under normal environmental conditions when oxidised by oxygen (sphalerite, galena, chalcopyrite). However, most sulphide minerals have the capabilities to generate acid regardless of the metal/sulphur ratio if oxidized by aqueous ferric iron (Fe^{3+}). Thus, the quantities of iron sulphides and crystalline structure of the sulphide minerals present in mine waste rock piles or tailings piles are of the utmost importance in determining the characteristics of the acid mine drainage (Simate & Ndlovu, 2014; Li *et al*., 2018)

Sulphate minerals have the ability to generate acid through equilibrium reactions (Dold, 2017). Sulphate minerals containing metals such as Al, Fe, and Mn can accumulate on the surface of the mine waste rock pile or tailings pile as an efflorescent salt. These efflorescent salts will generate acid immediately when exposed to water through dissolution. Efflorescent salts are a by-product of sulphide oxidation formed through the precipitation of secondary minerals in an Iron rich solution (Fosso-Kankeu *et al*., 2017). Table 2 summarises the most relevant sulphide oxidation reactions that may occur in mine wastes (Dold, 2017).

Table 2: Primary acid-generating sulphide mineral oxidation reactions

Sulphide mineral	Reaction
Oxidation of sulphide minerals via oxygen	
Pyrite (FeS_2)	$FeS_2 + 3.75O_2 + 3.5H_2O = Fe(OH)_3 + 2SO_4{}^{2-} + 4H^+$
Enargite (Cu_3AsS_4)	$Cu_3AsS_4 + 8.75O_2 + 2.5H_2O = 3Cu^{2+} + HAsO_4{}^{2-} + 4SO_4{}^{2-} + 4H^+$
Arsenopyrite (FeAsS)	$FeAsS + 2O_2 + 3H_2O = HAsO_4{}^{2-} + Fe(OH)_3 + SO_4{}^{2-} + 3H^+$
Pyrrhotite (Fe_xS)	$Fe_{0.9}S + 2.175O_2 + 2.35H_2O = 0.9Fe(OH)_3 + SO_4{}^{2-} + 2H^+$
Chalcopyrite ($CuFeS_2$)	$CuFeS_2 + 4O_2 + 3H_2O = Cu^{2+} + Fe(OH)_3 + 2SO_4{}^{2-} + 2H^+$
Covellite (CuS)	$CuS + 2O_2 = Cu^{2+} + SO_4{}^{2-}$
Galena (PbS)	$PbS + 2O_2 = Ps^{2+} + SO_4{}^{2-}$
Sphalerite (ZnS)	$ZnS + 2O_2 = Zn^{2+} + SO_4{}^{2-}$

Oxidation of sulphide minerals via ferric iron (Fe^{3+})	
Pyrite (FeS_2)	$FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4{}^{2-} + 16H^+$
Pyrrhotite (Fe_xS)	$Fe_{0.9}S + 7.8Fe^{3+} + 4H_2O = 8.7Fe^{2+} + SO_4{}^{2-} + 8H^+$
Arsenopyrite (FeAsS)	$FeAsS + 13Fe^{3+} + 8H_2O = HAsO_4{}^{2-} + 14Fe^{2+} + SO_4{}^{2-} + 15H^+$
Chalcopyrite ($CuFeS_2$)	$CuFeS_2 + 16Fe^{3+} + 8H_2O = Cu^{2+} + 17Fe^{2+} + 2SO_4{}^{2-} + 16H^+$
Enargite (Cu_3AsS_4)	$Cu_3AsS_4 + 35Fe^{3+} + 20H_2O = 3Cu^{2+} + HAsO_4{}^{2-} + 35Fe^{2+} + 4SO_4{}^{2-} + 39H^+$
Covellite (CuS)	$CuS + 8Fe^{3+} + 4H_2O = Cu^{2+} + 8Fe^{2+} + SO_4{}^{2-} + 8H^+$
Galena (PbS)	$PbS + 8Fe^{3+} + 4H_2O = Pb^{2+} + 8Fe^{2+} + SO_4{}^{2-} + 8H^+$
Sphalerite (ZnS)	$ZnS + 8Fe^{3+} + 4H_2O = Zn^{2+} + 8Fe^{2+} + SO_4{}^{2-} + 8H^+$

The quantity of acid generated per mole of sulphide depends on the crystalline structure of the sulphide mineral, as seen in Table 2. Sulphide minerals such as pyrite (FeS_2) are stable under reduction conditions. However, during mining operations, sulphide minerals are exposed to oxidising conditions. Equation (1) illustrates the oxidations of pyrite in the presence of atmospheric oxygen and water. During the oxidation of pyrite (Eq. (1)), 1 mole of Fe(III)hydroxide, 2 moles of sulphate and 4 moles of protons are produced. The quantity of acid (protons) produced depends on the sulphide mineral and the geochemical conditions (Chandra & Gerson, 2010; Dold, 2017).

$$\boldsymbol{FeS_2 + \frac{15}{4}O_{2(aq)} + \frac{7}{2}H_2O \rightarrow Fe(OH)_3 + 2SO_4{}^{2-} + 4H^+} \qquad (1)$$

When pyrite is oxidised by ferric iron in a ferric iron-rich solution, 1 mol of pyrite is oxidised to produce 16 mol of protons, as seen in Eq. (2). Ferric iron is a more aggressive oxidiser compared to oxygen (Dold, 2017). The rate of pyrite oxidation in the presence of ferric irons at acidic conditions (pH < 4) is two order magnitude higher than the rate of pyrite oxidation in an oxygen-saturated solution (Moses *et al.*, 1987; Appelo and Postma, 2005).

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

As seen in Eq.(3), galena (PbS) does not generate acid when oxidised by oxygen. However, galena becomes an acid-generating sulphide mineral when oxidised by ferric iron (Eq. (4)). Ferric iron is a more aggressive oxidiser, increasing the rate of acid generation and quantity of acid per mole of sulphide, enabling sulphide minerals that would not generate acid under normal environmental conditions to become acid-generating (Dold, 2017). It can thus be concluded that preventing mine waste rock or tailings from becoming acidic is of the utmost importance to prevent the oxidation of sulphide minerals via ferric iron to limit the rate and quantity of acid production.

$$\boldsymbol{PbS + 2O_2 = Ps^{2+} + SO_4{}^{2-}} \tag{3}$$

$$\boldsymbol{PbS + 8Fe^{3+} + 4H_2O = Pb^{2+} + 8Fe^{2+} + SO_4{}^{2-} + 8H^+} \tag{4}$$

2.3 Acid-neutralising minerals

There are acid-neutralising minerals in mine waste that neutralise the acid produced by acid-generating minerals. The most abundant acid neutralising minerals with their corresponding acid buffering pH range are summarised in Table 3. The dissolution of carbonates, iron hydroxides and aluminosilicates contribute the most to acid-neutralisation (Blowes et al., 2013; Usher et al., 2003).

Table 3: Acid neutralising minerals and corresponding pH buffering range

Acid-Neutralising Minerals	Molecular Formula	pH Buffering Range
Calcite	$CaCO_3$	5.5 - 6.9
Dolomite	$CaMg(CO_3)_2$	5.3 – 6.8
Ankerite	$Ca(Fe,Mg,Mn)(CO_3)_2$	5.2 – 6.8
Siderite	$FeCO_3$	5.1 – 6.0
Kaolinite	$Al_2Si_2O_5(OH)_4$	3.7 – 4.3
Gibbsite	$Al(OH)_3$	3.7 – 4.3
Ferric hydroxide	$Fe(OH)_3$	3.3 – 3.7
Goethite	$FeO(OH)$	2.1 – 2.2
Jarosite	$H_3OFe_3(SO_4)_2(OH)_6$	1.5 – 1.8

As seen in Table 3 and Figure 2, different acid neutralising minerals react with acid at different pH ranges maintaining the pH at a certain range depending on the minerals and crystalline structures present in the mine waste rock or tailings. Acid neutralising minerals are consumed or reacted to depletion resulting in the decrease in pH to the next pH buffering zone where the following acid neutralising minerals will react (Blowes *et al*., 2013; Usher *et al.*, 2003).

The quantity and rate of acid generation and metal dissolution increase as pH decreases. As the neutralising minerals are consumed, the pH continues decreasing in a step-like manner, as seen in Figure 2 (Blowes *et al*., 2013; Usher *et al.*, 2003).

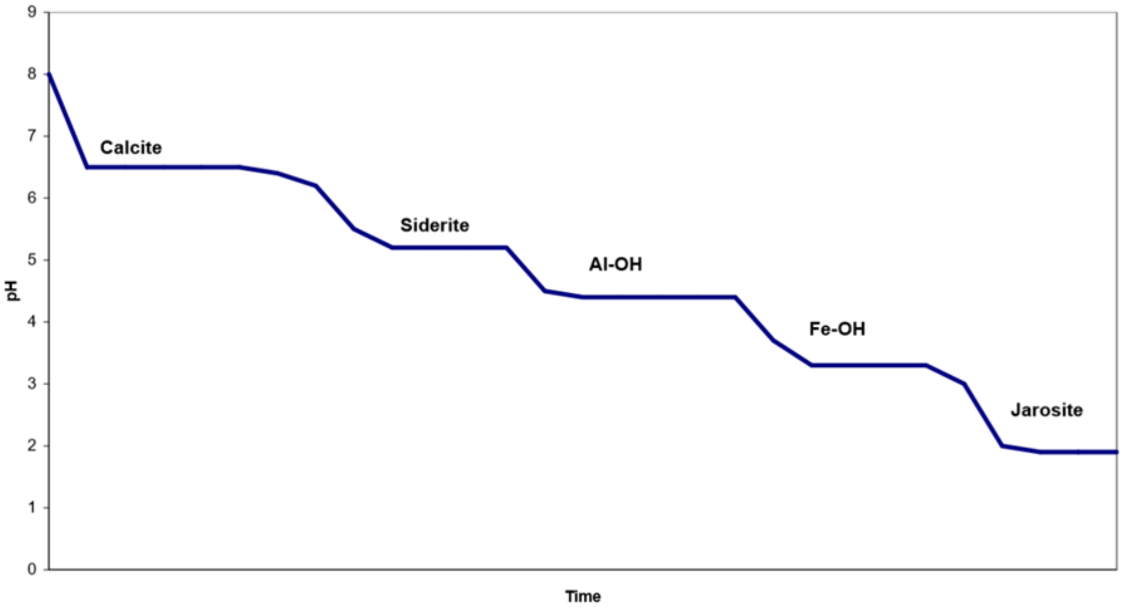

Figure 2: Stages of pH buffering (from Morin, 1983).

Carbonate minerals such as Calcite ($CaCO_3$) and Dolimite $MgCa(CO_3)_2$ are the most important acid neutralising minerals as they have the ability to maintain the pH of the tailing at near neutral conditions. Reaction equation (Eq. (5)) presents the chemical reaction by which calcite reacts with acid to maintain the pH at near neutral or alkaline conditions.

$$\boldsymbol{CaCO_3 + H^+ \leftrightarrow Ca^{2+} + HCO_3{}^-} \qquad (5)$$

Reaction equation Eq. (6) presents the reaction between calcite and acid at a low pH range.

$$\boldsymbol{CaCO_3 + 2H^{2+} \leftrightarrow Ca^{2+} + CO_2 + H_2O} \qquad (6)$$

When comparing reaction equations Eq. (5) to Eq. (6), it can be seen that one mole of calcite reacts with 2 moles of hydrogen ions under neutral conditions compared to the one mole of hydrogen ions that calcite reacts in acidic conditions. Thus, calcite is able to neutralise twice the quantity of acid at low pH levels (Blowes *et al*., 2013; Dold 2017).

Sulphuric acid (H_2SO_4) is the most common acid generated in waste rock or tailings. Reaction equation Eq. (7) represents the most common acid neutralising reaction that occurs in waste rock tailings (Blowes *et al*., 2013).

$$2CaCO_3 + H_2SO_4 \rightarrow 2Ca^{2+} + 2HCO_3^{-} + SO_4^{2-} \quad (7)$$

The pH of mine waste rock tailings is maintained at near neutral or alkaline conditions through the dissolution of carbonate minerals. The most reactive and soluble acid neutralising minerals are consumed first. Calcite ($CaCO_3$) will most likely react first, followed by dolomite ($CaMg(CO_3)_2$), ankerite ($Ca(CO_3)_2$) and then finally siderite ($FeCO_3$). At many or most mining sites, the acid generation minerals content exceeds the acid neutralising mineral content. AMD will most likely occur at these mining sites (Blowes *et al*., 2013).

At some mining sites, the acid neutralising mineral (especially carbonates) content exceeds the acid-generation minerals content (sulphide minerals); thus, AMD will most probably not occur. However, metal-rich neutral mine drainage (NMD) may still occur (Dold. 2017).

2.4 AMD prevention and treatment methods

Mine waste management relies on either AMD prevention or AMD treatment as primary AMD remediation strategies. AMD prevention strategies prevent AMD from occurring by inhibiting acid generation at the source by minimising the contact between acid-generating sulphide minerals, oxygen, water and bacteria (Aubertin *et al*., 2016). This method is a permanent solution as it prevents AMD generation entirely and does not require further treatment, such as secondary mineral removal or sludge disposal (Moodley *et al*., 2018).

Moodley *et al*., (2018) state that treatment (as opposed to prevention) is considered to be the best AMD remediation option, which involves collecting and treating AMD through active or passive means. Active treatment consists of continuously adding alkaline substrates to neutralise the pH of the mine waste, subsequently removing metals through precipitation. Passive treatment consists of natural and biological processes to treat AMD (Moodley *et al*., 2018).

Many AMD treatment and prevention techniques can be implemented to mitigate AMD formation. However, there are many disadvantages associated with using traditional/conventional materials in the implementation of AMD mitigation techniques, such as toxicity, expensive, poor performance, design inaccuracies, depleting of natural resources and generating additional waste (Table 4). New studies have been conducted on utilising waste/by-products from other industries in AMD treatment and prevention, providing more sustainable and environmentally friendly AMD treatment and prevention strategies (Moodley et al., 2018).

2.4.1 Neutralising material

Adding an alkaline material or substrate to an acid-generating mine waste is one of the most widely used AMD treatment techniques. Alkaline materials neutralise acid generated by acid-generating mine waste, increasing mine waste's pH and allowing the removal of metal/metalloids through precipitation. However, using alkaline materials such as lime, limestone, and slag can produce large quantities of secondary sludge (Wingenfelder et al., 2005).

Acid-neutralising waste materials or by-products such as paper mill by-products, steel mill by-products and phosphate waste rock have gained much attention in AMD treatment and prevention. Other industrial by-products studied include fly ash, wood ash, green liquor dregs, mesa lime, argon oxygen decarburization (AOD) slag and basic oxygen furnace slag (BOF slag) (Moodley et al., 2018).

