Acid Mine Drainage Treatment with Uncalcined Waste Coal

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DECLARATION

I, Sibabalwe Mxinwa, declare that this research report is my own unaided work. It is being submitted for the partial fulfilment of the Degree of Master of Science in Engineering to the University of the Witwatersrand, Johannesburg. It has not been submitted before for any other degree or examination in any other university.

Sibabalwe Mxinwa

Abstract

The generation of acid mine drainage (AMD) in the mining industry has been identified as a significant threat to water security by the South African government, research community and civil society. AMD is characterized by low pH and high concentrations of metals and sulphate. Several types of treatment techniques such as neutralisation, ionic resins, flotation, adsorption, coagulation, precipitation, flocculation and filtration processes have been developed to mitigate the AMD threat and produce solutions of acceptable standard for re-use or discharge. The high complexity and capital costs associated with the above processes, however, has led to a search for inexpensive and simpler process routes. The aim of this study was to evaluate the process of neutralising AMD with uncalcined waste coal discards, in order to generate a solution with water quality suitable for domestic, livestock drinking, irrigation and industrial use

Neutralisation tests were conducted in polypropylene columns, loaded with waste coal samples from Exxaro, Forzando and Vlakfontein coal mines. The columns were irrigated continuously in an open circuit with AMD solution at 0.44 mL/minute and 2.01 mL/minute irrigation rates, at a set point temperature of 25°C. The treated solutions were collected at the bottom of the columns and accumulated in tanks. The waste coal samples were crushed to -40 mm, -12.5 mm and -6.3 mm respectively, to investigate the effect of particle size. The treated AMD solution had a pH of 2.82 as well as high concentrations of sulphate (19365 mg/L), iron (6325 mg/L), calcium (492 mg/L), aluminium (424 mg/L), manganese (103 mg/L), silicon (90.6 mg/L), zinc (12.5 mg/L) and copper (10.9 mg/L). The Exxaro, Forzando and Vlakfontein waste coals contained a neutralising potential (NP) of 0.49 %, 2.33% and 2.32 % respectively, expressed as calcium carbonate equivalent. The coal samples also contained 0.4 % to 1.2% inorganic sulphur, which is potentially acid generating.

Neutralising capacities for Exxaro coal in columns were between 0 and 292 L AMD / t coal at crush sizes of -12.5 mm and -6.3 mm respectively. Neutralising capacities for Vlakfontein were between 0 and 2118 L AMD / t coal at crush sizes of -40 mm and -6.3 mm respectively. The neutralising capacity of the Forzando coal was 929 AMD / t coal at a crush size of -6.3 mm. The higher neutralising capacities exhibited by the Vlakfontein and Forzando coals is consistent with the higher NP values and the presence of calcite and dolomite identified by XRD in the Vlakfontein head. The results indicated that the neutralising capacities increased with a decrease in crush size, as well as a decrease in irrigation rate. It was believed that the alkaline minerals in coal were more liberated in smaller particles than in coarse particles. Therefore, the increase in the neutralising capacities with a decrease in crush size may be due to higher degree of liberation of alkalinity in the finer particles.

The alkalinity in the waste coals and concentrations of calcite, dolomite and kaolinite minerals decreased extensively during AMD neutralisation, suggesting that these minerals were responsible for neutralisation. For example, the Vlakfontein waste coal contained kaolinite (>50%), calcite (5 to 15%) and dolomite (<5%) minerals before AMD treatment. After AMD treatment, the levels were reduced to 15 - 30% (kaolinite), <3% (calcite) and <3% dolomite, which proved that they took part in the neutralisation reaction. This is consistent with literature, which suggests that out of the many types of alkaline compounds present in rocks, only carbonates and clays are the most effective neutralising minerals. The alkaline minerals were not completely consumed during AMD neutralisation. This therefore suggests that the waste coal samples are not likely to produce AMD after use.

The treatment of AMD with waste coals resulted in the extensive removal of metals such as aluminium (98-100%), copper (84-87%), silicon (91-98%), iron (100%), zinc (36-89%) and sulphate (72-82%). However, the concentrations of undesirable species in AMD such as sulphate and magnesium (-125 – 28%) still remained above the minimum criteria required for water for domestic, livestock drinking, aquatic ecosystem, irrigation and industrial use. Furthermore, there was an indication of a significant leaching of magnesium from the waste coal into the solution. An additional polishing step should therefore be added to reduce magnesium and sulphate further to acceptable levels, for example, the Mintek SRB (sulphate reducing bacteria) process.

A desktop economic model was developed to compare the neutralisation of waste coal with the traditional route of lime neutralisation in tanks. The model was based on an AMD production of 1750 m^3 / day, a neutralising capacity of 1.4 m^3 AMD / t coal, a solids bulk density of 1 t / m^3 and a heap height of 6 m. A lime cost of R2000 per tonne and a lime neutralising capacity of 12 kg $Ca(OH)_2$ / m^3 AMD was used, as well as an electricity cost of 86 cents / kWh.

Capital costs were estimated at R18 million for lime neutralisation, R63 million for coal neutralisation and operating costs were estimated at R24.5 million for lime neutralisation and R18 million for coal neutralisation. Although the capital cost for waste coal neutralisation exceed the capital costs for lime neutralisation, the operating costs for AMD treatment with waste coal are significantly lower than the operating costs for AMD treatment with lime. Therefore, the investment spent on capital costs for waste coal neutralisation could be recovered over time due to the saving in the operating costs (lower than that lime neutralisation operating costs) of this option.

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Special thanks to my siblings for the support and encouragement that they accorded throughout my studies.

“The steadfast love of the Lord never ceases; his mercies never come to an end; they are new every morning…” **Lamentations 3:22-23 English Standard Version (ESV)**

DEDICATION

This thesis is dedicated to my late parents who always encouraged me to study. It is also dedicated to my siblings: Xolani, Fezeka, Siphokazi, Zandile, Andiswa, Zikhona, Tyanikazi, Ongezwa, Bonga, Bongile, Kayakazi and Samkelo as well as my daughter, Kungawo Mate. Finally, to the poor and marginalised people of our continent. One day a total emancipation of our people from the shackles of poverty will come.

“The first duty of a revolutionary is to be educated.”

— Ernesto Che Guevara

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Chapter 1

Introduction

Mining makes an important contribution to the South African economy (Mxinwa *et al*., 2017). However, the environmental and potential health impacts of mining on local communities are a concern (Mxinwa *et al*., 2017). Most mines are surrounded by areas containing pulverised material or mine waste from extraction and beneficiation processes, which are known as tailings, leach dumps or stockpiles. The formation of acid mine drainage (AMD) from mine tailings waste is the largest environmental problem facing the gold and copper mining industry today (Dold, 2014). This type of mine waste is derived mainly from metallurgical processes such as physical separation, flotation and leaching of ore types that are likely to produce AMD. Tailings require large areas of land and have great potential to cause ground and surface water contamination as a result of AMD. In the copper and gold mining industries, this type of material is generally composed of important concentrations of sulphide minerals that may undergo oxidation, producing acid and metal contamination (Dold, 2014). All sulphide-bearing ores lead to AMD formation, especially in tailings storage facilities (Blowes and Jambor, 1990; GARD, 2010; Edraki *et al.*, 2014).

In South Africa, AMD or acid rock drainage (ARD) has in the past 10 years become a focus of government and academic research. Acid mine drainage is not only affecting drinking water in central Gauteng, South Africa, but it is also affecting the Cradle of Humankind international heritage site (CSIR, 2009; DWA, 2010; Ewart, 2011; McCarthy, 2011).

AMD may be characterised by one or more of the following: low pH, high total dissolved solids (TDS), high sulphates (SO_4^{2-}), and/or high levels of heavy metals, especially aluminium (Al), iron (Fe), manganese (Mn), nickel (Ni) and/ or cobalt (Co) (Scott, 1995). These dissolved metals are commonly removed from the solution through precipitation using a lime neutralization process, which produces a low density (2-5% solids) sludge that is difficult to thicken and filter (SGS, 2013). Several types of treatment techniques for AMD have been proposed. In general, the treatment of AMD is carried out by the use of precipitation, ionic resins, flotation, adsorption, coagulation, flocculation and filtration processes to remove metals (Netto *et al*., 2013). However, these processes require a number of stages and are expensive, necessitating a search for new treatment technologies that use cheaper materials with improved capabilities to treat AMD (Netto *et al*., 2013).

Coal mining generates large amounts of pyritic wastes that are stockpiled. The recycling and re-use of wastes in the coal industry has been the subject of much investigation, for example, the use of waste coal in cement manufacture and as filler in road construction has been proposed (Vegas *et al*., 2015; Taha *et al.*,2017). These applications however, do not consume enough material to use up the large amount of stockpiles available. The stockpiling of wastes tends to lead to the formation of AMD and surface pollution (Francisconi *et al*., 2013). In addition to (acid-generating) pyritic wastes, coal mining also generates alkaline-rich materials (Skousen *at al*., 2000). Therefore, the neutralisation of AMD with alkaline-rich uncalcined waste coal could provide an alternative low-cost process route that may be implemented to replace lime neutralisation (Perry and Brady, 1995). The concept was tested on calcined waste coal by Francisconi *et al*. (2013).

According to Francisconi *et al.* (2013), Geremias *et al*. (2008), Geremias *et al.* (2012) and Netto *et al.* (2013), the treatment of AMD with calcined waste coal results in an increase in pH from 2.6 to 7.8, with the removal of elements such as Al (100 %), Fe (99.8 %), Mn (93.1 %) and zinc (Zn) (81.5 %) (Francisconi *et al*., 2013; Geremias *et al*., 2008; Geremias *et al*., 2012; Netto *et al*., 2013). This could be due to the presence of metal oxides such as SiO_2, Al_2O_3 and Fe_2O_3 in the calcinated waste coal, which could adsorb the H_3O^+ present in the solution, thereby increasing the pH with subsequent formation of oxides and insoluble metal hydroxides (Geremias *et al*., 2008). However, since the calcination process would be energy intensive and therefore expensive, the use of uncalcined coal would be preferable, and is therefore the focus of this research. The use of uncalcined waste coal in the AMD treatment will eliminate liming and energy costs. According to Van den Berg *et al*. (2001), toxic elements contained in coal could leach out when the coal material is mixed with water after calcination. However, this may not be as significant if the sample is not calcined. The potential drawback that may arise in the use of uncalcined waste coal to treat AMD is that the solution pH may not increase to levels high enough to remove all major elements. According to Skousen *at al*. (2000) and Madzivire *et al*. (2011), the pH required to precipitate most metals from AMD ranges from pH 6 to 9 and between 11 and 13 to precipitate magnesium.

Although some attention has been given to the use of calcinated waste coal for AMD treatment, no effort has been made to evaluate the economic use and efficacy of treating AMD with uncalcined waste coal containing alkaline-rich materials such as carbonate minerals and metal oxides. The calcination process requires heating the waste coal to 800°C for 1 hour in a furnace, which is very costly (Netto *et al*., 2013). Coal is calcinated to eliminate organic matter and obtain metal oxides (Francisconi *et al*., 2013). Even though coal mining generates large portions of pyritic waste which creates AMD, it also generates alkaline-rich materials which produce alkaline drainages instead of creating AMD. This indicates that not all coal mines generate AMD (Skousen *at al*., 2000). The alkaline content of waste coal determines whether there is enough inherent neutralization potential (NP) to counteract the acid produced from pyrite oxidation.

Mintek currently performs an acid-base accounting (ABA) method to characterise the ore, with respect to acid generating potential (AP) and NP. The neutralisation potential is determined by the alkalinity of the ore and the acid generating potential is determined by the presence of sulphur species, which may oxidise and form acid in the presence of water. The ABA method provides a useful way of preliminary screening the waste coal samples (Ramatsoma *et al*., 2018)

It is proposed that the uncalcined waste coal sample be utilised to neutralise AMD by percolating the solution over the coal stockpile and collecting the neutralised solution from the base of the pile in ponds. After completion, the waste coal material may be returned to the pit.

This test work simulates this process with column percolation tests. For the sample to be suitable for this process, the material must meet threshold values of NP greater than 3% (expressed as $CaCO_3$ content) and sulphur (S) less than 0.5%, and the ore bed must also be permeable to the AMD solution (Skousen *et al.*, 2000; Guzman, 2008). The permeability of the ore bed is a function of the fines content, and excessive slumping during column percolation indicates the potential of permeability restraints, which may become more pronounced on an actual pile (Guzman, 2008). The crush size of the ore also plays a role in that a finer crush will generate more available reaction surface for neutralisation and at the same time, may inhibit the percolation. Moreover, some metals in AMD precipitate at elevated pH levels (up to 13) and the use of uncalcined waste may not achieve these high levels.

In this study, AMD neutralisation with alkaline-rich waste coal was tested on uncalcined waste coal discards from Exxaro and Vlakfontein coal mines. The test work was performed in polypropylene columns, charged with coal and irrigated with AMD in order to simulate neutralisation over heaps.

A desktop economic model was also developed in this study to compare the economics of AMD neutralisation with waste coal to the traditional lime neutralisation route. Two flowsheets were developed: (1) neutralisation with uncalcined waste coal only and (2) neutralisation with lime only. The reason for this approach was to determine if the costly lime neutralisation route could be completely replaced with a coal neutralisation route. Design criteria, reagent consumptions and reagent costs based on experimental and published data were used to calculate capital and operating costs for each process option.

1.1. Problem identification

Acid mine drainage formation has been widely recognised as one of the major environmental problems caused by mining worldwide, as evidenced by numerous studies (Kalin, 2006; Klapper and Geller, 2002; Doupé and Lymbery, 2005; McCullough and Lund, 2006; McDonald *et al.*, 2006; Saarinen *et al.*, 2013). Acid mine drainage on the Witwatersrand, in South Africa, has reached a crisis point (Manders *et al.*, 2009). This is because some mining companies allow acid mine water to flow into streams, dams and sources of groundwater. The potential volume of AMD for the Witwatersrand Goldfield alone amounts to an estimated 350ML/day (Manders *et al.*, 2009). This represents 10% of the potable water supplied daily by Rand Water to municipal authorities for urban distribution in Gauteng province and surrounding areas. There is an estimated 62 million L/day of AMD from coal mines in the Highveld Coalfield, South Africa (Vegas *et al.*, 2015; Taha *et al.*,2017). In West Rand, toxic water has already destroyed life in the WonderfonteinSpruit, Tweelopiespruit, Tudor Dam and the Robinson Lake near Randfontein (Manders *et al.*, 2009).