2.4.2 Using lime and limestone as AMD remediation

Lime and limestone are considered to be a resource and not waste materials. Vast quantities of lime and limestone must be continuously added to treat AMD at mining waste disposal sites. Most metals/metalloids are removed by adding lime or limestone, and sulphate is removed through precipitating, resulting in the formation of gypsum. The neutralisation of acid and removal of sulphate by the addition of lime and limestone are represented by equations Eq. (8) and Eq. (9), respectively (Li et al., 2018).

$$\boldsymbol{Ca(OH)_2(s) + 2H^+ + {SO_4}^{2-} \rightarrow CaSO_4 \cdot 2H_2O(s)} \tag{8}$$

$$\boldsymbol{CaCO_3(s) + 2H^+ + {SO_4}^{2-} + H_2O \rightarrow CaSO_4 \cdot 2H_2O + CO_2(g)} \tag{9}$$

The use of lime and limestone to remove sulphate from AMD with high sulphate concentrations through gypsum crystallization has been reported to be a cost-effective process due to the low cost of lime and limestone in many countries (Hammarstrom *et al*., 2003, Tait *et al*., 2009). However, lime and limestone addition are not sustainable in the long term from a financial and resource availability perspective (Li et al., 2018).

Table 4: AMD prevention technique

Prevention technique	Mechanism/Principle	Material used	Advantage	Disadvantage	References
Passivation/ Microencapsulation.	A thin organic or inorganic coating is applied to the surface of the sulphide ore. The coating consists of a network of covalent and ionic bonds that prevent water and oxygen ingress.	Lime, limestone, fly ash, phosphate, permanganate, silica, sodium oleate, 8-hydroxyquinoline and phospholipids	It can be used as an alternative as opposed to using low permeability grout to seal mines.	Are usually unstable at low pH levels. Can affect the environment negatively and is prone to hydrolysis. Toxic oxidizing agents are used in the pre-treatment.	Diao *et al*., (2013); Shu *et al*., (2013)
Backfilling	Opencast or underground mines are refilled with waste rock after a mine has been closed.	Soil, tailings and waste rock	The volume of waste rock that requires treatment is indirectly minimised. Safe containment for waste rock.	Alkalinity is most likely needed. Expensive Waste rock requires pre-treatment due to the veins and cracks in the waste rock, which can lead to AMD formation.	Villain *et al*., (2013)
Waste-heap dry covers	A system with a single or multiple layers consisting of non-reactive low permeable solid material placed on waste rock heap or tailings.	Soil, sewage sludge, clay, kiln dust or cement.	Mine sites are reclaimed and rehabilitated. The use of waste allows for the disposal of waste.	Does not prevent the acid generation and AMD completely.	Borghetti Soares *et al*., (2009)

Source: Moodley et al. (2018).

The extent to which sulphate can be removed depends on the solubility of gypsum, which depends on the solution's composition and ionic strength. It is recommended to use lime and limestone as the first step in AMD treatment, especially AMD with elevated sulphate concentration, to reduce the sulphate content to a concentration lower than 1200 mg/L (Geldenhuys et al., 2003; Li et al., 2018).

Limestone usually becomes covered with aluminium and iron precipitates, lowering the activity to a point where limestone can fail as an AMD treatment method. Limestone is not a recommended AMD treatment method for waste material with an iron concentration greater than 5 mg/L or with an acidity greater than 50 mg/L as calcium carbonate ($CaCO_3$) (Skousen et al., 1990)

2.4.3 Utilising Industrial acid-neutralising waste or by-products in AMD remediation

Using industrial acid-neutralising waste or by-products in AMD treatment and prevention techniques has received much attention in the past decade, particularly waste produced by steel and paper mills. Waste from steel and paper mills may serve as an alternative to lime with additional benefits that will eliminate some of the disadvantages associated with the use of lime. Additionally, industrial acid-neutralising waste or by-products such as mesa lime, green liquor dregs (GLDs), fly ash (FA), wood ash (WA), basic oxygen furnace slag (BOFS) and argon oxygen decarburization slag (AODS) have been studied with regards to acid-neutralisation (Moodley et al., 2018).

2.4.3.1 Fly ash

Fly ash is a by-product produced by the burning of fossil fuels. Fly ash consists primarily of carbonates and calcium oxides which increase the pH allowing for the precipitation of metals (Moodley et al., 2018). Fly ash is an unconventional low-cost, environmentally friendly alternative to absorbent compared to using activated carbon and can be used as a pre-treatment agent alternative to limestone and dolomite. Fly ash has been used in AMD treatment to remove toxic heavy metals such as iron, manganese, zinc, cadmium, cobalt, aluminium and nickel (Saha & Sinha, 2018).

2.4.3.2 Slag

BOF and AOD slags are produced during steel refining processes. Both AOD and BOF slag consists of oxides and calcium silicates which help the sludge settlement post-treatment (Heviánková *et al*., 2014).

In a study by Name & Sheridan (2014); BOF and stainless-steel slag were assessed as potential alternatives to lime in treating AMD. The worst-case AMD was modelled with a pH of 2.5, 5000 ppm sulphate and 1000 Fe concentration. The study concluded that the stainless-steel slag would not be suitable as it was highly ineffective. The BOF slag has highly effective as it removed 99.7 % of soluble iron and 75 % of sulphate and increased the pH to 12.1.

2.4.3.3 Bauxite residue

Bauxite residue, or red mud, is a by-product/waste produced in significant quantities during the Bayer process in alumina refining. Bauxite residue is considered a solid waste with high alkalinity and fine particle size. Recently, much attention has been placed on using bauxite residue as an effective replacement for lime as it has acid-neutralising minerals such as carbonate, aluminate, hydroxide, aluminate, and other minerals. Bauxite residue has excellent adsorption properties due to the large specific area of the insoluble metal oxide the residue (Rios et al., 2008; Li et al., 2018)

A study by Doye & Duchsne (2003) concluded that bauxite residue has exceptional short-term acid-neutralising capabilities. Paradis *et al*. (2007) improved the long-term acid-neutralising capabilities through modifying the bauxite residue by adding brine. The brine converted each soluble alkalinity to less soluble alkalinity. The addition of brine did not affect the short-term acid-neutralising capabilities of the bauxite residue.

2.4.3.4 Phosphatic waste-rock

Ouakibi *et al*. (2014) conducted experiments showing the use of phosphatic waste rock to be an effective replacement for lime and limestone. The results of the experiment showed that the phosphatic waste-rock effectively neutralised the AMD with a decrease in Fe (600 to120mg/L), Cu (23 to 0.002 mg/L) and Al (160 to 1.7 mg/L). Phosphatic waste rock has high acid-neutralising capabilities due to its high carbonate content such as calcite and dolomite, which place the largest role in acid neutralisation (Ouakibi et al., 2014).

2.4.4 Covers

Preventing AMD formation at the source by separating the sulphide minerals from water or oxygen is a much more sustainable option for long-term AMD mitigation than AMD remediation using alkaline materials (Li *et al*., 2018).

Acid-generating mine tailings are covered with a layer of sediment or organic material to reduce the contact between oxygen and water, preventing acid generation. The sediment and organic material cover limit the oxygen ingress from the environment. This method depends on sufficient water content to effectively limit the oxygen ingress. The effectiveness of these covers is affected by intense wet and dry seasons, particularly when the covers dry and crack (Li *et al*., 2018).

One method of preventing AMD is the use of an oxygen barrier to reduce the oxygen availability to the acid-generating mine material underneath. An oxygen barrier can be created by using oxygen-consuming materials such as wood waste, straw mulch or other organic residues as an oxygen-consuming material (Bussière *et a*l., 2004). Covers with capillary barrier effects (CCBE) is another effective method to limit oxygen migration. CCBE's rely on the ability of the covers to retain moisture (Bussière *et al*., 2004).

AMD effluent treatment is used during mining operations but is not sustainable or a long-term solution (Aubertin et al., 2015, 2016). AMD management is much more effective but preventing oxidation reactions from occurring within the tailings. Cover systems are one of many control and reclamation approaches. Cover systems aim to control the water content or fluxes to the reactive tailings (Pabst *et al.*, 2018).

2.4.5 CCBE covers

Covers with capillary barrier effects (CCBE) have been seen to be extremely effective in AMD prevention techniques. CCBEs are, in many cases, the only practical alternative to control AMD formation, even though the construction of a CCBE has a relatively high cost of construction (Bussière *et al*., 2004).

The primary role of a CCBE is to limit oxygen diffusion to the underlying acid-generating material, thus reducing acid generation. The cover must retain a high moister content in one or more of its soil layers to accomplish this oxygen diffusion limitation. The saturated soil can lower the diffusion of gas to such an extent that it effectively limits the influx of oxygen from the atmosphere to the acid-generating waste material beneath (Bussière *et al*., 2004).

The ability of CCBE covers to maintain a high degree of saturation depends on the capillary barrier effect. The capillary barrier effect is present when fine-grainer material is placed over a coarse material. The two materials have different particle size distributions resulting in different hydrogeological properties. The fine-grained material layer will retain water easier as it has smaller interstitial pores, and capillary forces allow for higher water retaining capacity. The coarse material drains during desaturation, and the interconnectivity of water-filled voids is reduced by the presence of gas in the coarse material pore space, reducing its hydraulic conductivity (k). The vertical flow of water between the fin-grained material layer to the coarse material layer is decreased by the low hydraulic conductivity of the coarse material. The fine-grained material layer remains almost fully saturated, resulting in a reduced oxygen flux (Bussière *et al*., 2004)

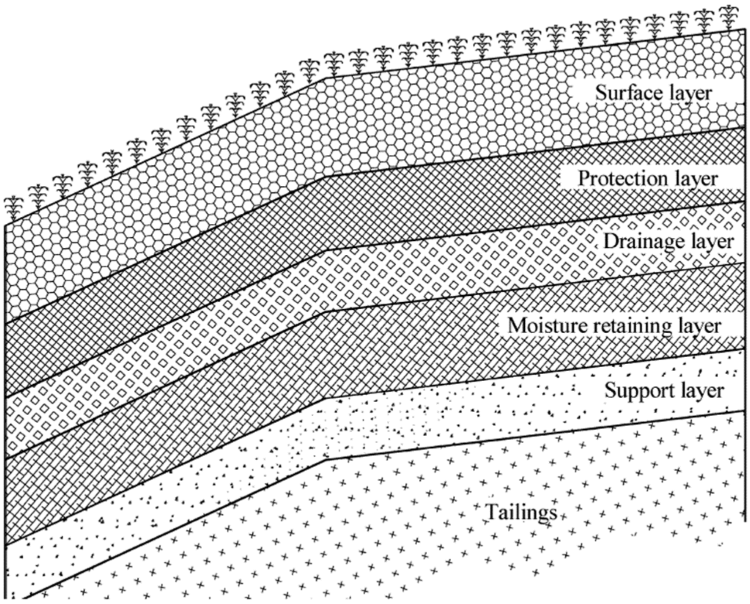

Figure 3: CCBE configuration (Source: Bussière *et al*., 2004)

A CCBE usually consists of three to five layers made of different materials. Each layer has its own purpose. Figure 3 illustrates the typical configuration of a CCBE (Aubertin *et al*., 1995). The first layer (bottom support layer) placed above the acid-generating tailings is made of a coarse-grained material that acts as a capillary break and mechanical support. The second layer, the moisture-retaining layer, consists of fine-grained material. This layer is used as the moisture-retaining layer and is placed above the first layer to create the capillary barrier effect. The third layer (drainage layer) consists of another coarse-grained material that helps with lateral draining and prevents water loss through evaporation from the moisture-retaining layer. The protection and surface layers protect the core of the CCBE from bio-intrusion and erosion (Bussière *et al*., 2004).

The proposed use of low sulphide, non-reactive, non-acid generating mine tailings as the moisture-retaining material layer in the CCBE would reduce the cost of construction of a CCBE cover system. Low sulphide tailings are usually found in abundance in many mining areas.

Utilising low sulphide-containing tailings as moister-retaining material has already demonstrated its feasibility at an LTA site in Quebec, where it lowered the cost of construction significantly (Ricard *et al*., 1997; Bussière *et al*., 2004).

Bussière *et al*. 2004 conducted a leach column test where the moisture-retaining layer of the CCBE consisted of slightly reactive low sulphide tailings. The study's results concluded that the low sulphide tailings effectively limited the acid generation and release of sulphates and heavy metals from the acid-generating tailings underneath. The study further showed that the low sulphide tailings could improve the CCBE's ability to limit gas diffusion through consuming a portion of the migrating oxygen.

Utilising industrial waste material or by-products in AMD prevention and treatments resonates with sustainability, particularly if the source of acid generation is considered to be acid-generation for the foreseeable future. The use of industrial waste material or by-products may benefit multiple industries simultaneously. However, the cost of transportation and implementation should be considered when considering a waste material to be used in the prevention or treatment of AMD at a disposal site to ensure that the AMD treatment or prevention strategy to be implemented will be economically viable (Moodley et al., 2018).

2.5 Acid mine drainage prediction methods

Developing and implementing an effective AMD mediation strategy requires assessing the acid generating capabilities of the waste rock or tailing. The acid-generating evaluation test are either static or kinetic, depending on the experimental procedure and timeframe (Smart *et a*l., 2002; Stewart *et al*., 2006; Oh *et al*., 2017). Predicting whether or not mine waste will produce AMD is a challenging task, as AMD generation depends on chemical hydrological, microbiological, and mineralogical factors (Blowes et al., 2013, Karlsson *et al*., 2018)

Static tests only predict the acid-forming potential and the relative quantity of acid that may be generated. Static tests are relatively inexpensive and conducted in a relatively short timeframe. Static tests do not provide information on the rate of acid generation and the duration (Oh *et al*., 2017).

Static tests such as the ABA, NAG and ABCC tests are initially conducted as prelimanary screening tools,to identify samples that may generate acid that may lead to AMD. ABA and NAG tests are the two static tests that are most widely used to evaluate the acid-forming potential and to predict AMD (Bouzahzah *et al*., 2015). Static tests such as ABA and NAG provide information on the balance between the theoretical acid-generating and acid-neutralising components (Smart *et al*., 2002; Stewart *et al*., 2006; El Amari & Hibti, 2019).

A Kinetic test attempts to mimic the natural reactions that would occur at the mining or waste rock disposal site. The Kinetic test, such as humidity cells, are generally used to determine whether or not the waste rock will generate an acidic effluent. Additionally, leach columns may provide information on the rate of acid generation, sulphide reactivity, metal solubility and oxidation kinetics. The results obtained from kinetic tests are known to be relatively credible (Lapakko, 2003; Oh *et al*., 2017).