Several methods have been proposed for the treatment of AMD, including the use of ionic resins, flotation, adsorption, coagulation, precipitation, flocculation and filtration processes to remove deleterious elements (Netto *et al.*, 2013). Most of these processes, however, require a number of stages and a large financial investment, making the search for new treatment technologies using low-cost resources with better contaminant-removal properties a priority

(Faulkner, 1996). In terms of the Mineral and Petroleum Resources Development Act 28 of 2002 (MPRDA), mines are now legally obliged to plan for rehabilitation after mining activity has ceased, and to consider the lagged social and environmental impacts of mining in the short term (Bobbins, 2015). Mining companies are obliged to allocate funds for environmental rehabilitation upon the decommissioning or termination of mining activities. Therefore, it is necessary to consider a cheap AMD treatment programme since the current AMD treatment methods are expensive.

Studies have shown that the treatment of AMD using calcined waste coal can decrease the toxic effects, which could be associated with the removal of toxic metals through their adsorption onto the surface of metal oxides such as SiO_2, Al_2O_3 and Fe_2O_3 (Francisconi *et al*., 2013; Geremias *et al*., 2008; Geremias *et al*., 2012; Netto *et al*., 2013). Studies have shown that the presence of metal oxides such as SiO_2, Al_2O_3 and Fe_2O_3 in calcined waste coal results in adsorption of H_3O^+, which in turn results in an increased pH (Geremias *et al*., 2008). It has also been shown that the treatment of AMD with the calcined waste coal results in increased pH and removal of metal ions. However, the energy costs associated with calcination are high (54 KJ/m^3 AMD treated) (Geremias *et al*., 2008). Skousen *et al*, (2000) have shown that alkaline-rich minerals with $\geq$ 3% NP as calcium carbonate equivalent and S < 0.5% can produce alkaline drainages. Therefore, uncalcined waste coal with high NP and low S can be investigated as an alternative and low cost method for AMD neutralisation, rendering an economic use for these wastes and reducing their impact on the environment.

1.2. Research aim and objectives

The main aim of this research was to evaluate the use of uncalcined waste coal as a low-cost alternative for the treatment of AMD in order to meet the South African water quality standards for domestic, livestock drinking, irrigation and industrial use.

The objectives of this study were:

- To determine the effect of crush size on the neutralising capacity.
- To determine the neutralising potential of the waste coal expressed in litres AMD per ton of waste coal.
- To determine the removal efficiency of dissolved species such as Al, Fe and sulphate in AMD.
- To undertake a preliminary comparison of AMD neutralisation with uncalcined waste coal, with the economics of the traditional lime neutralisation process.

1.3. Hypothesis

Southern African waste coal samples can be used as a low-cost alternative to treat AMD and precipitate deleterious metal species in order to meet requirements for disposal of the water.

1.4. Research questions

- What is the effect of *crush size* on the neutralising capacity and the permeability? For example, a finer crush generates more fines, which generate more reaction area but reduce void space.
- What is the *neutralising potential* of the waste coal expressed in litres AMD per ton of waste coal?
- What is the removal efficiency of other dissolved species such as Al, Fe and sulphate in AMD?
- How do the economics of AMD neutralisation with uncalcined waste coal compare with the economics of the traditional lime neutralisation process?

1.5. Research approach

Waste coal and AMD solutions were collected from Mpumalanga. AMD neutralisation test work was conducted in columns in order to simulate percolation over piles. The coal samples were crushed to the target crush size and loaded into polypropylene columns (160 mm ID). The AMD was irrigated into the top of the columns and percolated by gravity through the columns. The pH of the AMD was expected to increase due to the alkalinity of the waste coal, resulting in the precipitation and removal of deleterious metals, which remain in the coal bed. The drainages were collected from the bottom of columns, and the mass, pH and volume of the drainages were recorded daily. The waste coal (head and residue) was analysed for NP, S and AP. The AMD solution and drainages were analysed for heavy metals. The composition of the drainage was also compared to the South African Water Guidelines.

Chapter 2

Literature Review

2.1. Acid mine drainage

AMD is the flow of polluted acidic water from metal and coal mines. It occurs when the sulphide minerals in the rocks are exposed to oxidising conditions in the coal and metal mining or other large scale excavations. The most common sulphide minerals that cause AMD are pyrite and pyrrhotite (Faulkner, 1996). When pyrite is exposed to oxygen and water, it forms sulphuric acid, which dissolves toxic metals such as arsenic (As), lead (Pb), cadmium (Cd), copper (Cu), Zn and Ni. Since AMD is a threat to water resources such as rivers and the environment as a whole, it must be treated before it is discharged to any site of the environment (Faulkner, 1996).

2.2. Formation of AMD

Coal-bearing rocks and gold-bearing rocks contain sulphide minerals that can generate AMD. The main cause of AMD formation is the oxidation of the sulphide minerals due to exposure to oxygen, water and bacteria. Although the AMD generation process is known to occur naturally, mining and related activities speed up the process because such activities increase the exposure of sulphide-bearing rocks to air, water and bacteria. As a result, AMD generation and accumulation is prominent in operating and abandoned mining areas, especially in both coal and gold mines in South Africa; in underground tunnels and mine shafts, open pits, milling tailings and mine dumps. Although AMD is less critical when the mine is still operating since the ground water table levels are kept low by pumping processes, it is a serious challenge in closed and abandoned mines where pumping has stopped, resulting in increased underground acidic water levels (McCarthy, 2010; Skousen *at al.*, 2000).

The most common sulphide minerals are pyrite and pyrrhotite (Akcil and Koldas, 2005; Johnson and Hallberg, 2005; Peppas *et al.*, 2000; Schippers *et al.*, 2007 and Salmon and Malström, 2004). Pyrite will break down under oxidising conditions to form dissolved iron, sulphate and hydrogen ions as shown in the following reaction (Johnson and Hallberg, 2005):

$$4FeS_2 + 15O_2 + 14H_2O \rightarrow 4Fe(OH)_3 + 8SO_4^{2-} + 16H^+ \qquad (1)$$

For pyrrhotite, the oxidation reaction is as follows (GARD, 2010):

$$Fe_{1-x} + \left(2 - \frac{x}{2}\right) O_2 + xH_2O \ \rightarrow (1-x)Fe^{2+} + SO_4^{2-} + 2xH^+ \qquad (2)$$

The oxidation of sulphide minerals can be affected by the presence of microorganisms in the mine water. The rate of oxidation of ferrous iron to ferric iron can be increased by an order of magnitude of 6 times if iron-oxidising bacteria are present in the water (GARD, 2010).

$$Fe^{2+} + O_2 + 4H^+ \xrightarrow[bacteria]{} Fe^{3+} + 2H_2O \qquad (3)$$

The process of AMD production is complicated because it includes chemical, biological, physical and electro-chemical reaction processes that differ according to the environment and local geological conditions. Several sulphide minerals found in different ore bodies are formed in reducing environments in the absence of oxygen. The exposure of these various sulphide minerals to water with oxygen or atmospheric oxygen due to mining, mineral processing, excavation or other earthmoving processes (for example road construction) causes the sulphide minerals to be unstable and then oxidise to form acid (Antonio *et al*., 2014).