Leach column tests are conducted over a 6 to 12-month period. Leach column tests are incredibly time-consuming and expensive. Thus, other geochemical tests such as ABA, NAG and ABCC tests are conducted initially to evaluate the acid generation capabilities of mine waste rock and tailings. Results obtained from the static tests are used to identify samples that require additional testing, such as leach column tests (Smart *et al*., 2002).

The end goal of conducting static and kinetic tests, together with other mine waste evaluation methods, is to provide reliable and accurate information to develop suitable treatment or prevention strategies that are environmentally sound in the management of mine waste (Lapakko, 2003).

2.5.1 Acid-Base Accounting (ABA)

The ABA test evaluation method can be conducted in a relatively short time frame and is a relatively inexpensive analytical procedure to assess the chemical and physical properties of mine waste rock tailings (Skousen, 2017). The ABA procedure, as described in Sobek *et al.* (1978), utilises three parameters, namely paste pH, maximum potential acidity (MPA) and acid neutralisation capacity (ANC), to assess the acid generating capabilities of mine waste. These MPA and ANC are used to calculate the net acid production potential (NAPP) and ANC/MPA ratio. The NAPP, ANC/MPA and the associated classification criteria are used to classify the acid-generation capabilities of mine waste as potential acid forming (PAF), non-acid forming (NAF) or uncertain (UC) (Usher *et al*., 2003).

2.5.1.1 Paste pH

Paste pH (Soil pH) is one of the most common physical aspect measures in mine waste. The paste pH test involves mixing the mine waste sample with water with a 2:1 waste-to-water weight ratio, creating a paste-like sludge, after which the pH is measured (Sobek *et al*., 1978).

The paste pH test is an extremely simple, inexpensive test used to evaluate a sample's readily available alkalinity/acidity. Only highly reactive minerals and highly soluble salts are assessed due to the short time duration of the paste pH test (Weber *et al*., 2006; Skousen, 2017).

A paste pH below 4 strongly indicates that the sample will likely be a potential acid forming (PAF). A sample with a pH below 4 will immediately generate acid upon exposure to water and may contain stored acidity of up to 30 kg H_2SO_4/t. Samples with a paste pH between 4 and 5, will most likely PAF with a stored acidity up to 9 kg H_2SO_4/t. Weber *et al*. (2006) suggest that samples with a paste pH below 5 should be classified as PAF with a high priority for further testing. Samples with a paste pH above 7 indicate that the samples may be NAF due to a higher neutralising capacity, most likely due to the presence of highly reactive carbonates. However, samples with a pH above 7 may generate AMD if the acid-neutralising minerals are consumed to the point of depletion before acid-generating sulphides (Weber *et al*., 2006; Skousen, 2017; Nieva *et al*., 2018).

2.5.1.2 Maximum potential acidity (MPA)

It is necessary to determine the sulphide and sulphur content to calculate the quantity of theoretical acid that may be generated per ton of material, which is refers to as the maximum potential acidity of a sample (Dold, 2017). The MPA is determined by multiplying the total sulphur or sulphide content by a factor of 30.6, as seen in Eq. (10) (Sobek *et al*., 1978; Bouzahzah *et al*., 2015; Smart *et al*., 2002).

$$\boldsymbol{MPA} = (\%)\boldsymbol{S} \times \mathbf{30.6} \qquad (\mathbf{10})$$

The MPA of a sample is calculated based on the assumption that the total sulphur or total sulphide content in a sample occurs mostly in the form of pyrite. However, this assumption may overestimate the actual acid generating capabilities of the sample if sulphur or sulphide content occurs in other forms that do not generate, such as galena, gypsum and barite. The MPA can be adjusted if the sulphur and sulphide speciation is known (Sobek *et al*., 1978; Bouzahzah *et al*., 2015; Smart *et al*., 2002; Stewart et al., 2006).

2.5.1.3 Acid neutralisation capacity (ANC)

The ANC evaluates the quantity of acid-neutralising that a sample may neutralise due to its acid-neutralising mineral content. The ANC test protocol digests a sample in highly acidic conditions at high temperatures, which may allow acid neutralising minerals to contribute to acid neutralisation that would not normally contribute to acid neutralisation under normal environmental conditions. The true or effective ANC may thus be overestimated (Bouzahzah *et al*., 2015; Stewart *et al*., 2006).

Reaction equation Eq. (11) represents the dissolution of siderite. Siderite reacts with 2 moles of hydrogen ions to form ferrous iron (Fe^{2+}), thus contributing to acid neutralisation (Bouzahzah *et al*., 2015; Stewart *et al*., 2006).

$$\boldsymbol{FeCO_3 + 2H^+ = Fe^{2+} + 2CO_2 + H_2O} \qquad (\mathbf{11})$$

Ferrous iron continues to neutralise acid when oxidised by oxygen, consuming 1 mole of hydrogen ions to produce ferric iron (Fe^{3+}), as seen in Eq. (12) (Bouzahzah *et al*., 2015; Stewart *et al*., 2006).

$$\boldsymbol{Fe^{2+} + \frac{1}{4}O_{2(aq)} + H^{+} \rightarrow Fe^{3+} + \frac{1}{2}H_2O} \qquad (\mathbf{12})$$

However, the acid neutralised by the dissolution of siderite and the oxidation of ferrous iron is released back into the solution through the hydrolysis of ferric iron and subsequently precipitation of ferric oxyhydroxides ($Fe(OH)_3$) as seen in Eq. (13). Siderite may thus falsely contribute to acid neutralisation, resulting in an overestimation of the ANC (Stewart *et al*., 2006; Blowes *et al*., 2013).

$$\boldsymbol{Fe^{3+} + 3H_2O \leftrightarrow Fe(OH)_3(s) \downarrow + 3H^{+}} \qquad (\mathbf{13})$$

To overcome the acid-neutralising contribution of siderite, two drops of hydrogen peroxide (H_2O_2) are added to the ANC solution during the back titration at a pH of 5 to promote the oxidation of dissolved ferrous iron (Eq. (12)), hydrolysis of ferric iron (Eq. (13)). Samples with a siderite content high than 15% by weight should utilize a modified H_2O_2 ANC method (Stewart *et al*., 2006).

2.5.1.4 ABA evaluation parameters

The net acid production potential (NAPP), acidity ratio (AR), and paste pH are utilised to classify the sample's acid generating potential as potential acid forming (PAF), non-acid forming (NAF) or as uncertain (UC) (Smart *et al*., 2002; Stewart *et al*., 2006)

The NAPP refers to the theoretical quantity of acid that will be released if AMD occurs and is calculated by subtracting the ANC from the MPA as seen in Eq. (14). The AR is calculated by dividing the ANC by the MPA, as seen in Eq. (15), representing the balance between acid neutralisation and acid generation minerals. The calcification criteria using the NAPP and AR values are found in Table 5 (Usher *et al*., 2003; Stewart *et al*., 2006).

$$\boldsymbol{NAPP = MPA - ANC} \qquad (\mathbf{14})$$

$$\boldsymbol{AR = \frac{ANC}{MPA}} \qquad (\mathbf{15})$$

The NAPP and AR do not provide any information on the relative reactivity or rate of reactions of the acid generating or acid neutralising minerals within the sample. Additionally, the NAPP and AR do not provide any information on the lag time that will occur before the onset of acidic conditions (Stewart *et al*., 2006).

Table 5: ABA classification criteria using NAPP and AR

NAPP (kg H_2SO_4/t)	**AR**	**Classification**	**Comment**
NAPP > 20	**AR < 1**	**PAF**	Will likely generate AMD.
NAPP < -20	**2 < AR**	**NAF**	AMD will most likely not be generated.
-20 < NAPP < 20	**1 < AR < 2**	**UC**	Will possibly generate AMD if acid neutralising minerals are depleted at a fast rate than acid-generating minerals or if the acid neutralising minerals are not readily available of acid neutralisation.

Paste pH is not definitively used to classify waste rock samples' acid generating capabilities. However, paste pH can be very useful as it quickly indicates a sample's readily available alkalinity/acidity. Paste pH helps to prioritise samples if large quantities of samples need to be tested (Weber *et al*., 2006). Weber *et al*. (2006) state that samples with a paste pH < 5 should be classified as high-priority samples that require immediate further testing.

2.5.2 Net acid generation (NAG)

The NAG test assesses the total or net acid that a mine waste may generate instead of assessing the acid-generating and acid-neutralising capabilities separate as done in the ABA method (Smart *et al*., 2002; Weber *et al*., 2006). The NAG test compensates for some of the limitations and uncertainties associated with using the ABA method. The NAG value obtained from the NAG test is essentially the same as the NAPP obtained in the ABA but just determined differently. The ABA and the NAG test results are commonly used in conjunction to provide a more accurate classification system (Weber *et al*., 2006).

The organic acid formed by carbonaceous material during the NAG test may overestimate the acid generation capabilities of a sample. An organic material content of as little as 3% may significantly affect the NAG results (Pope *et al*., 2010). Karlsson *et al*. (2018) suggest that slow-reacting minerals such as silicates require a longer reaction time to react with the hydrogen peroxide to contribute to acid neutralisation. The time specified in current methods could thus neglect the acid neutralising contributions of slow weathering minerals and thus underestimate the true acid neutralising capabilities of the tailing or waste rock sample.

2.5.2.1 NAG test

A NAG test involves a single addition of 250 mL of hydrogen peroxide (H_2O_2) with a purity of 15 wt% and a pH of 4.5 to a 2.5 g (particle size < 75 µm) waste rock sample. The NAG solution is allowed to react overnight. The NAG solution is then gently heated to encourage the release of inherent acid-neutralising capacity, promote the oxidation of remaining sulphides and remove excess H_2O_2 which has not reacted. The solution is left to cool down to room temperature, after which the pH of the NAG solution is measured. The NAG solution's pH is then measured and referred to as the NAGpH (Stewart *et al.,* 2006; Weber *et al*., 2004; Smart *et al.,* 2002).

The solution is titrated to a pH of 4.5 using sodium hydroxide (NaOH). The volume and concentration of sodium hydroxide used during the titration procedure are used to calculate the theoretical NAG value using Eq. (16) which expresses the NAG value kg H_2SO_4/t (Stewart *et al.,* 2006; Weber *et al*., 2004; Smart *et al.,* 2002).

$$\boldsymbol{NAG = (49 \times V \times M)/w} \qquad (\mathbf{16})$$

The NAGpH and the NAG value are used to evaluate the acid-generating capabilities of waste rock samples. The NAGpH is usually used to classify the acid generating capabilities as PAF, NAF or UC. The NAG value is usually used to evaluate the quantity of acid that may be generated and is usually compared to the NAPP value obtained in the ABA method. A waste rock sample is categorized as PAF if the NAGpH has a value below 4.5 and NAP if the NAGpH has a value above 4.5 (Weber *et al.,* 2004; Stewart *et al*., 2006).

The single additional NAG test may underestimate the NAG value if the hydrogen peroxide is completely depleted or decomposed before all the sulphides have been oxidised. Smart *et al.* (2002) state that waste rock samples with a pyritic-S content > 1% will lead to incomplete sulphide oxidation.

2.5.2.2 NAG classification criteria

The classification criteria used when only considering the NAG results are summarised in Table 6 (Smart *et al.,* 2002).

Table 6: NAG Classification Criteria

NAGpH	NAG (kg H_2SO_4/t)	Classification
> 4.5	0	NAF
< 4.5	$\leqslant$ 5	PAF with low capacity
< 4.5	> 5	PAF

2.5.3 Acid buffering characteristic Curve (ABCC)

The ABCC test method was first developed in 1995 by Miller & Jeffery. The ABCC involves partially dissolving a 2 g sample in 100 mL of deionised water followed by incrementally titrating with hydrochloric acid to a pH of 2.5 whilst continuously stirring using a magnetic stirrer. After each incremental addition, the solution is left to react with the hydrochloric acid, after which the pH is recorded before each addition (Smart *et al*., 2002; Stewart *et al*., 2006).

The ABCC method provides information on the portion of the ANC measured in the ABA that is readily available for neutralising acid. The ABCC is extremely useful as it has the ability to resolve conflicts between the NAG and ABA results (Smart *et al*., 2002; Stewart *et al*., 2006).

The volume and concentration of hydrochloric acid used during the titration procedure is converted to the kilograms of sulphuric acid added per ton material (kg H_2SO_4/t) equivalent. The recorded pH is plotted against the acid that was added during the titration, as seen in Figure 4.

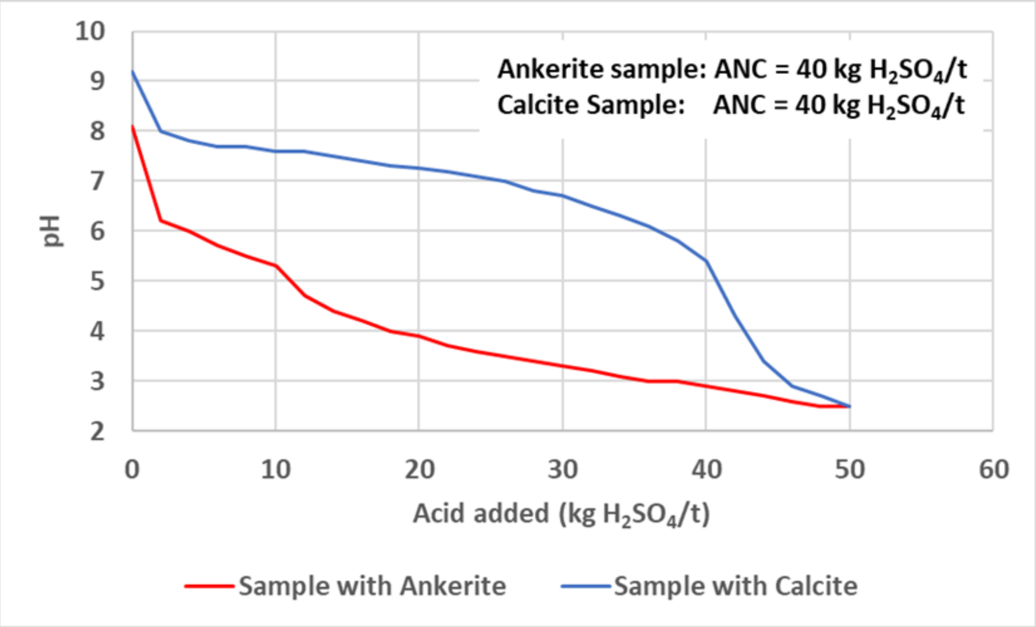

Figure 4: The ABCC of a sample containing calcite and a sample containing ankerite (Source: Smart *et al*., 2002).

Figure 4 depicts the ABCC profile of a sample containing calcite ($CaCO_3$) and a sample containing ankerite (Ca-Mg-Fe carbonate). Both samples have an ANC of 40 kg H_2SO_4/t as determined by the ABA method. However, the reactivity of the samples differs dramatically. As seen in Figure 4, the sample containing calcite maintained the pH of the solution above 4 until the equivalent of 42 kg H_2SO_4/t had been neutralised. Thus, all of the ANC, as determined by the ABA method, are readily available for acid neutralisation. The ankerite sample maintained the pH of the solution above a pH of 4 up until the equivalent of 18 kg H_2SO_4/t of acid had been neutralised, indicating that only 45% of the ANC measured using the ABA method is readily available for acid neutralisation (Smart *et al.,* 2002).

2.5.4 Classification criteria

The ABA and NAG test methods utilise different classification criteria to classify a sample's acid generating capabilities as potential acid forming, non-acid forming or uncertain. However, it is best to practise using the ABA and NAG results in conjunction to ensure classifications with a high degree of confidence, eliminating some of the limitations associated with using ABA and NAG separately. The NAPP of the ABA test method and NAGpH of the NAG test method are the parameter of concern when classifying the acid generating capabilities of sample’s as PAF, NAF or UC (Table 7) (Oh *et al.,* 2017; Smart *et al*., 2002).

Table 7: Classification Criteria

Classification	Test Criteria
NAF	NAPP $\leqslant$ 0 and NAGpH $\geqslant$ 4.4
PAF	NAPP > 0 and NAGpH < 4.4
UC	(NAPP $\leqslant$ 0 and NAGpH < 4.5) or if (NAPP > 0 and NAGpH $\geqslant$ 4.5)

2.5.5 Leach column tests

AMD formation occurs as a result of complex geochemical reactions taking place in waste rock tailings. Kinetic tests such as the leach column test are experimental systems where some factors are induced, manipulated and monitored. Various factors include moisture content, water and oxygen availability, microbial activity, pH, and temperature (Blowes *et al*., 2013; Wang *et al*., 2019).

Kinetic tests are time-dependent weathering tests conducted to obtain mine waste's drainage quality. The most common kinetic test involves laboratory-based columns, humidity cells and field-based test pads (Bowell *et al*., 2006).

Kinetic tests such as the humidity cell test (HCT) are commonly used in conjunction with static tests and are complementary to static tests. Kinetic tests attempt to mimic the natural and accelerated weathering of mine tailings under controlled conditions. Kinetic tests provide information on the rate of acid generation, contaminant release and leachate quality. Kinetic tests become very useful when static tests do not provide clear information on the acid-generating capabilities of tailing samples (El Amari & Hibti, 2019).

Aerated cells are subject to a weekly aeration cycle, which includes 3 days of dry air exposure, 3 days of exposure to humidified air and the flushed on the 7th day. Non-aerated cells are cells that do not undergo the 6-day exposure procedure. Non-aerated cells are left between cycles and only flushed at the end of each cycle (Bowell *et al*., 2006).

The water used to flush the waste rock remains in contact with the waste rock for approximately 2 hours. The columns are then drained, and the column effluent is then analysed. The pH, conductivity, sulphate concentration, acidity, alkalinity and metal concentration using ICP are typical parameters that are analysed. The effluent analysis data can be used with effluent volume to calculate leaching rates (Morin & Hutt 1997; Lapakko, 2003).

Benzazoua *et al.* (2004) presented a new approach when evaluating leach column results. The accumulation of sulphate (SO_4^{2-}) mass versus the accumulation of Mn, Ca and Mg mass, is plotted and referred to as the oxidation-neutralisation curve. This oxidation-neutralisation curve is used to evaluate the acid-generating potential of mine tailings. Sulphate represents the primary product of oxidation resulting in acid generation. The sum of Ca, Mg and Mn represent the products of carbonate dissolution resulting in acid neutralisation.

2.5.5.1 Particle size distribution

The particle size distribution of the sample will determine the surface area that will be available for kinetically controlled reactions. A decreased particle size will result in an increased surface area available for chemical reactions to occur (Bowell *et al*., 2006). According to Bowell et al., 2006 the fine material in a leach test will contribute proportionally more to the mass transfer from the solid to the dissolved phase.

Water retention in the leach column is another important aspect, especially for non-aerated columns. Finer particles tend to retain more water during flushing cycles and could impact the reactivity of sulphide-rich samples (Bowell *et al*., 2006).

Figure 5 illustrates the possible influence that partial size has on the rate of pyrite oxidation in laboratory weathering cells. Particle size is especially relevant to non-aerated leach columns (Bowell *et al*., 2006).

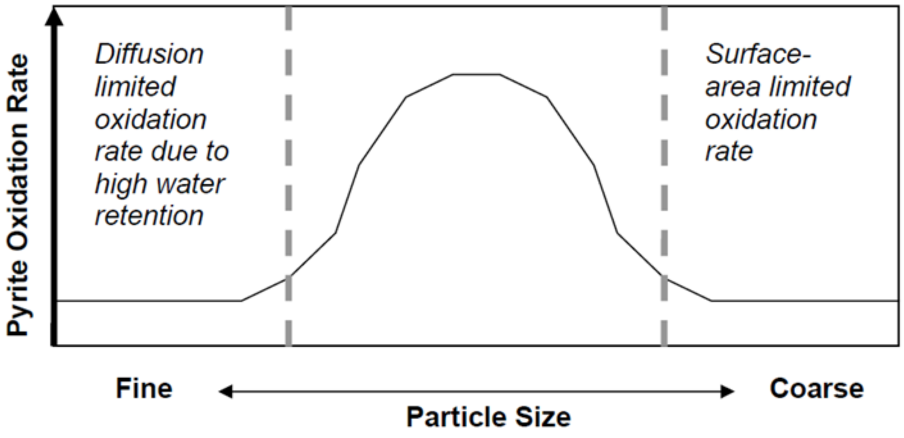

Figure 5: Theoretical effect of particle size on the rate of pyrite oxidation (Source: Bowell *et al*., 2006).

2.5.5.2 Effects of aeration versus non-aeration

The forced aeration is intended to ensure that the oxygen-consuming sulphide oxidation reactions are not limited by the rate of oxygen supply by diffusion. Forced aeration is commonly incorporated in leach column cells. Aeration of the leach column cells involves exposing the sample to dry and humid air cycles (Bowell *et al*., 2006). Studies by Lapakko &

White. (2000), Frostad *et al.* (2002) and Bowell *et al*. 2006 on samples with sulphide content up to 7% suggest that aeration of a cell does not have a significant effect on the weathering rates. Bowell *et al*. (2006) state that the low oxidations rates will be a result of low sulphide content and will not be affected by oxygen diffusion rate that will be fast enough to supply enough oxygen to the sulphide surface. Furthermore, that caution should be used when considering such studies where aqueous releases are dominant resulting from the dissolution of sulphate salts since such processes are independent of oxygen supply.

A study conducted by Bowell *et al*., (2006) showed that a non-aerated cell produces a variable sulphate release rate and that most of the peaks of the non-aerated cells are smaller than the peak releases for the aerated cells. Bowell *et al*., (2006) suggest that the complete drying of the cell contents may suppress sulphide oxidation rate as the interstitial water is, which prevents the accumulation of aqueous ferric iron (Fe(III)), which oxidises sulphide minerals far more aggressively under acidic conditions.

Studies have found that leach columns with weekly dry-air and wet-air cycles retain less pore water than leach columns with no weekly dry-air and wet-air cycles. The drainage quality of the leach columns with no weakly aeration cycle had a high calcium and magnesium release rate due to the superior retention of pore water during the weekly cycle. It is believed that the higher pore water content of the leach columns with no aeration cycle favours the dissolution of calcium and magnesium minerals as it enables the transport of acidic reaction products from the surface of iron sulphide minerals to the calcium and magnesium carbonate minerals (Lapakko & White, 2000; ASTM D5744-18).

2.5.5.3 Effects of flushing frequency and secondary mineral interaction

Secondary minerals precipitate when the dissolution products become saturated within the interstitial water within the cell. The flushing frequency of the cells should be frequent enough to ensure that the dissolution products are removed to prevent the precipitation of secondary minerals. Flushing frequency is particularly important for sulphate release as sulphate is used as a tracer to trace the sulphide oxidation rate (Bowell *et al*., 2006).

The time duration between flushing (or leaching) will control the time duration available for the soled phase to react with the interstitial water. Bowell *et al*., 2006 state the 7-day cycle has been set arbitrarily, most probably for convenience. Reaction rates such as the oxidation of sulphide minerals are controlled concentration of dissolved species in the interstitial water thus, the time duration between flushing (or leaching) controlled by the flushing frequency may affect rection rates by allowing the build-up of reactants (e.g., H^+ and sulphates) in the solution (Bowell *et al*., 2006).

Studies done by Bowell *et al*. 2006 suggest that increased time duration between flushing encourages secondary mineral precipitation. According to the common humidity cell protocols of Morin & Hutt (1997) and Price (1997), the precipitation of secondary minerals is unwanted. Suppose sulphate concentration is used to calculate the rate of sulphide oxidation. In that case, precipitation of secondary minerals such as gypsum and jarosite will remove sulphate from the solution providing a false impression that sulphide oxidation is slower (Bowell et al., 2006).

2.5.5.4 Test duration

The test duration of a humidity cell test varies in literature. Most recent protocols conduct humidity cell tests for 40 weeks. It has been recognised that the concentration in the leachate tends to stabilise at a period of 40 weeks. The leachate is geochemically stable when the weekly release varies less than a factor of 2 from the previous 5 week's average release (Price 1997; Lapakko 2003). A study done by Morin & Hutt (2000) suggests that there is a 50% chance that the humidity cell leachate will stabilize within a year. The humidity cell test duration is normally limited to a year due to the practicalities in time involved with mining permits (Bowell *et al*., 2006).

The test duration of the leach column test will ultimately depend on the objective of the test, which may be site specific.

2.5.5.5 Leaching

Leachate collection vessels are weighed before and after the leachate is collect from leaching columns. Samples may become less permeable as the leach column test continues and thus require a longer leachate collection time, extending two to four hours into the day after the leaching day. The leach columns are weighed before and after leaching to determine the retained pore water mass (ASTM D5744-18).

2.5.5.6 Leachate interpretation

Studies have found that the anionic and cationic load in the leachate of week 0 are commonly high due to the dissolution of soluble pre-existing soluble oxidation salts present in the samples. The first three to five weeks of leaching are often required to flush out pre-existing salts (Alpers & Blowes, 1994). The flushing of pre-existing soluble salts is only required if it is part of the test objectives (ASTM D5744-18).

It is recommended that the sulphate, magnesium, calcium, sodium and potassium concentration of the leachate of a mine waste sample containing iron sulphides be recorded and monitored as they are critical measurements to understand the mass release associated with iron sulphide mineral oxidation, magnesium carbonate, calcium carbonate, magnesium silicate, calcium silicate, potassium silicate mineral dissolution. Iron concentration is also of interest when the pH is lower than 3.5. Finally, trace metals should be measured and monitored using IPC-MS to be able to identify problematic leachable chemical species (ASTM D5744-18).

2.6 Mineralogy

The correlation between AMD and sulphide oxidation, dissolution and precipitation process of minerals and metals has been studied extensively over the past 70 years (Moses *et al*., 1987; Jambor, 1994; Wang, *et al*., 2019). However, minimal research has been conducted on the mineralogy and geochemical interactions that take place in the mine waste rock or tailings. Understanding the parameters that control acid mine drainage formation is essential to construct an effective remediation strategy (Dold 2010; Kalin, *et al*., 2006).

AMD's drainage quality depends on the quality and ratio between acid-generating and acid-neutralising minerals. Mineralogical calculations can thus be used to predict the occurrence of AMD (Karlsson *et al*., 2018).

Different geological samples contain different minerals or mineral groups such as carbonates, silicates, oxides, sulphides and sulphates. Many minerals or mineral groups can generate acidity (e.g., oxidation of sulphides, Fe(III) hydroxides, and the equilibrium reactions of sulphates, which means these minerals and reactions allow the liberation of protons (H^+) and elements into the water. Elements such as Fe, Al and Mn can hydrolyse and deprotonate water resulting in the liberation of protons and causing acidification of water. Acid-neutralising minerals or mineral groups such as carbonates, hydroxides and silicates can be found in mine waste. These acid-neutralising minerals neutralise protons ad can control the pH at certain values. It is thus necessary to know the quantity of each mineral (composition and trace element composition) in order to predict whether mine waste rock or tailings will release an acidic, neutral or alkaline effluent into the environment (Dold 2017).

A study by Karlsson et al., 2018 found that silicate minerals contributed the most to acid neutralisation (ANC) at 60% of the invested mine sites. It would appear that silicate minerals play a larger role in acid neutralisation and AMD generation. Karlsson *et al*., 2018 state that their results show that mineralogical calculations using SEM analysis are a the least as accurate as those of commonly used static tests such as the ABA and NAG.

Acid-generating sulphide minerals commonly appear as iron sulphides, such as pyrite (FeS_2) and pyrrhotite ($Fe_{1-x}S$). The acid-neutralising minerals are commonly present in the form of highly reactive carbonates such as calcite ($Ca(CO_3)_2$) and dolomite ($CaMg(CO_3)_2$) (Becker *et al*., 2015, Karlsson *et al*., 2018)

X-ray diffraction (XRD) and optical microscopy are two traditional analytical techniques used to characterise crystalline structures of minerals. Both techniques have limitations for quantification. XRD has a high detection limit (2 - 5%) and is thus not suitable for detecting trace elements (Dold 2017). Optical microscopy uses point counting for a semi-quantification analysis. However, optical microscopy in very labour intensive and expensive.

2.7 Mineralogy and mineralogical calculations

The mineral phases and elemental composition of tailing samples can be determined using X-ray diffraction (XRD) and X-ray fluorescence (XRF). The mineralogy is essential to identify reactive minerals present in the tailings. Crystal habit and species of neutralising and sulphur-bearing minerals are of particular interest. Identifying the different phases of sulphide minerals and acid naturalising minerals present in the tailings allows for a more comprehensive understanding of the acid generating capabilities of the tailings (Smart *et al*., 2002; Bouzahzah *et al*., 2015)

The MPA is calculated based on the assumption that the total sulphide or sulphur content occurs in the form of pyrite. However, not all sulphide or sulphur content within tailings occurs as Pyrite. Thus, identifying the non-acid generating sulphur or sulphide minerals present allows for corrections to be made to the MPA. Identifying the acid neutralising minerals present in the tailing's samples would assist in understanding the ANC determined using the ABA method and in predicting the availability of these minerals to neutralise acid.

The mineralogy of the waste rock can be used to determine the mineralogical acid neutralising capacity (ANC_{min}) and mineralogical maximum potential acidity (MPA_{min}) (Karlsson *et al*., 2018).