2.3. AMD characterisation

AMD from coal mines is characterised by elevated levels of dissolved Fe and Mg at low pH levels. Manganese compounds also leach into AMD and rise to fairly high levels, sometimes 20 ppm to 100 ppm. Such pollution can contaminate the downstream water supplies. Typical compositions of AMD resulting from coal mining are shown in Table 2.1 (Richards *et al*., 1993). This quality of mine water is not suitable for livestock drinking, irrigation and industrial use according to the South African water quality standards.

Table 2.1: Typical compositions of the AMD from coal mining (Richards et al., 1993)

Parameter	**Concentration**
pH	3.0-5.5
Al (ppm)	50
Ca (ppm)	200
Fe (ppm)	50-300
Mg (ppm)	80
Mn (ppm)	20-300
SiO_2 (ppm)	90
SO_4^{2-} (ppm)	20-2000

The quality of AMD produced in gold mining areas differs from area to area, depending on the local composition of rocks containing he pyrite minerals that lead to AMD generation. In the Witwatersrand area, the AMD quality differs from the Western Basin, the Eastern Basin and the Central basin. The AMD composition also differs with seasonal variations, especially with the rainfall pattern. The interconnection of abandoned and unknown underground tunnels also affects the quality of AMD. In areas where mining is still active, it is possible that the miners may be dumping their waste water into the mining voids, which are already full of AMD. This has resulted in unexpected AMD quality variations. Table 2.2 summarises the differences in AMD quality according to the regions in the Witwatersrand area (Mutanga and Mujuru, 2016). Most of the parameters presented in Table 2.2 are far above the water quality guidelines provided by the Department of Water and Sanitation (DWA, 2010).

Table 2.2: AMD quality according to areas located close to gold mines in the Witwatersrand area (Mutanga and Mujuru, 2016)

Parameter	Western Basin	Eastern Basin	Central Basin
pH	3.5	6.65	2.8
Fe (ppm)	800	38	112
TDS (ppm)	6580	2041	4936
SO_4^{2-} (ppm)	4800	1037	3700

2.4. AMD neutralisation and removal of metals

Sufficient alkalinity must be added to raise the pH of AMD so that insoluble metal hydroxides precipitate and settle out of the AMD. The types and amounts of metals in the water heavily influence the selection of an AMD treatment technique. The pH required to precipitate most metals from water ranges from pH 6 to 9 (except Fe^{3+}, which precipitates at pH >3.5). Aluminium hydroxide precipitates at pH above 5 but also enters solution again at a pH 9. Mn precipitation is variable due to its many oxidation states, but will generally precipitate at a pH of 9 to 9.5. The appropriate treatment chemical can depend on both the oxidation state and concentrations of metals in the AMD (Skousen at al., 2000). Interactions among metals also influence the rate and degree to which metals precipitate. For example, Fe precipitation will greatly remove Mn from the water at pH 8 due to co-precipitation, but only if the Fe concentration in the water is much greater than the Mn content (about 4 times more or greater). If the Fe : Mn ratio is less than 4, Mn cannot be removed by co-precipitation and a solution pH greater than 9 is necessary to remove it from solution (Skousen *at al*., 2000).

2.5. Current technologies used in AMD treatment

Several types of technologies for AMD treatment have been proposed, always taking into account the volumes of treated solution produced, in addition to qualitative and quantitative analysis of contaminants. An effective treatment should be capable of raising the pH as well as removing toxic metals in the environment (Faulkner, 1996). The following section gives an outline of some of the current processes used for AMD treatment.

2.5.1. Limestone and burnt lime

Limestone and burnt lime are used to raise the pH and precipitate the metals in AMD (Scott, 1995). The neutralization of AMD using burnt lime depends on the insolubility of heavy metals and the alkaline condition. The pH is controlled to the set point of 9.5 and metals such as Fe, Zn and Cu as well as other metals get precipitated. Limestone is directly dumped into the AMD stream. This process is mostly applied in the case where the pH is low and where acidity is relatively high. It is carried out in the abandoned mines and reclaiming projects and by operators wishing to reduce chemical treatment costs (Scott, 1995). The disadvantages include slow reaction time and when exposed to AMD containing Al^{3+} and Fe^{3+}, solids quickly form. These solids foul the limestone, decreasing its effectiveness (Wolfe and Hedin, 2010).

When the limestone comes into contact with AMD, it dissolves, while producing alkalinity to increase pH and remove soluble Al, Fe and Mn due to mineral precipitation. The following reactions take place during the process (Madzivire, 2009):

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \tag{4}$$

$$Fe^{3+} + 3HCO_3^- \rightarrow Fe(OH)_3(s) + 3CO_2(\text{g}) \tag{5}$$

$$Al^{3+} + 3HCO_3^- \rightarrow Al(OH)_3(s) + 3CO_2(g) \tag{6}$$

Sulphates in the AMD precipitate as gypsum:

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4.H_2O \tag{7}$$

2.5.2. Hydrated lime

Hydrated lime is the most commonly used chemical for treating AMD in the industry. Hydrated lime is cost-effective if it is used in large flow high acidity situations, where a lime treatment plant with a mixer is constructed to help dispense and mix the chemical with water (Skousen *et al.*, 2000). Hydrated lime is not effective when a high pH is required to remove ions such as Mn. Operators of lime treatment systems frequently increase lime application as Mn levels increase in the water. However, due to the kinetics of lime dissolution, increasing the rate of lime increases the volume of unreacted lime that enters the metal floc settling pond (Madzivire, 2009). Following dissolution of the hydrated lime in mine waters, the pH is increased, metal ions are precipitated as hydroxides and $SO_4^{2-}$are removed from the water in the form of gypsum (Equation 9) (Madzivire, 2009).

$$Me^{2+} + 2OH^- \rightarrow Me(OH)_2 \tag{8}$$

$$Ca^{2+} + SO_4^{2-} + 2H_2O \rightarrow CaSO_4.2H_2O \tag{9}$$

Chemical treatment of AMD using hydrated lime or limestone will remove SO_4^{2-} to between 1500 ppm to 2000 ppm depending on the solubility of gypsum. Gypsum solubility depends on the composition and ionic strength of the solution (Wolfe and Hedin, 2010). Operators prefer to use bulk lime due to cost and handling advantages (Madzivire, 2009).