2.7.1 Mineralogical acid-neutralising capacity (ANC_{min})

The theoretical mineralogical ANC (ANC_{min}) can be calculated using the acid neutralising mineral content of the sample. Some of the most common acid neutralising minerals that occur in mine waste rock are highly reactive carbonates (calcite and dolomite) and low reactive silicates (mica and chlorite) (Karlsson et al., 2018). Calcite is one of the most critical acid neutralising minerals due to its high reactivity and ability to maintain the pH at near-neutral conditions.

Table 8 summarises the most common acid-neutralising minerals found in mine waste rock tailings with their relative reactivity (RR) at their respective concentration. The minerals are divided into six groups: carbonates, fast-weathering, intermediate-weathering, slow-weathering, very slow-weathering and inert, which categorizes them according to their ability to reactively. The reactivity of each mineral or mineral group is incorporated into the ANC_{min} calculations to account for the difference in reactivity based on concentration and mineral speciation. Minerals found in the slow-weathering, very slow-weathering and inert groups are not included in ANC_{min} calculations, as their contributions to the ANC are considered insignificant due to their low reactivity (Karlsson *et al*., 2018).

Table 8: Acid neutralising minerals and their corresponding relative reactivity

Mineral Class	Mineral	Relative reactivity (RR)			
		Average mineral content wt%			
		100%	30%	3%	0.3%
Carbonates	Calcite, magnesite, dolomite, brucite, aragonite	1	1	1	1
Fast-weathering	Olivine, anorthite, diopside, jadeite, garnet, wollastonite, leucite, nepheline, spodumene.	0.6	0.67	0.3	0.1
Intermediate-weathering	Hornblende, enstatite, actinolite, augite, tremolite, biotite, serpentine, zoisite, chlorite, talc, epidote, hedenbergite, anthophyllite, glaucophane, phlogopite.	0.4	0.2	0.03	0.01
Slow-weathering	Kaolinite, plagioclase, gibbsite, vermiculite, montmorillonite.	0.02	0.013	0.002	-
Very slow-weathering	Muscovite, k-feldspar	0.01	0.007	0.001	-
Inert	Rutile, Quartz, Zicon	0.004	0.0007	-	-

2.7.2 Mineralogical maximum potential acidity (MPA_{min})

The ABA method determines the MPA based on the assumption that a waste rock sample's total sulphur or sulphide content occurs primarily in the form of pyrite. This assumption can drastically overestimate the true acid generating capabilities of that waste rock sample as all sulphur and sulphide minerals do not generate acid. The true acid generating capabilities can be evaluated more accurately by conducting a mineralogical investigation and determining the sulphide mineral speciation and content. The sulphur or sulphide mineral speciation may provide information on the portion of sulphur of sulphide that may occur in the form of acid-generating minerals (Karlsson *et al*., 2018).

The mineralogical maximum potential acidity (MPA_{min}) is calculated by multiplying the weight percentage of the acid-generating mineral present in the sample ($wt\%_{AG,min}$) with the weight percentage of sulphur in the mineral ($wt\%_{s,min}$) and with maximum potential acidity constant (C_{MPA}) (Karlsson *et al*., 2018).

CHAPTER 3: MATERIALS AND METHOD

3.1 Sample collection

The alkaline and acidic gold mine tailing piles are located approximately 3.8 km apart in the Sabie district in the Mpumalanga province, South Africa (Figure 6). Sabie has a high yearly rainfall, averaging 1195 mm a year. Additionally, Sabie has a high relative humidity ranging from 58% (August) to 80% (January) (CLIMATE SABIE, SOUTH AFRICA, 2022). High yearly rainfall in conjunction with high relative humidity provides ideal conditions for sulphide oxidation and dissolution of minerals.

Studies conducted by Rudzani, L. *et al.* (2018) found that one tailing pile found is Sabie district in the Mpumalanga province, South Africa had become acidic, and another tailings pile in Sabie district in the Mpumalanga province, South Africa had alkaline properties. This study was considered when selecting tailings to be sampled.

Both the alkaline and acidic gold mine tailings consist of fines, which have a large surface area allowing for the increasing rate and extent of sulphide oxidation and mineral dissolution. Currently, no tailing impoundments operations are in place, emphasising the need to investigate environmentally and economically sustainable remediation strategies.

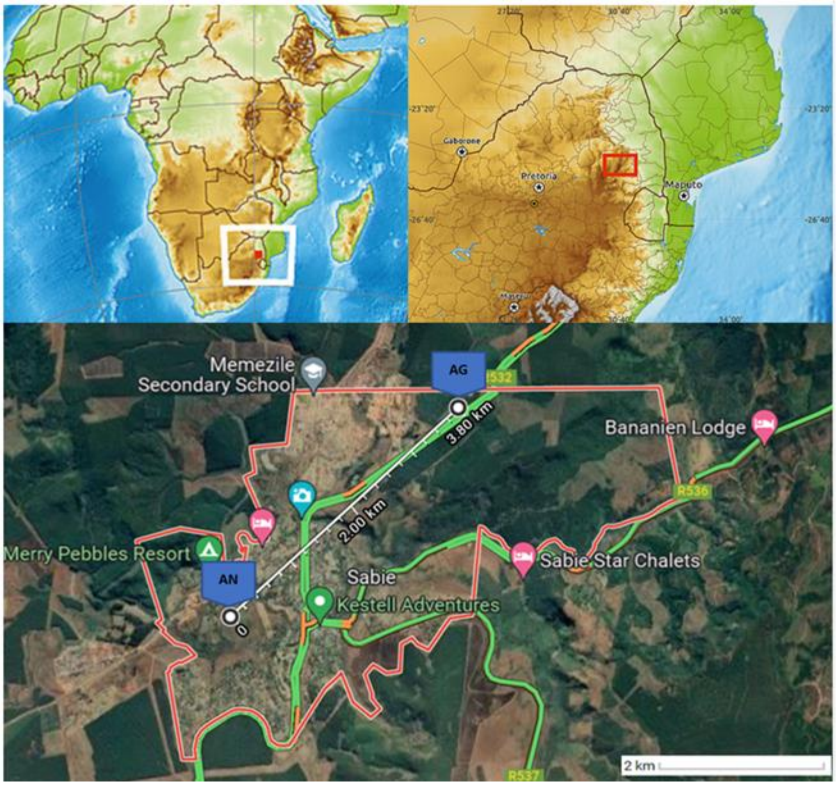

Figure 6: Study area location

Samples were collected during July 2019, which falls in the dry winter season for Sabie. Three sample sets were collected from the acidic gold mine tailing pile, and three sample sets were collected from the alkaline gold mine tailing pile. Samples were collected from the surface at the base of the tailings pile, the surface at the top of the tailings pile and 30 cm below the surface at the top of the tailings pile. Three samples were collected to ensure the mineralogy and properties of the tailing were consistent throughout the tailings pile. During sample collection, it was observed that there was no plant growth on the surface of the acidic gold mine tailings (Figure 7), providing an initial indication the tailings have either become acidic or toxic. Additionally, it was observed that there is substantial plant growth on the surface of the alkaline gold mine tailings (Figure 8). Plant growth prevents erosion and minimises the extent to which water and oxygen penetrate the tailings piles, thus minimising sulphide oxidation and mineral dissolution.

Figure 7: Acidic gold mine tailings pile

Figure 8: Alkaline gold mine tailings pile

3.2 Sample preparation

Each sample set consisted of at least Twelve (12) kilograms of material. The sample was sieved using a 200-mesh sieve to obtain a partial size distribution smaller than 75 µm following static and kinetic test procedures (ASTM D5744-18; Smart et al., 2002; Stewart et al., 2006). Airtight containers were used to store the samples to limit pre-oxidation (ASTM D5744-18).

Two sample mixtures were prepared, namely MIX25 and MIX50. MIX25 was prepared by mixing the acidic and alkaline samples with a 3:1 weight ratio, respectively. The MIX 50 was prepared by mixing the acidic and alkaline samples with a 1:1 weight ratio. MIX25 and MIX50 acid generating capabilities were evaluated using the same static and kinetic test used to evaluate the acid generation of the alkaline and acidic gold mine tailings.

3.3 Acid-Base Accounting

3.3.1 Paste pH

50 mL of deionised water was added to each 25 g sample and mixed to obtain a paste-like slurry. The pH was measured after 2 hours and is referred to as the paste pH (Smart *et al*., 2002).

3.3.2 Acid Neutralising Capacity (ANC)

The standard acid neutralising capacity measures a mine waste material's inherent neutralising ability or buffering capability. The ANC was determined by adding a predetermined quantity of hydrochloric acid (HCl) to a pulverised sample, allowing time to react and then back titrating the solution with sodium hydroxide (NaOH) to determine the amount of hydrochloric acid consumed by the sample due to acid neutralising reactions (Sobek *et al.,* 1978).

The modified ANC method is essentially the same as the standard ANC method but with a different back titration procedure. This procedure is conducted to overcome the effect of siderite on the measured ANC (Stewart *et al*., 2006). The following method of determining the modified ANC, as reported by Stewart *et al*., 2006, is a modified version of the stander procedure derived by Sobek *et al*. (1978).

3.3.3 Determining Acid Neutralising Capacity

1. Two drops of 1:3 HCl (about 8% HCl) were added to 0.5 g sample of AG, AN, MIX25 and MIX50 to determine the fizz rating. No reaction was observed for AG, suggesting

that AG will have a low acid neutralising mineral content. A slight reaction was observed from MIX50, and MIX25, indicating a low to moderate calcite content. AN observed a slightly aggressive reaction, indicating a high content of acid neutralising carbonates. A fizz rating of 0, 2, 3 and 4 was allocated to AG, MIX50, MIX25 and AN, respectively.

Table 9:"Fizz Rate" and corresponding concentration and quantities of acid used in the ANC test

Reaction	Fizz Rating	HCl Molarity (M)	HCl volume (mL)	NaOH molarity (M)
No reaction observed	0	0.5	4	0.1
Slight reaction observed	1	0.5	8	0.1
Moderate reaction observed	2	0.5	20	0.5
Strong reaction observed	3	0.5	40	0.5
Very strong reaction observed	4	1	40	0.5
Extreme reaction observed	5	1	60	0.5

2. Exactly 2 grams of AG, MIX25, MIX50 and AN were accurately weighed into four Erlenmeyer flasks. 4 mL of 0.5 M HCl was added to AG based on its fizz rating of 0 (Table 9). 20 mL of 0.5 M HCl was added to MIX25. 40 mL of 0.5 M HCl was added to MIX50, and 60 mL of 1 M HCl was added to AN (Table 9). 20 mL of distilled water was added to each sample.

3. The sample solutions were heated on a hotplate to a temperature of about 85°C. A magnetic stirrer was used to stir the solution during heating continuously. The samples were heated for 2 hours, the solution was maintained at the temperature between 80 °C – 90°C.

4. The solutions were allowed to cool down to room temperature, after which the pH of the solution was measured. The pH of the solutions were 0.8, 1.4, 1.2, and 0.6 for AG, MIX25, MIX50 and AN, respectively. According to Stewart *et al*. 2006, the sample solution should be between 0.8 to 1.5 to ensure complete digestion of acid-neutralising components.

5. A blank was prepared for each sample following the same procedure.

6. Deionised water was added to AG, MIX25, MIX50, AN and each blank to obtain a total solution volume of 125 mL

7. The AG, MIX25, MIX50, AN and blank solutions were back titrated to a pH of 5 using a 50 mL burette and 0.5 M sodium hydroxide (NaOH) corresponding to a fizz rating of 3 (Table 9).

8. Two drops of 30% hydrogen peroxide (H_2O_2) were added at a pH of 5 to encourage the oxidation of ferrous iron and the precipitation of ferric hydroxide ($Fe(OH)_3$) (Stewart et *al*., 2006).

9. The back titration was continued to a pH of 7 and 8.3. The volume of NaOH used to titrate the solutions to a pH of 7 and 8.3 were recorded.

10. The ANC is calculated using Eq. (17).

$$\mathbf{ANC} = \frac{\left(\mathbf{V_{HCl}} - \left[\mathbf{V_{NaOH}} \times \frac{\mathbf{V_{HCl\,,Blank}}}{\mathbf{V_{NaOH\,,Blank}}}\right]\right) \times \mathbf{M_{HCl}}}{\mathbf{m}} \times \mathbf{C} \qquad (\mathbf{17})$$

V_{HCl} = Volume HCl acid used (mL)

$V_{HCl\ Blank}$ = Volume acid added to the blank (mL)

V_{NaOH} = Volume NaOH used (mL)

$V_{NaOH\ Blank}$ = Volume NaOH added to blank (mL)

M_{HCl} = Molarity of HCl acid used (M)

m = Sample weight (g)

C = Conversion factor with a value of 49 to obtain the ANC in kg H_2SO_4/t.

3.3.4 Maximum Potential Acidity (MPA)

The total sulphide weight percentage in each sample was used to calculate the MPA (kg H_2SO_4/t) using equation Eq. (18) (Smart *et al*., 2002).

$$\boldsymbol{MPA} = (\boldsymbol{S}\%) \times \mathbf{30.6} \qquad (\mathbf{18})$$

The total sulphur and sulphide content (weight percentage) were determined utilising an ELTRA CS 2000, which consists of a weighing scale, computer with required programs, ELTRA induction and resistance furnace, as seen in Figure 9.

Figure 9: ELTRA CS 2000 Carbon Sulphur Determinator PC controlled.

The following procedure of determining the total sulphur, sulphide and carbon weight percentage was constructed using the ELTRA CS 2000 operating manual. The induction furnace was used to determine the total sulphur and total carbon content of the sample. The resistance furnace was used to determine the total sulphide content.

1. The computer was switched on, and the oxygen and pressure valves were opened.
2. The main power switch of the induction and resistance furnaces was turned to position 1 to allow them to warm up and stabilise. The furnaces warmed up and stabilised after about two hours.

Induction furnace

3. The main power switch of the induction furnace was turned to position 3.
4. Quality checks

Quality checks were conducted to assess whether the induction and resistance furnace accurately detects the carbon and sulphur content of the sample. The quality checks were done by analysing standards which has a known carbon and sulphur content.

5. Analysing sample.

   5.1 0.7 g of tungsten and 1 g of steel shavings were accurately weighed into a ceramic crucible.

   5.2 The crucible was placed on a scale connected to the computer system. 2 g of a sample was weighed into the crucible.

   5.3 The weighing function was activated by pressing F5 on the keyboard to allow the computer to import the weight of the sample as measured by the scale.

   5.4 The crucible was then placed into the induction furnace.

   5.5 The analysis was initiated by pressing F4 on the keyboard to allow the furnace to conduct the sulphur and carbon analysis.

   5.6 The results were obtained after a few minutes and were recorded.

Resistance furnace

6. Analysing sample.

   6.1 A ceramic crucible was placed on the scale.

   6.2 0.5 g of the sample was weighed into the crucible.

   6.3 The weighing function was activated by pressing F5 on the keyboard to allow the computer to import the weight of the sample as measured by the scale.

   6.4 The analysis was initiated by pressing F4 on the keyboard to allow the furnace to conduct the sulphide analysis.

   6.5 The crucible was loaded into the furnace after the analysis has been initiated.

   6.6 The results were obtained after a few minutes and were recorded.

3.4 Net acid generation (NAG) test

3.4.1 Single addition net acid generation (NAG) test

Single addition NAG tests are appropriate for samples with a total pyritic-sulphur content less than 1 (%wt.). The following procedure was conducted as described by Smart *et al*. 2002.

Procedure

1. 2.5 g of samples AG, MIX25, MIX50 and AN were accurately weighed into a 500 mL Erlenmeyer flask.
2. 250 mL of 15 (%vol.) H_2O_2 was added to each sample using a graduated cylinder to obtain a solution referred to as the NAG solution.
3. The Erlenmeyer flask was covered with a watch glass, placed in a fume hood, and left to reach overnight.
4. The NAG solutions were heated until gently bubbling for 2 hours to remove excess H_2O_2 and to encourage the release of inherent acid neutralising capacity. The NAG solutions were continuously stirred during heating using a magnetic stirrer.
5. The sample solutions were allowed to cool down to room temperature.
6. Deionised water was added to the solution to obtain a volume of 250 mL
7. The pH of the NAG solutions was measured and is referred to as the NAGpH.
8. The NAG solutions were titrated with 0.1 M NaOH to a pH of 4.5, and the volume of NaOH used during the titration was recorded.

The volume and concentration of NaOH were used to calculate the NAG value using Eq. (19).

$$\boldsymbol{NAG = (49 \times V \times M)/w} \qquad (\mathbf{19})$$

NAG = Net acid generation (kg H_2SO_4/t)

V = Volume of NaOH used during the titration (mL)

M = Concentration of NaOH used during the titration (mol/L)

W = Weight of the soil sample (g)

3.5 Acid Buffering Characteristic Curve (ABCC) Test

The following procedure was conducted as described by Smart *et al.*, 2002:

1. 100 mL of deionised water was added to 2.5 g sample in a 250 mL Erlenmeyer flask.

2. 0.2 mL of 0.1 M hydrochloric acid (HCl) was incrementally added to the solution using a single channel micro manually adjustable volume pipet. The solution was continuously stirred during the incremental addition with the use of a magnetic stirrer.

3. The pH of the solution was measured 17 min after each addition. The following HCl incremental addition would follow directly after the pH was measured for the previous addition.

4. HCl was incrementally added up until the solution reached a pH of 2.5.

5. The concentration and volume of HCl acid used during incremental additions were converted to the kg H_2SO_4/t equivalent using equation (20).

$$\boldsymbol{H_2SO_4\ added\ (kg/t) = (V \times C \times 49)/W} \qquad (\mathbf{20})$$

6. The measured pH was plotted against the quantity of acid added to obtain the acid buffering characteristic curve.

3.6 Leach column test

The kinetic leach column tests entail a laboratory leaching procedure which enhances the reaction-product transport from a solid phase material sample into aqueous leachate. Additionally, it allows for measurable rates of weathering products released by the solid phase material into the leachate. A fixed volume of aqueous leach is used to mobilise weathering products collected weekly. The leachate is analysed for acidity/alkalinity, pH, sulphate, specific conductance and other selected analytes (ASTM 2018).

The leach columns (option B) were constructed using ASTM D5744-18, the most widely used standard test method for laboratory weathering solid materials using a humidity cell. ASTM D5744-18 provides detailed instruction on the design of the columns, materials to be used, significant uses of the columns, sampling procedure, sample preparation, apparatus assembly, operating procedure etc.

One set of columns were constructed using the ASTM D5744-18. The leach columns were built with an inside diameter of 20.3 cm and a height of 10.2 cm (F) to accommodate the gold mine tailings with an extremely small partial size distribution (< 150 µm).

Figure 10: Leach Column Components

3.6.1 Sample preparation

The air-dried gold mine tailings were screened using a 150 µm (100 mesh) screen.

3.6.2 Column configuration

1. Each leach column cell was weighed with the lid connected to the closeted 0.1 g (M_c)
2. One layer of filter media (polypropylene membrane) was cut to the inner diameter size to fit snugly in the column, supported by the perforated plate. Each column's layers of filter media were weighed (M_{fm}) to the closest 0.1 g. Each column with its respective filter media was weighed to the closeted 0.1 g (M_{Cfm}).
3. Three columns were filled with 1 kg acid-generating mine tailing (Figure 11) and then weighed to the nearest 0.1 g (M_{AGG}).
4. Three columns were filled with 1 kg of acid-neutralising gold mine tailings (Figure 12) and then weighed to the nearest 0.1 g (M_{ANG}).
5. Three columns were filled with 0.75 kg of acid-generating gold mine tailings followed by the additional filling of 0.25 g of acid-neutralising gold mine tailings (Figure 13) and then weighed to the nearest 0.1 g.

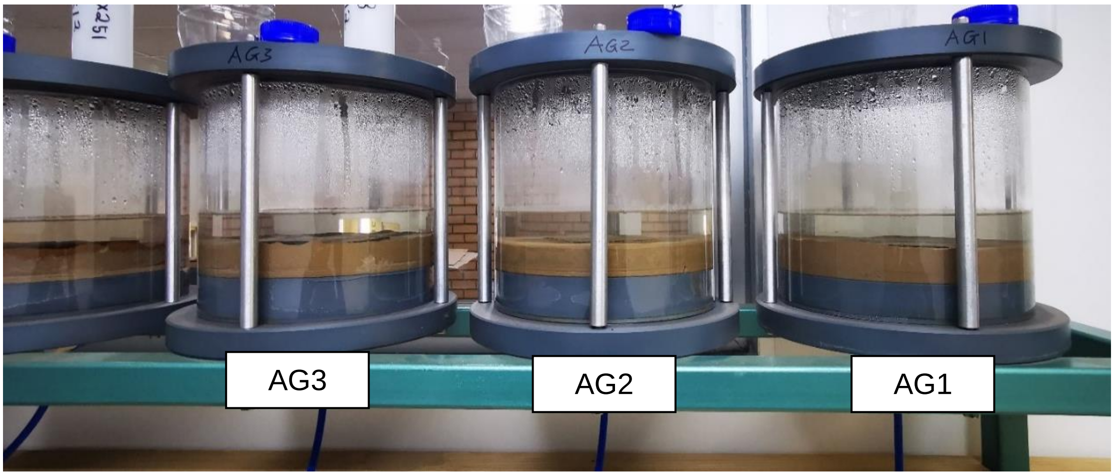

Figure 11: AG Leach Columns

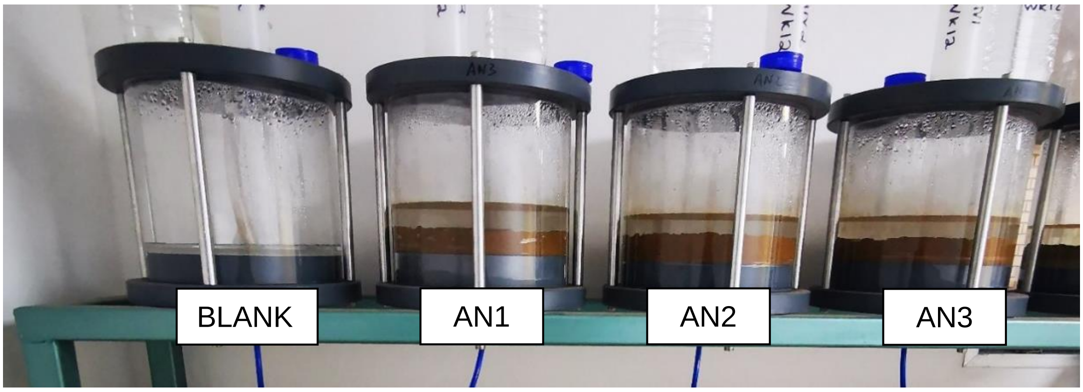

Figure 12: AN and Blank Leach Columns

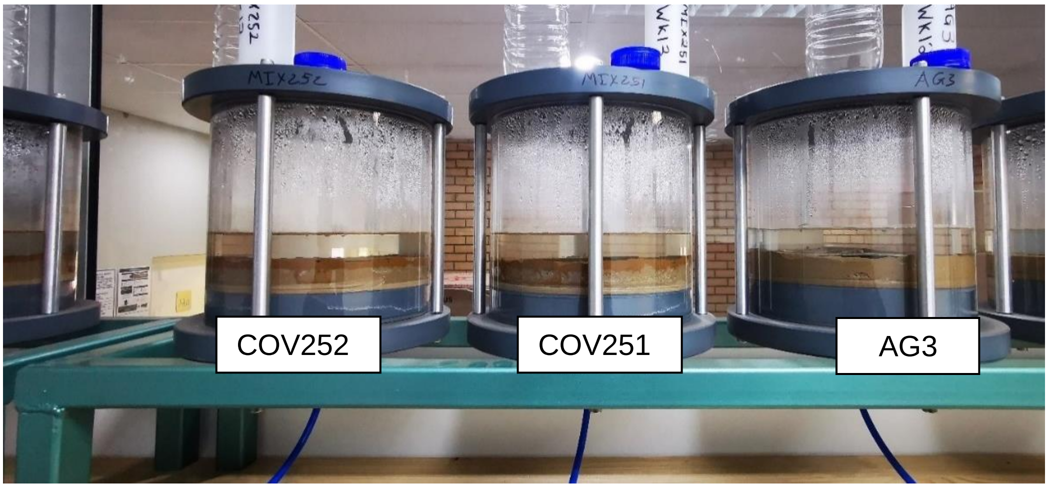

Figure 13: COV25 and AG Leach Columns

3.6.3 Leaching protocol

The leach column test is designed to follow a seven-day leach cycle, requiring the leaching procedure to be completed on the same day of the week (for example, every Wednesday). The removal of the pre-oxidation product was not required for the study; thus, three consecutive leaches on the first week (week 0) were not performed. Each leach was conducted using 750 ml of deionised water, which falls between the leach volume boundary of 500 mL to 1000 mL, which are the respective lower and upper boundaries of the required leach volume (ASTM D5744-18). The leach column was flooded with deionised water for a period of 1 hour. The lid of the columns remained connected to prevent external airborne contamination and to limit the effect of evaporation. The columns were drained after the 1 hour had passed. The drainage process was initiated by opening the drainage valve allowing the leachate to drain into the collection vessel. The drainage process was allowed to continue for the rest of the leaching day. The collection vessels were then set aside for leachate analysis.

3.6.4 Leachate analysis

The mass of the container collecting the leachates were measured before and after leaching. Leachate collected from the columns and deionized water used to perform leachate were sent for analysis to determine the following chemical parameters summarised in Table 10.

Table 10: Deionized water and leachate water analysis

Measurements
pH
Electrical Conductivity (EC) (mS/m)
Total Dissolved Solids
Total Alkalinity/Acidity
Mass of leachate collection container before leaching
Mass of leachate container after leaching
Mass of leachate
Volume of leachate
Sulphate-SO_4

Leachate collected from the columns was filtered using a 0.45 µm filter and sent for elemental analysis (ICP-MS) to determine the following concentrations summarized in Table 11.

Table 11: Deionised water and leachate elemental analysis

Element (mg/l)	Abbreviation (mg/l)
Silver	Ag
Aluminium	Al
Arsenic	As
Barium	Ba
Beryllium	Be
Calcium	Ca
Cadmium	Cd
Cobalt	Co
Chromium	Cr
Copper	Cu
Iron	Fe
Potassium	K
Magnesium	Mg
Manganese	Mn
Sodium	Na
Nickel	Ni
Lead	Pb
Titanium	Ti
Vanadium	V
Zinc	Zn

3.7 Mineralogy

The XRD and XRF analysis were conducted by Belinda Venter at the XRD and XRF laboratory at the Centre for Water Science and Management, North-West University (NWU) Potchefstroom Campus. The different crystalline phases in the samples were identified and quantified using X-Ray diffraction (XRD), a non-destructive analytical technique. The samples were prepared using a backloading preparation method. The samples were analysed using PANalytical X'Pert Pro multipurpose diffractometer with X'Celerator detector and fixed slits with Fe-filtered Co-Kα radiation.

PANalytical Highscore^{+}program, ICDD PDF 4+ and PAN ICSD database were used to identify the crystalline mineral phases present in the samples. The Rietveld method was used to determine relative phase amount or quantity (wt %).

The concentration of elements present in the samples were determined using X-Ray Fluorescence (XRF) which is a non-destructive analytical technique. The samples were analysed using a PANalytical Axios^{mAX} XRF spectrometer, equipped with a 50 kV Rh-anode

X-ray tube and a high-resolution silicon drift detector. The calibration was done using and calibrated using a number of international and national certified reference materials.

3.7.1 Mineralogical ANC (ANC_{min})

The total acid-neutralising capabilities of AN based-on mineralogy (ANC_{min}) were calculated using Eq. (21) (Karlsson *et al.,* 2018).

$$\boldsymbol{ANC_{min} = ANC_{min,c} + ANC_{min,nc}} \tag{21}$$

The acid neutralisation capabilities of AN based on the carbonate minerals ($ANC_{min,c}$) were calculated using Eq. (22) (Karlsson *et al*., 2018).

$$\boldsymbol{ANC_{min,c} = 83.3 \times \left[\frac{MW_c}{MW_{c,min}}\right] \times wt\%_{c,min} \times CF} \tag{22}$$

- $ANC_{min,c}$ is the ANC contribution of carbonate minerals to the total ANC_{min}.
- MW_c is the carbon molar weight of carbon present in the mineral in the form of a carbonate.
- $MW_{c,min}$ is the molar weight of and carbonate mineral, respectively (g/mol).
- $wt\%_{c,min}$ is the weight percentage of carbonate mineral in the sample.
- CF is a conversion factor with a value of 0.98 to convert the unit of ANC_{min} from kg $CaCO_3$/t to kg H_2SO_4/t.

The ANC contribution of other non-carbonate minerals ($ANC_{min,nc}$) was calculated using equation Eq. 23 (Karlsson *et al.*, 2018).

$$\boldsymbol{ANC_{min,nc} = \left[\frac{MW_{calcite}}{MW_{nc,min}}\right] \times \left[\frac{wt\%_{nc,min}}{100}\right] \times \left[\frac{1000\ kg}{1\ t}\right] \times RC \times CF} \tag{23}$$

- $ANC_{min,nc}$ is the ANC contribution of no-carbonate minerals to the total ANC_{min}
- $MW_{calcite}$ and $MW_{nc,min}$ represent the molar weight of calcite and non-carbonate minerals respectively.
- $wt\%_{nc,min}$ is the weight percentage of non-carbonate mineral in the sample.