2.5.3. Ammonia

Ammonia is a gas at an ambient temperature. It is compressed and stored as a liquid but it returns to the gaseous state when it is released into water. In a gaseous state, ammonia is extremely soluble and reacts rapidly. It behaves as a strong base and can easily raise the pH to the value that is required, mostly 9.2. At pH 9.2, it buffers the solution to further pH increases, and therefore, very high amount of ammonia must be added to elevate the pH beyond 9.2. When added into the AMD, ammonia quickly raises the water pH, helping to neutralize the pH of the AMD. Ammonia must be handled very carefully since it is very hazardous; potential biological implications and the consequences of excessive ammonia application rate are dangerous (Scott, 1995). Since ammonia is a base, it reacts with sulphuric acid, forming a salt and that is how neutralization occurs. Most metals that are present in aqueous solution will react with ammonia, producing metals hydroxide as shown in the following reactions (Skousen, 2000):

$$2NH_3 + H_2SO_4 \rightarrow (NH_4)_2SO_4 \quad (10)$$

$$2NH_3 + 2H_2O + FeSO_4 \rightarrow (NH_4)_2SO_4 + Fe(OH)_2 \quad (11)$$

$$MS + nNH_3 + 2O_2 \rightarrow [M(NH_3)_n]^{2+} + SO_4^{2-} \quad (12)$$

Where M is the metal species.

Ammonia is effective in treating AMD having a high ferrous iron and/or manganese content. However, ammonia is difficult and dangerous to use and can affect biological conditions downstream from the mining operation and the costs associated with the use of ammonia to treat AMD renders the technology cost extensive (Scott, 1995).

2.5.4. Biological process

The sulphate reduction bacteria (SRB) process is a common biological process that is used for treating AMD. SRB obtain their energy by oxidizing organic compounds or hydrogen while reducing sulphate to hydrogen sulphide. Most SRB can also reduce other oxidized inorganic sulphur compounds, such as sulphite and thiosulphate/elemental sulphur. SRB occur naturally in surface waters, including seawater (Odom and Singleton, 1993). The SRB used to treat AMD are able to survive at different pH levels, but the higher the pH, the more effective it is to precipitate the metals. SRB can only be used in low concentrated AMD to prevent the bacteria from dying from elevated concentrations of dissolved metals (Doshi, 2006; Koschorreck, 2008).

SRB are a large and diverse physiological group of anaerobic bacteria, which are defined by their capability to use inorganic sulphate in an adenosine triphosphate requiring reaction as one of their terminal electron acceptors (Sheela, 2006). The chemical basis of SRB remediation involves microbially-mediated sulphate reduction coupled with organic matter (represented by CH_2O in equation 13) oxidation (Sheela, 2006).

This process takes place via the following reaction:

$$2CH_2O + SO_4^{2-} \rightarrow H_2S + 2HCO_3^- \quad (13)$$

The sulphate in AMD may be converted to H_2S or HS^- during the sulphate reduction process, depending on the surrounding redox environment. The initial step of biological sulphate reduction involves the transportation of exogenous sulphate across the bacterial cell membrane into the cell (Sheela, 2006).

It also involves the chemical reaction of metal (Me) precipitation:

$$H_2S + Me^{2+} \rightarrow MeS + 2H^+ \quad (14)$$

Cd, Cu, Fe, Pb, Hg, Ni, and Zn are some of the metals that precipitate as metal sulphides. In addition, As, Sb, and Mo form more complex sulphide minerals (Sheela, 2006). Metals such as Mn, Fe, Ni, Cu, Zn, Cd, Hg, and Pb may also be removed to some extent by co-precipitation with other metal sulphides. Moreover, SRB species that can reduce certain metals to a more insoluble form, such as reduction of $U6^+$ to U^{4+} have been found (Sheela, 2006). Sulphate reduction also consumes acidity, increasing the pH. Raising the pH facilitates the above precipitation reactions and creates suitable conditions for precipitation of metal hydroxides (Sheela, 2006). The advantage of this process is that it produces treated AMD of similar quality to treated sewage effluent. The disadvantage of SRB process is that it could be destabilised by toxins, fluctuating feed water quality or unfavourable environmental conditions (Mottay and Van Staden, 2018).

2.5.5. CSIR alkali barium calcium (ABC) process

In this process, $BaCO_3$ is effectively used for the removal of sulphates from sulphate rich industrial waste waters through the precipitation of barite. The CSIR ABC process have exhibited a number of advantages over the use of other chemicals (Maree *et al.*, 2004). The process uses barium salts to further reduce the sulphate concentration to acceptable levels with the added advantage that sulphate removal can be controlled due to the low solubility of $BaSO_4$. The precipitation of barite is favoured due to the low solubility of barite in water (0.0015 g/L). However, the use of $BaCO_3$ in mine water treatment for sulphate removal results in the production of large amounts of barite sludge. Besides its numerous existing uses, barite can also be thermally processed back to barium sulphide, which then can be used as a starting material for the production of $BaCO_3$, thereby increasing the viability of the overall process and reducing environmental pollution (Maree *et al.*, 2004).

The current ABC process makes provision for three sludge processing stages: pre-treatment with lime and CaS to remove free acid and metals; $BaCO_3$ treatment to form barite; waste processing to recover alkali, barium and calcium in coal-fired kiln (Merta, 2015). The modified ABC process has been designed to minimize the gypsum generation, thereby reducing the quantity of gypsum crystallized during the water treatment stage, with all the sulphate removed as barite. This design increases the sludge load to the barium sludge processing stage, significantly reducing the gypsum sludge processing, whose capex alone is estimated at about R1 billion (Maree *et al.*, 2004).

The disadvantage of this process is that the barium carbonate used in CSIR ABC process is very toxic and if any unreacted barium carbonate were to pass through to the effluent stream, it would have catastrophic consequences. The energy requirement for the CSIR ABC process is also high due to the thermal reduction in the barium sludge processing step, which is required for $BaCO_3$ recycling (Mottay and Van Staden, 2018).

2.5.6. Sulf-IX for Sulphate and TDS control process

The Sulf-IX™ process is a continuous flow, two-step process that is used to remove calcium associated sulphate from AMD. AMD first passes through a cationic circuit where a strong acid cation (SAC) resin exchanges two hydrogen ions for a calcium ion, as shown in equation 15 (Doughty and Littlejohn, 2015).

$$Ca^{2+} + 2RH \rightarrow 2RCa + 2H^+ \tag{15}$$

The effluent from the cationic columns is then transferred to the anionic circuit. The cationic effluent, now the anionic feed, enters the anionic columns, which contain a weak basic anion (WBA) resin for the removal of the H_2SO_4 molecule present in the water, as shown in equation 16 (Doughty and Littlejohn, 2015).

$$2H^+ + SO_4^{2-} + R \rightarrow RH_2SO_4 \quad (16)$$

The anionic effluent is discharged from the plant with both calcium and sulphate levels significantly reduced. The regeneration cycle begins once the anionic and cationic resin beds reach their respective working capacities. The cationic regeneration solution consists of a dilute H_2SO_4 solution, which strips the SAC resin of calcium and replaces it with two hydrogen ions. The anionic solution (regenerated) is a lime solution which releases the H_2SO_4 solution from the WBA resin. Each spent solution (regenerated) is sent to its respective solids handling loop to relieve the gypsum super-saturation and replenish the regenerated solution prior to the next regeneration cycle. As part of the process, the solution passing through the fluidized bed changes depending on the current cycle. However, the resin remains in the same column for the entire process (Doughty and Littlejohn, 2015).