- RC is a reactivity coefficient of neutralising mineral identified in the sample and is summarised in Table 12 (Karlsson *et al.*, 2018).

Table 12: Relative reactivity of identified neutralising minerals

Mineral Class	**Mineral**	**Relative reactivity (RC)**			
		Average mineral content			
		100%	30%	3%	0.3%
Carbonates	Calcite	1	1	1	1
Fast-weathering	None	0.6	0.67	0.3	0.1
Intermediate-weathering	None	0.4	0.2	0.03	0.01
Slow-weathering	Kaolinite	0.02	0.013	0.002	-
Very slow-weathering	Muscovite	0.01	0.007	0.001	-
Inert	Quartz	0.004	0.0007	-	-

CHAPTER 4: RESULTS AND DISCUSSION

4.1 Acid-base accounting

The results obtained from the ABA test method are summarised in Table 13. As seen in Table 13, the paste pH of AG is extremely low, with a value of 2.5. A paste pH of 2.5 confirms that the acidic gold mine tailings (AG) are acidic, indicating that AG is an acid-generating sample and may contain a high concentration of stored acidity. According to Weber *et al*. (2006), a sample with a paste pH below 4, may contain up to 30 kg H_2SO_4/t, which will be released instantaneously when exposed to water. AN has a relatively high paste pH of 7.7. The high paste pH of AN provides an initial indication that AN may contain a high quantity of highly soluble acid neutralising minerals such as carbonates that may contribute to acid neutralisation indicating that it may be a non-acid generating sample containing a high concentration. However, samples with a pH above 7 may still generate AMD if the acid-neutralising minerals are consumed to the point of depletion before acid-generating sulphides (Weber *et al*., 2006; Skousen, 2017; Nieva *et al*., 2018).

MIX25 and MIX50 have paste pH’s of 5.1 and 6.1, respectively, which is relatively high when compared to the paste pH of AG. The high paste pH of MIX25 and MIX50 indicates AN portion of the mixture contains a high quantity of readily available acid neutralising minerals, capable of neutralises acid generated by the AG portion of the mixtures, as the paste pH test procedure only assesses the acidity or alkalinity released by highly reactive minerals and highly soluble salts due to the short time frame in which the paste pH test is conducted. This provides an initial indication that both mixtures may be a suitable option for neutralising acid generated by the AG portion of the sample.

AG has no acid-neutralising capabilities, as seen in Table 13. The acidic gold mine tailings pile (AG) is thus unable to neutralise any acid generated by AG, which corresponds to the low paste pH of AG. Thus, when calculating the NAPP by subtracting the ANC from the MPA, AG will have a NAPP of 13 kg H_2SO_4/t. Thus, AG may generate up to 13 kilograms of sulphuric acid per ton of material before the acid generating capabilities of AG are depleted. It is important to note that the ABA method calculated MPA by assuming that all of the sulphur contained within the AG sample occurs only in the form of Pyrite, which may overestimate the MPA to a certain extent. However, due to the acidic conditions of the AG tailings, ferric iron will be the primary oxidiser of sulphide minerals which means the true maximum potential acidity may be up to four times greater than the calculated MPA found in Table 13.

As seen in Table 13, AN has an extremely high ANC of 184 kg H_2SO_4/t, which confirms that AN contains a high concentration of acid neutralising minerals. When comparing the ANC of AN (184 kg H_2SO_4/t) to the MPA of AN (2 kg H_2SO_4/t), AN's acid neutralising capabilities overwhelm to acid-generating capabilities of AN. AN has a NAPP of -182 kg H_2SO_4/t and RANC/MPA of 86 and is thus classified as a non-acid forming sample using conventional ABA classification criteria (Table 5).

MIX25 and MIX50 have ANC values of 56 and 96 kg H_2SO_4/t, respectively, which are relatively high when compared with their MPA values of 10 and 8 kg H_2SO_4/t, respectively. The large difference in ANC and MPA of MIX25 and MIX50 suggests that MIX25 and MIX50 may contain a sufficient quantity of acid neutralising minerals to neutralise, and the acid generated by the AG portion of the mixtures. Using ABA classification criteria (Table 5), MIX25 and MIX50 are considered to be non-acid generating samples. However, the ABA test method does not provide any information on the availability of acid neutralisation. MIX25 and MIX50 may be acid generating if the rate of acid generation is substantially high than the rate of acid neutralisation.

Table 13: ABA results

Sample	Paste pH	ANC (kg H_2SO_4/t)	S_{Total}	MPA (kg H_2SO_4/t)	NAPP (kg H_2SO_4/t)	$R_{ANC/MPA}$
AG	2.5	0	0.43	13	13	0
MIX25	5.1	56	0.34	10	-46	5
MIX50	6.1	96	0.25	8	-89	13
AN	7.7	184	0.07	2	-182	86

4.2 Net Acid Generation (NAG)

As seen in Table 14, AG has a NAGpH of 2.7 and a NAG value of 6.9 kg H_2SO_4/t. Thus, according to the NAG test procedure and interpretation, AG will generate up to 6.9 kg of sulphuric acid per ton of material. Utilising the NAG classification criteria summarised in Table 6, AG is classified as a potential acid-forming sample. MIX25, MIX50 and An have NAG values of 0 kg H_2SO_4/t, suggesting that MIX25, MIX50 and AN will neutralise any acid generated and will not release any acid. MIX25, MIX50 and AN have NAGpH values of 4.9, 5 and 5.9, respectively. MIX25, MIX50, and AN have NAGpH greater than 4.5 and are thus considered to be non-acid forming using the classification criteria summarised in Table 6, as the sample will contain sufficient readily available carbonates to render it non-acid producing.

Table 14:NAG results

Sample	NAGpH	NAG (kg H_2SO_4/t)	NAG Classification
AG	2.7	6.9	Potential Acid Forming
MIX25	4.9	0	Non-Acid Forming
MIX50	5	0	Non-Acid Forming
AN	5.9	0	Non-Acid Forming

4.3 Acid Buffering Characteristic Curve (ABCC)

The ABCC test was conducted as the ABA and NAG test methods do not provide insight into the readily availability of acid neutralisation. The quantity and rate of acid generation increase substantially when the pH of tailings drops below a pH of 4 as ferric iron becomes the primary oxidiser at low pH conditions. Thus, the effective or readily available acid-neutralising capacities refers to the quantity of acid neutralised before the pH of the solution drops to a value of 4.

AG does not have any acid neutralising capabilities and thus does not have an ABCC curve. As seen in Figure 14 and Table 15, AN able to neutralise up to 170 kg H_2SO_4/t before the pH of the solution drops to a pH of 2.5, which corresponds closely to the ANC of 184 kg H_2SO_4/t determined using the ABA test method. The ABCC thus confirms that AN has high acid neutralising capabilities. Most importantly, as seen in Figure 14, AN is able to neutralise up to 155 kg H_2SO_4/t before the pH of the solution drops to a pH of 4. This suggests that up more than 80% of ANC of AN is readily available for acid neutralisation.

MIX25 and MIX50 have the ability to neutralise 53 and 87 kg H_2SO_4/t, respectively, before the pH of the solution drops below a pH of 2.5, which corresponds closely to the ANC results determined using the ABA method (Table 15). MIX25 and MIX50 have high readily available acid neutralising capabilities as they are able to neutralise up to 35 and 77 kg H_2SO_4/t, respectively, before the pH of the solutions drops to a pH of 4.

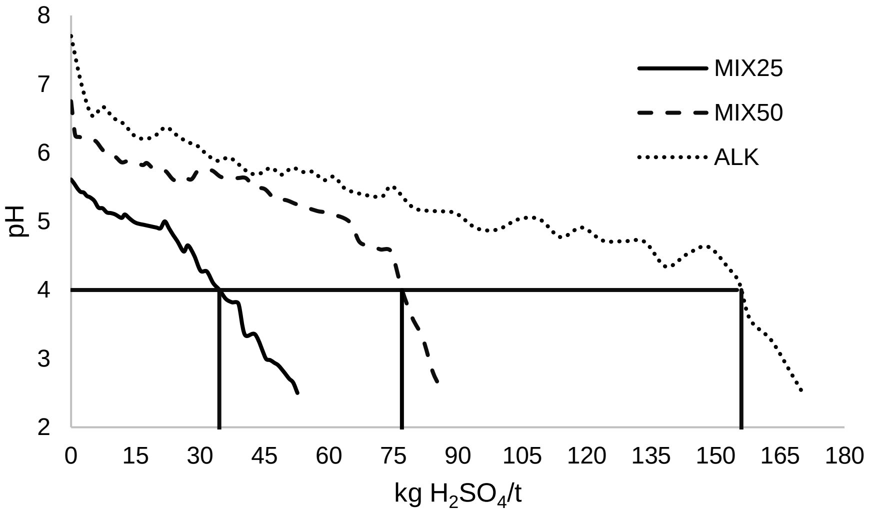

Figure 14: ABCC of MIX25, MIX50 and AN

Thus, the large portion of the ANC of MIX25, MIX50, and AN determined using the ABA method is readily available for acid neutralisation. The AN potion of MIX25 and MIX50 will thus be able to neutralise acid generated by the AG portion of MIX25 and MIX50. Furthermore, it can be concluded that the acid neutralising capabilities of MIX25, MIX50 and AN are not overestimated and will be readily available for acid neutralisation. The high readily available acid neutralising capabilities is most like due to the occurrence of highly reactive and soluble carbonate minerals such as calcite or dolomite in AN.

Table 15: ANC comparison

Sample	ANC (ABA) (kg H_2SO_4/t)	ANC ($ABCC_{pH=2.5}$) (kg H_2SO_4/t)	ANC ($ABCC_{pH=4}$) (kg H_2SO_4/t)
MIX25	56	53	35
MIX50	96	87	77
AN	184	170	155

4.4 Final classification

Using the NAPP, NAGpH and the classification criteria summarised in Table 7, the acid-generating capabilities of AG, MIX25, MIX50 and AN can be classified as PAF, NAF, NAF and NAF, respectively, with a high degree of confidence (Table 16).

Table 16: Final classification

Sample	NAPP (kg H_2SO_4/t)	NAGpH	Classification
AG	13	2.7	PAF
MIX25	-46	4.9	NAF
MIX50	-89	5	NAF
AN	-182	5.9	NAF

4.5 Mineralogy

The minerals found in the AG and AN samples using XRD analysis (Appendix A and Appendix B) are summarised in Table 17. As seen in Table 17, AN has a high dolomite content of 22.4%. Dolimite is a highly reactive acid-neutralising carbonate mineral, confirming AN's highly readily available acid neutralising capacity. As seen in Table 17, AG does not contain any carbonate minerals or fast weathering acid neutralising minerals, confirming that AG has no acid neutralising capabilities.

Table 17: Mineralogy

Mineral	Molecular formula	AN	AG
Quartz	SiO_2	65.4	86.9
Dolomite	$MgCa(CO_3)_2$	22.4	0
Muscovite	$(KF)_2(Al_2O_3)_3(SiO_2)_6$	6.2	10.2
Goethite	FeO_2H	4.6	2.7
Hematite	Fe_2O_3	0.7	0.1
Gypsum	$CaSO_4 \cdot 2H_2O$	0.6	0

As seen in Table 17, The slow-weathering acid-neutralising mineral Muscovite was found in AN and AG. That acid neutralising contributions of Muscovite is considered to be negligible and will thus not be considered in further calculations (Karlsson *et al.,* 2018).

4.5.1 Mineralogical acid neutralising capabilities (ANC_{min})

The acid-neutralising based on mineralogy (ANC_{min}) of AN was calculated using equation (23), and the weight percentage of dolomite present of 22.4 % (Table 17), as seen in (24). The molecular weight (MW_c) of carbon was multiplied by 2 as there are 2 carbon atoms in a dolomite molecule, as seen in Table 17. The ANC_{min} AN was calculated to be 238 kg H_2SO_4/t. The calculated ANC_{min} of 238 kg H_2SO_4/t correlates to the acid neutralising capabilities of AN determined using the modified ABA and ABCC, confirming AN has high acid neutralising capabilities.

$$\boldsymbol{ANC_{min,c} = 83.3 \times \left[\frac{MW_c}{MW_{c,min}}\right] \times wt\%_{c,min} \times CF} \tag{24}$$

$$\boldsymbol{ANC_{min,c} = 83.3 \times \left[\frac{2 \times 12.01}{184.41}\right] \times 22.4 \times 0.98}$$

$$\boldsymbol{ANC_{min,c} = 238\ kg\ H_2SO_4/t}$$

4.6 Leach column

4.6.1 Leach Column pH

The leach column leachate pH results of the AG gold mine tailings columns (AG1, AG2 and AG3) are presented in Figure 15. As seen in Figure 15, the leachate pH of AG1, AG2 and AG3 are extremely low from the first week of leaching, with a pH of 2.2 (week 1), which is indicative of a release of stored acidity. The pH of the leachate of AG1, AG2 and AG3 increase slightly to a pH of 3, maintaining an acidic pH throughout the leach column experiment, confirming the static test results. The leach column leachate pH results confirm that the AG tailings have become acidic and will continue to generate an acidic effluent for the foreseeable future.

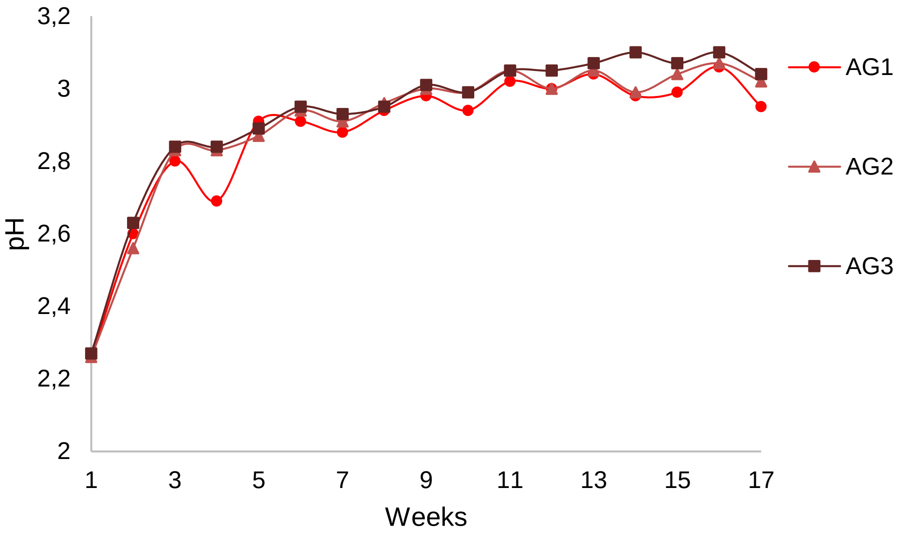

Figure 15: AG1, AG2 and AG3 Leachate pH

The pH of the leachates of AN gold mine tailings (AN1 and AN3) are presented in Figure 16. The leachate pH results of AN2 were compromised due to the occurrence of channelling, rendering the results unusable and will thus not be discussed. As seen in Figure 16, the pH of AN1 and AN3 remained alkaline throughout the leach column experiment, gradually increasing to a pH of 8.2 at the end. The slight increase of the leachate pH of AN1 and AN3 from 7.5 (week1) to 8.2 (week17) may indicate an increase in the rate of dissolution of acid neutralising minerals (dolomite) as time progresses. Additionally, the leach column leachate pH results confirm that the AN gold mine tailings are non-acid.