Removal of sulphate to meet new regulations worldwide is more efficient using the Sulf-IX™ process when compared with biological sulphate reduction and membrane technology. The process is typically applied following a lime plant and it allows for low cost removal of sulphate to less than 500 mg/L, while producing a clean gypsum product that can provide added-value as a construction material. The treated water product from a Sulf-IX™ plant can be discharged directly to the environment or recycled (Industrial, nd).

2.5.7. ChemSulphide process

ChemSulphide process is used to treat AMD, industrial wastewater and contaminated groundwater. The metal rate of recovery is greater than 99%, and the recovered metal products are of a sufficiently high grade to be suitable for refining (Stedman, 2010).

In this process, chemical sulphide material is added to the contactor tank where it mixes with the water to be treated under controlled conditions to selectively precipitate metals as a metal sulphide. The precipitated metals and water are pumped to a clarifier tank where the treated water is separated from the metal solids and discharged or recycled. The solids containing metals are then filtered to remove excess water, producing a high-grade metal sulphide product suitable for refining. To recover separate metal sulphide products, separate contactor and clarifier tanks are set up in series. The metals that can be recovered through this process include Cu, Zn, Ni and Co. Toxic metals such as As, Sb, Pb, Cd, and Mn are also removed from the water (Stedman, 2010).

2.5.8. GYP-CIX process

GYP-CIX process uses ion exchange resins to remove the toxic metals. The resins are regenerated in a novel way using lime and sulphuric acid, whereby gypsum is precipitated in the regeneration stage and is the only waste product generated by the process. The GYP-CIX process can be used in an economic and cost-effective way to remove scaling elements so that water can be recycled and re-used. Desalination of scaling effluents which was not possible in the past is now possible (Du Plessis and Gussman, 1993). The GYP-CIX process can tolerate relatively high concentrations of calcium, however, the TDS needs to be less than 4000 mg/L (Mottay and Van Staden, 2018).

2.5.9. *The Slurry Precipitation and Recycle Reverse Osmosis (SPARRO) process*

The SPARRO process is a novel design developed in South Africa by the Chamber of Mines. It is developed from a seeded reverse osmosis (RO) concept invented in the USA (Industrial, nd). It is a membrane desalination process designed to treat calcium sulphate scaling mine water. Figure 2.1 presents the basic flow chart of the SPARRO process. The process is based on the protection of the membrane surfaces by providing a slurry suspension onto which the precipitation products can form (Mutanga and Mujuru, 2016). Two of the main advantages of the process are that it forms a high quality solid gypsum by-product, which could be sold and can operate at very high recovery ratios, reducing the quantity of brine disposal. The quality of the treated water is related to the overall water recovery and this would be adjusted to each raw mine water treated. The process has been successfully tested at a pilot scale on scaling mine water from East Rand Proprietary Mines (ERPM) Hercules Shaft. However, the severe shortcomings of this process are that it entails high capital, maintenance and operational costs, and membrane fouling can occur (Mutanga and Mujuru, 2016).

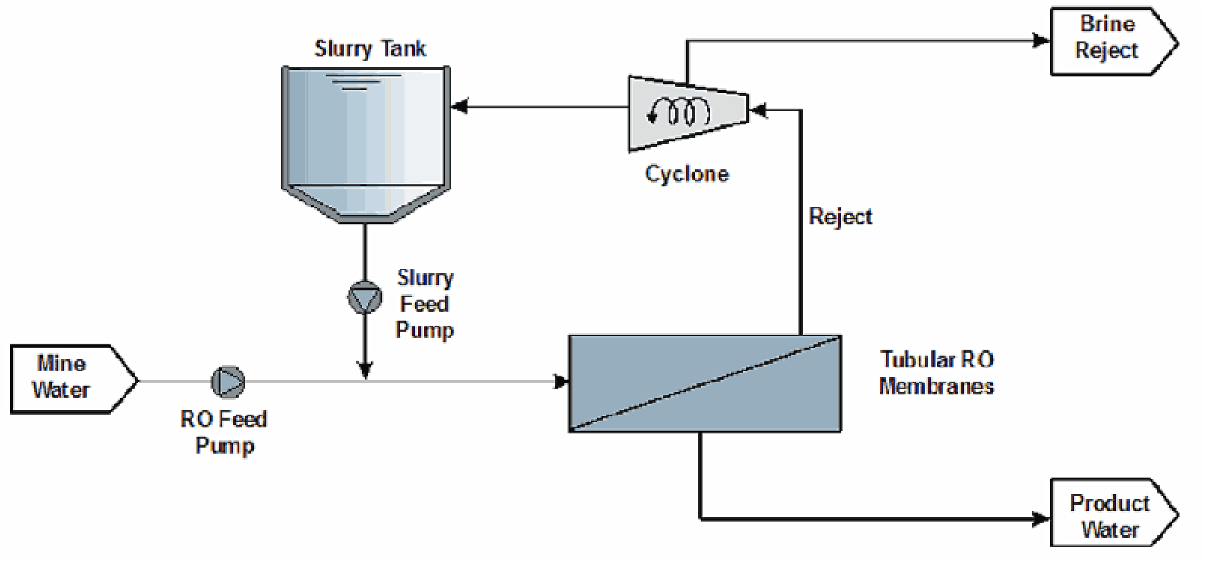

Figure 2.1: SPARRO Process Flow Chart from Mutanga and Mujuru, 2016

The process incorporates three major treatment improvements over the conventional RO processes: independent control of gypsum seed, lower power consumption and utilisation of a novel pumping system. The pre-treatment stage includes the use of the pH adjustment. This is followed by the removal of the suspended solids through coagulation, settling and filtration. The resultant feed water is pumped into a storage tank from which it is mixed with recycle gypsum seed from the reactor before it is pumped to the RO membrane module tank (Mutanga and Mujuru, 2016).

As the water is concentrated along the membranes, calcium sulphate ($CaSO_4$), silicates and other scaling salts are preferentially precipitated on the seed material, rather than on the membranes. The treated water from the module is stored. The flow concentrate from the cyclone vessel is further subdivided with one part returned to the reactor and the other blown up as brine (overflow) and as seeds (underflow) (Mutanga and Mujuru, 2016).

2.5.10. High density sludge (HDS) process

As mentioned above, the dissolved ions in AMD are commonly precipitated using a lime neutralisation process, which produces a low density (2-5% solids) sludge that is difficult to thicken and filter. The HDS process is an improvement on low-density treatment method and acts to greatly reduce the sludge volume by greatly increasing its density. In this process, limestone/lime and recycled sludge are added to the lime-sludge mix tank at the beginning of the process and the lime becomes the main neutralisation agent (SGS, nd).

Some gold mines currently use lime treatment in order to precipitate the majority of heavy metals in the AMD as metal hydroxides. A schematic diagram of the HDS process is shown in Figure 2.2. When this process is implemented, the toxicity of the clarified AMD waters is reduced to the extent where the treated water is, in most cases, regarded as non-toxic to animals and indicator organisms (Corbett, 2001).

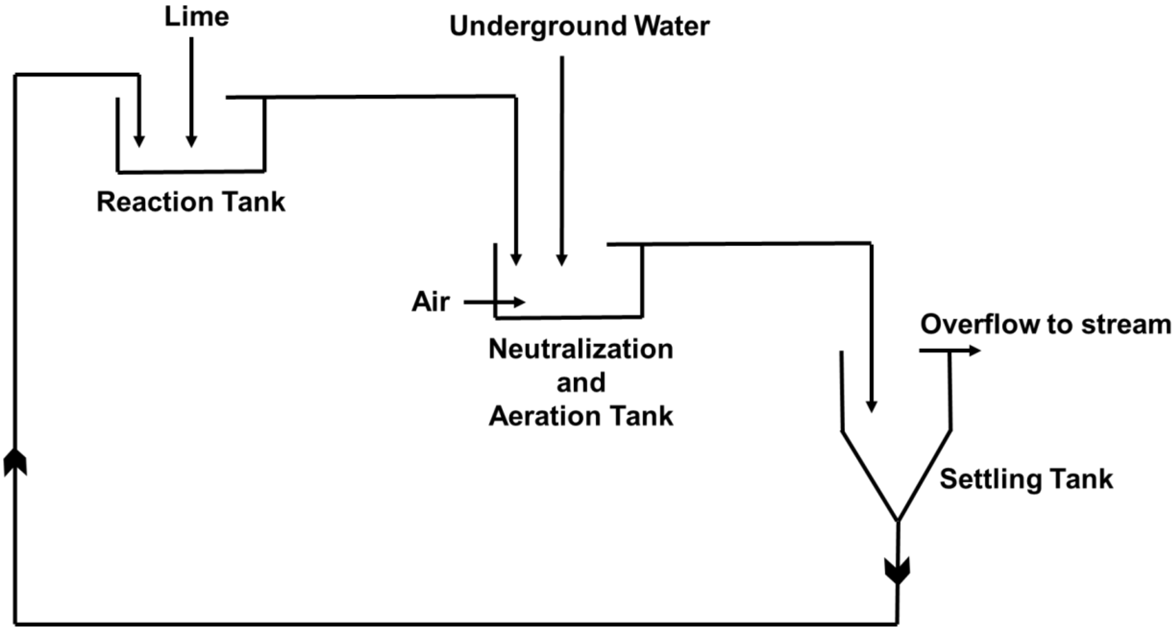

Figure 2.2: Systematic diagram of the HDS Treatment Process from Corbett, 2001

The advantages of high-density sludge process are that it is well established and has been in operation for many years. Government, as a short-term intervention for AMD treatment in the Witwatersrand Basin in Gauteng installed three high-density sludge treatment plants in Krugersdorp, Germiston, and the most recent commissioned in Springs during February 2017. These plants can treat 50 ML/d, 82 ML/d, and 110 ML/d of decant respectively, after which it is released into nearby water resources (Grewar, 2019). The major problem with this solution, however, lies in the fact that water treated by HDS has sulphate levels that are well above those allowable for discharge, in addition to a number of issues surrounding storage and disposal of the sludge produced (Grewar, 2019).

2.5.11. High Recovery Precipitating Reverse Osmosis (HiPRO) process

HiPRO process consists of three stages, each configured with pre-treatment, ultrafiltration and reverse osmosis (Figure 2.3). Each stage produces treated water of potable water quality, through the reverse osmosis unit process, while the reject produced product becomes the feed for the next stage. In doing so, greater than 98% overall plant recovery is attained with minimal waste production (Karakatsanis and Cogho, 2010).

Pre-treatment:
In this stage, Fe and Mn are removed from feed water to levels suitable for reverse osmosis (RO) treatment. Ozone is the preferred route for Fe and Mn removal. After ozonation, any solid debris in the mine water feed, together with the oxidised Fe and Mn, will settle out in the stage 1 clarifiers. An anionic polymer flocculant is dosed into the clarifier feed water in order to promote solids agglomeration. The stage 1 clarified water is then filtered through sand filters prior to further treatment by ultrafiltration. Pre-treatment in stage 2 and 3 is quite different to that of stage 1 due to the nature of the feed water. Stage 2 and 3 are fed with RO reject from the previous stage, which is in a state of supersaturation. The salts in the reject are removed by means of precipitation at an elevated pH, which is achieved by the addition of lime. Gypsum and magnesium hydroxide are the salts that predominantly precipitate in the precipitation reactors and they are kept in suspension by means of large agitators in the reactors. The slurry in the reactors is classified by means of hydrocyclones. The hydrocyclone overflow, containing the small particles, is introduced into the respective stage 2 and 3 clarifier. The underflow from the hydrocyclones contain the larger gypsum particles, which are dewatered by means of a vacuum belt filter (Karakatsanis and Cogho, 2010).

Ultrafiltration:
Ultrafiltration is the final solids-removal process before introducing the water to the RO’s. Each UF skid has 38 modules installed (maximum 44 available). The UF’s are operated in dead-end mode and each skid is intermittently backwashed in order to remove the entrained solids. As per the sand filters, the backwash water is collected in the plants drains sump and returned to the Flash mixer for further treatment (Karakatsanis and Cogho, 2010).

Operation of the UF system automatically initiates the dosing of antiscallant in preparation for RO treatment. In order to protect the UF’s from this source fouling, the antiscallant is dosed upstream of the UF’s in stage 1. In the case of the stage 2 and 3 UF’s, the antiscallant is dosed post UF's. In addition, sulphuric acid is dosed in the UF product water for pH correction prior to the RO's. The antiscallant dosing and acid correction is implemented post UF's so that any small precipitates of calcium sulphate remaining in suspension after clarification, may still be removed by the UF's (Karakatsanis and Cogho, 2010).

Reverse Osmosis:
The final treatment process is reverse osmosis. The design of the RO skids for each stage is specific to the feed water quality and subsequent allowable recovery. The stage 1 RO feed water typically has a $CaSO_4$ saturation level of 90 - 95%, but the recovery is limited by the $CaCO_3$ scaling potential. In addition, the stage 1 RO design makes use of nanofiltration (NF) membranes in order to allow for the passage of the monovalent bicarbonate ion into the permeate stream. This has a two-fold advantage in that stability is provided to the low salinity permeate and that the lower levels of bicarbonate in the reject will place less demand on lime in the stage 2 precipitation reactors. The drawback of RO water is that it can significantly reduce minerals that can aid in overall heart and muscle health (Karakatsanis and Cogho, 2010).

The stage 2 and 3 RO designs differ in their allowable recoveries as a result of the ability of the precipitation reactors to remove $CaSO_4$. Therefore, the allowable recoveries of the stage 2 and 3 RO's are 65% and 60% respectively. The permeate stream from each Ro skid is collected in the common permeate header and routed to a potable water distribution. The reject from each stage is routed to the next stage, with a small amount of stage 3 reject routed to the brine pond.
This AMD treatment plant operates at 98% overall recovery. The remaining water stream is released with the three waste streams produced by the plant; mixed sludge, gypsum and brine (Karakatsanis and Cogho, 2010).