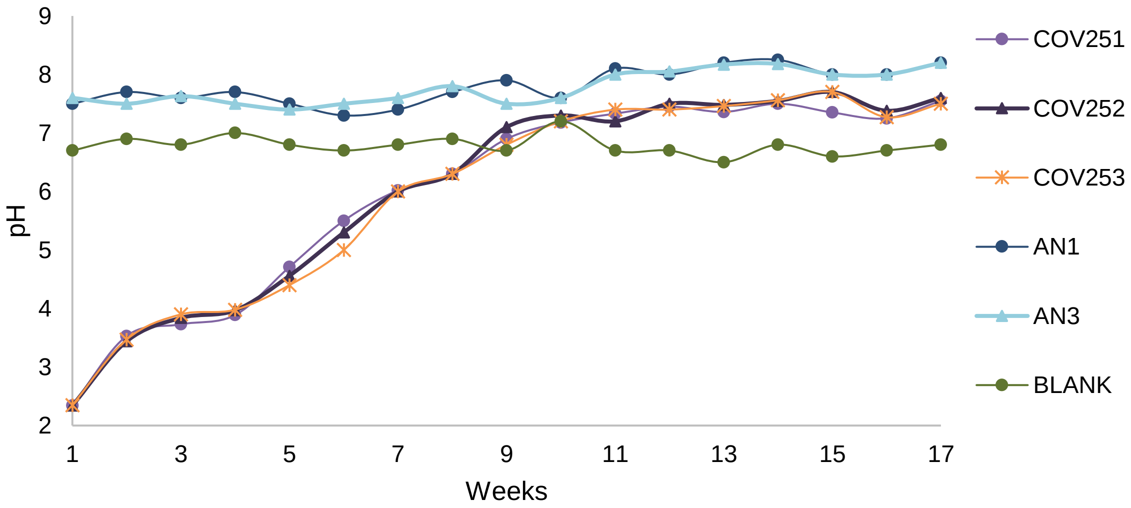

Figure 16: MIX251, MIX252, MIX253, AN1, AN2 and Blank leachate pH

As seen in Figure 16, the leach columns utilised AN gold mine tailings as a top acid neutralising cover with AN to AG weight ratio of 1:3 (COV251, COV252 and COV253) initially produced acidic leachates with a pH of 2.5 during the first week of leaching. The low initial leachate pH indicated a release of stored acid by the bottom AG layer of COV251, COV252 and COV253. The low leachate pH of COV251, COV252 and COV253 indicate that the neutralising minerals such as dolomite were not able to react or dissolve to such an extent to neutralise the sored acidity released by the AG. However, as the leach column test progressed, the leachate pH of the COV251, COV252 and COV253 increased substantially to neutral conditions (week 2-9), becoming alkaline after nine weeks of leaching. Thus the AN acid neutralising cover was able to neutralise acid generated by the bottom AG layer. Additionally, the increase in leachate pH suggests that the rate of acid neutralisation increases as time progresses.

4.6.2 Leach Column Acidity

The acidity results of the leach column test of AG1, AG2, AG3, COV251, COV252 and COV253 are summarised in Table 18. As seen in Table 18, AG1, AG2 and Ag leach columns released leachates with high acidity (weeks 1-2). The acidity of the leachates of AG1, AG2 and AG3 decreases substantially after the first two weeks of leaching. However, AG1, AG2 and AG3 continued to generate a acidic leachate throughout the leach column experiment. The high acidity of leach columns AG1, AG2 and AG3 confirm that AG gold mine tailings contain a substantial quantity of stored acidity which will be released immediately when exposed to water.

As seen in Table 18, the COV251, COV252, and COV253 leach columns generated leachate with a high acidity during the first week of leaching as the top acid neutralising layer (AN) was not able to neutralise the large quantity of acid released by the sored acidity of the bottom acid-generating layer (AG). The top acid neutralising layer was not able to neutralise the acid generated by the bottom acid-generating layer (AG) as the rate of dissolution of acid generating salts (stored acidity) of the bottom acid-generating layer (AG) is substantially higher compared to the rate of dissolution of acid neutralising minerals namely dolimite in the top acid neutralising layer (AN).

Keeping in mind that the AG columns were loaded with 1 kg of AG gold mine tailings and COV25 leach columns were loaded with 0.75 kg AG (bottom layer) and 0.25 kg AN as the top acid neutralising layer, it can be seen leach columns COV251, COV252 and COV253 release leachates of which the acidity was four less than the leachates produced by AG1, AG2 and AG3 (week 2-17). Thus, it can be concluded that AN does contribute to acid neutralisation and that prolonged exposure will ensure effective acid neutralisation.

Table 18: Leach Column Acidity

	Acidity (mg $CaCO_3$/L)					
Week	AG1	AG2	AG3	COV251	COV252	COV253
1	7900	8500	7820	6630	6580	6440
2	256	268	220	54	60	68
3	80	88	180	20	24	18
4	84	82	80	24	26	34
5	64	68	64	24	24	24
6	60	62	60	14	14	8
7	62	61	60	22	24	21
8	56	54	52	11	10	10
9	72	60	58	14	12	10
10	64	62	61	9	9	10
11	48	46	44	6	7	6
12	47	47	45	4	4	6
13	46	44	43	6	5	6
14	50	49	47	6	5	5
15	48	45	43	6	6	7
16	52	52	46	9	4	4
17	38	37	35	6	4	4

4.6.3 Leach Column Alkalinity

The leach column alkalinity results are presented in Table 19. The AG1, AG2 and AG3 leach column produced leachates with pH below 3.2 and thus have an alkalinity of 0 mg $CaCO_3$/L. As seen in Table 19, when excluding the first week of leaching, AN1 and AN3 produced leachate with alkalinity ranging from 60 – 70 $CaCO_3$/L confirming the occurrence of acid-neutralising mineral dissolution. Furthermore, the alkalinity of the leachates increased as the leach column experiment progressed, indicating that the rate of acid-neutralising minerals dissolution increased as time progressed.

As seen in Table 19, COV251, COV252 and COV253 produced leachate with 0 mg $CaCO_3$/L. However, after 5 weeks of leaching, COV251, COV252 and COV253 produced leachates ranging from 3 - 4 mg $CaCO_3$/L (week 6), which increased to 32 – 34 mg $CaCO_3$/L (week 17). The increase in alkalinity suggests that the rate of acid generation of the bottom acid-generating layer (AG) is lower than the rate of acid neutralisation due to dolomite dissolution of the top acid neutralising layer (AN), confirming that AN possesses that requires acid neutralising capabilities to neutralise acid generated by AG over a prolonged period of time.

Table 19: Leach Column Alkalinity

	Alkalinity (mg $CaCO_3$/L)				
Week	COV251	COV252	COV253	AN1	AN3
1	0	0	0	24	22
2	0	0	0	44	46
3	0	0	0	64	60
4	0	0	0	64	68
5	0	0	0	68	60
6	5	4	3	64	60
7	5	4	3	66	70
8	16	15	20	67	68
9	28	31	30	68	66
10	30	32	35	69	68
11	33	37	34	70	70
12	33	34	32	66	66
13	31	32	32	67	64
14	31	34	33	70	66
15	32	34	32	72	72
16	32	32	32	72	72
17	32	34	32	72	72

CHAPTER 5: CONCLUSION AND RECOMMENDATIONSs

5.1 Conclusion

When considering the ABA, NAG, ABCC and leach column test results, the AG gold mine tailing collected from the Sabie-Pilgrim's Rest Goldfields are considered to be acid forming. The low paste pH of AG confirms that AG has become acidic, and that AG has no acid neutralising capabilities. The AG leach column continuously produced acidic leachate throughout the leach column experiment, which implies that AG will generate an acidic effluent for the foreseeable future. Furthermore, the leach column test confirmed that AG has a high stored acidity content which will be lease immediately when exposed to water.

The AN gold mine tailing were classified as non-acid forming using conventional ABA and NAG test results and associated classification criteria. The ABA test indicated that AN has high acid neutralising capabilities of 184 kg H_2SO_4/t. The ABCC results indicated that most of the acid neutralising capacity of AN would be readily available for acid neutralisation. The AN leach column test produced alkaline leachate throughout the experiment, confirming that AN gold mine tailing would generate an alkaline effluent due to the occurrence of highly reactive carbonate minerals, namely dolomite, as determined using XRD.

The results of the COV251, COV252 and COV253 leach columns showed that the COV25 column generated acidic leachates at the start of the leach column test and continued to produce alkaline leachates after five weeks of leaching, indicating a delay in the remediations of the acid generation when using the AN tailing as an acid neutralising cover to neutralise age generated by the bottom acid-generating layer (AG tailings). However, prolonged exposure will ensure effective acid neutralisation and prevention of AMD over a certain period.

The alkaline gold mine tailings are located approximately 3.8 km from the acid-generating gold mine tailings. Thus, utilising the alkaline gold mine tailings as a pH neutralising cover would be one of the most economical options to neutralise acid generated by the acid-generating gold mine tailings and thus mitigate AMD generation. Therefore, it is recommended that the alkaline gold mine tailings be used as a pH neutralising cover material to mitigate AMD generated by the acid-generating gold mine tailings, aiming to prevent polluting of the receiving water in the Sabie-Pilgrim’s Rest Goldfields district.

5.2 Recommendations

It is recommended that further research should be considered in utilising a multi-layer or blend approach to increase the effective acid neutralising capabilities of the alkaline gold mine tailings and to neutralise the large quantity of acid initially released by the acid-generating gold mine tailings due to stored acidity. Additionally, research should also be conducted on using small quantities of industrial waste/by-products from other industries, such as fly ash from the fossil fuels industry, to increase the initial release of alkalinity.

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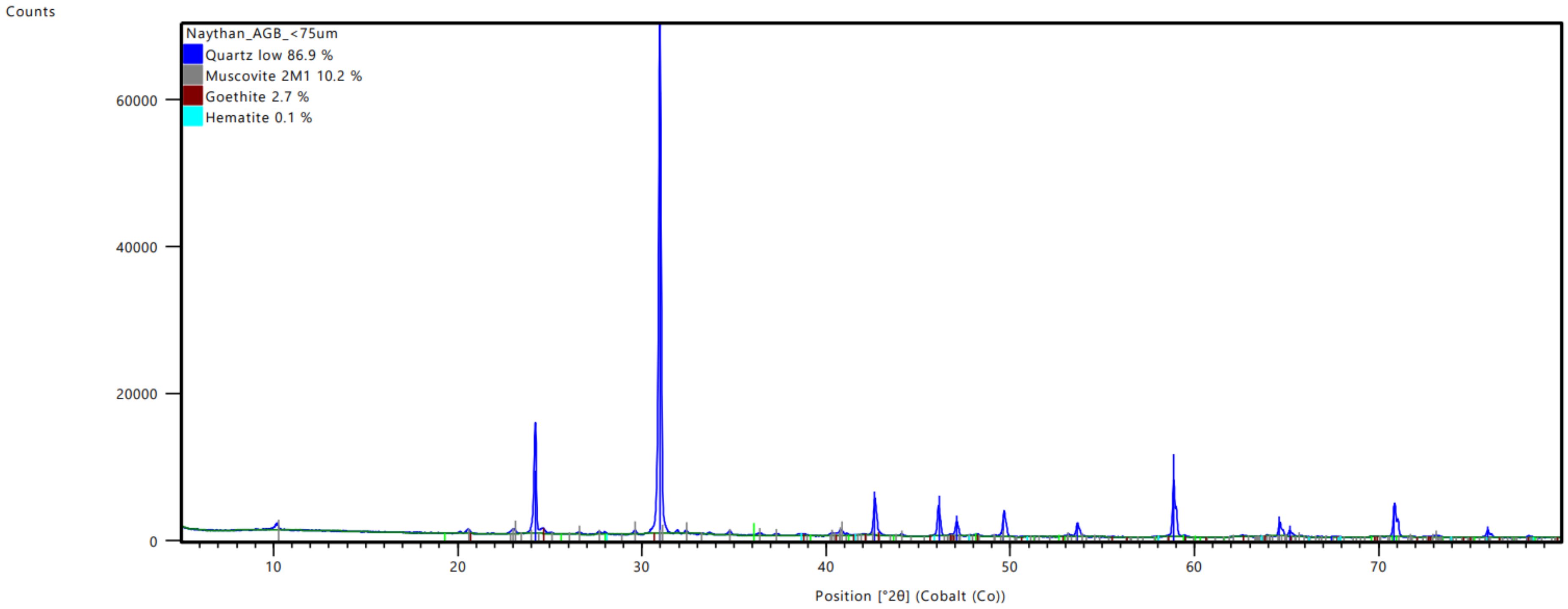
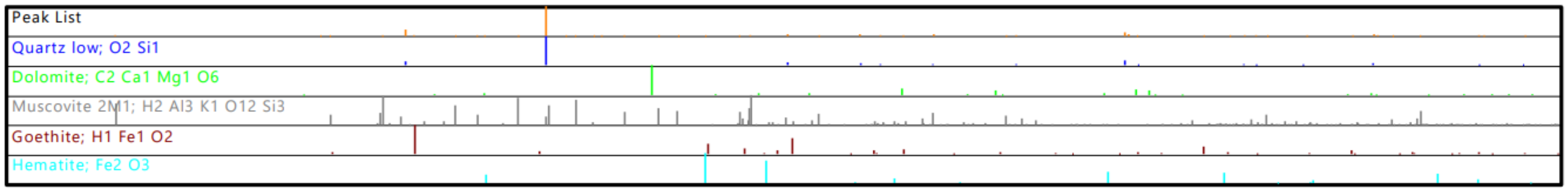
Appendix

Appendix A: Acidic gold mine tailing XRD Analysis





Appendix B: Alkaline Gold Mine Tailings XRD Analysis