Reverse osmosis is a membrane process that has reached the point of practical application in water or wastewater treatment. One of the disadvantages of reverse osmosis is fouling of the membrane by suspended solids, oil and grease, iron, manganese, microbial growth, and precipitation of calcium carbonate and magnesium hydroxide. Hence, extensive pre-treatment to prevent membrane deterioration and fouling may be required. Water softening processes, such as lime and soda ash, can be used to remove these interferences before applying a reverse osmosis treatment process. Membranes may also require frequent and specialized cleaning, which produces significant volumes of cleaning and rinse solutions that then require management (Nagy, 2019)

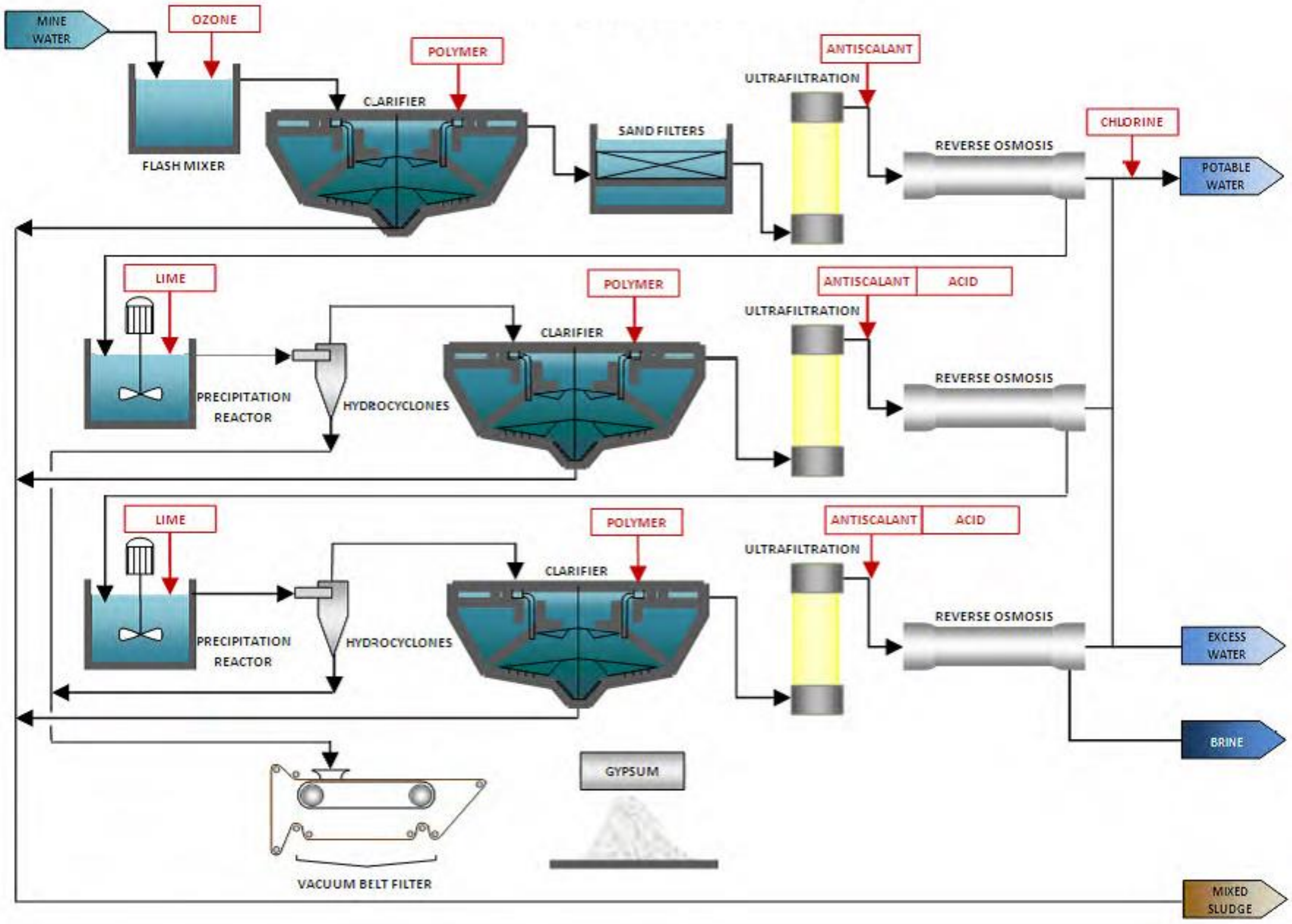

Figure 2.3: HiPRO Process Flow Chart from Karakatsanis and Cogho, 2010

2.5.12 SAVMIN process

SAVMIN was patented by Mintek in 1998 for the treatment of AMD. A key feature of SAVMIN is that it is able to decrease sulphate concentrations to less than 200 mg/L $SO_4{}^{2-}$ via the addition of aluminium hydroxide to form the highly insoluble ettringite precipitate. The OPEX costs are also lowered compared to typical chemical treatment processes as it includes regeneration and recycling of aluminium hydroxide. The process is run at ambient temperature and pressure and therefore electrical power consumption is also limited (Mottay and Van Staden, 2018). SAVMIN can recover >95 % of the water, reduce concentrations of trace metals and produce a non-saline effluent stream (Mottay and Van Staden, 2018). The disadvantage of this process is that the high concentration of calcium sulphate in solution, gypsum scaling could be problematic without a proper management plan.

The technology involves the removal of heavy metals, calcium and sulphate ions at ambient conditions (Karakatsanis, nd). Figure 2.4 shows the four- stage process (Smit, 1999).

SAVMIN stage 1 (Heavy metal precipitation)
In stage 1 heavy metals are precipitated using lime at pH above 11. The metals precipitate as metal hydroxide, together with the formation of gypsum. The solution is then separated and the precipitate is discarded as waste.

SAVMIN stage 2 (Ettringite precipitation)
In this stage, aluminium hydroxide and lime are added to the solution from stage 1 to remove Ca and SO_4^{2-} from solution by formation of an insoluble calcium-aluminium sulphate salt called ettringite. After thickening, the overflow solution is sent to stage 3 and the ettringite to stage 4.

SAVMIN stage 3 (Carbonation)
The water overflow from stage 2 is treated with carbon dioxide to lower the pH and cause the precipitation of calcium carbonate. The calcium carbonate can either be a by-product, recycled, or disposed as waste. The treated water is then ready for use.

SAVMIN stage 4 (Recovery of aluminium hydroxide)
The final stage of the process consists of the recovery of aluminium hydroxide via ettringite decomposition. Sulphuric acid and make-up aluminium sulphate are added to the ettringite slurry (underflow from stage 2). Aluminium hydroxide and gypsum precipitate during the decomposition. Aluminium hydroxide needs to be separated from the gypsum in order to be recycled to the stage 2 ettringite precipitation. The 'clean' gypsum is recovered as a by-product or waste. The overflow, saturated in gypsum, is recycled to stage 1 to ensure precipitation of metals such as magnesium (Mg) that might have entered the circuit through the lime. The separation of aluminium hydroxide and gypsum crystals is carried out by means of a hydrocyclone.

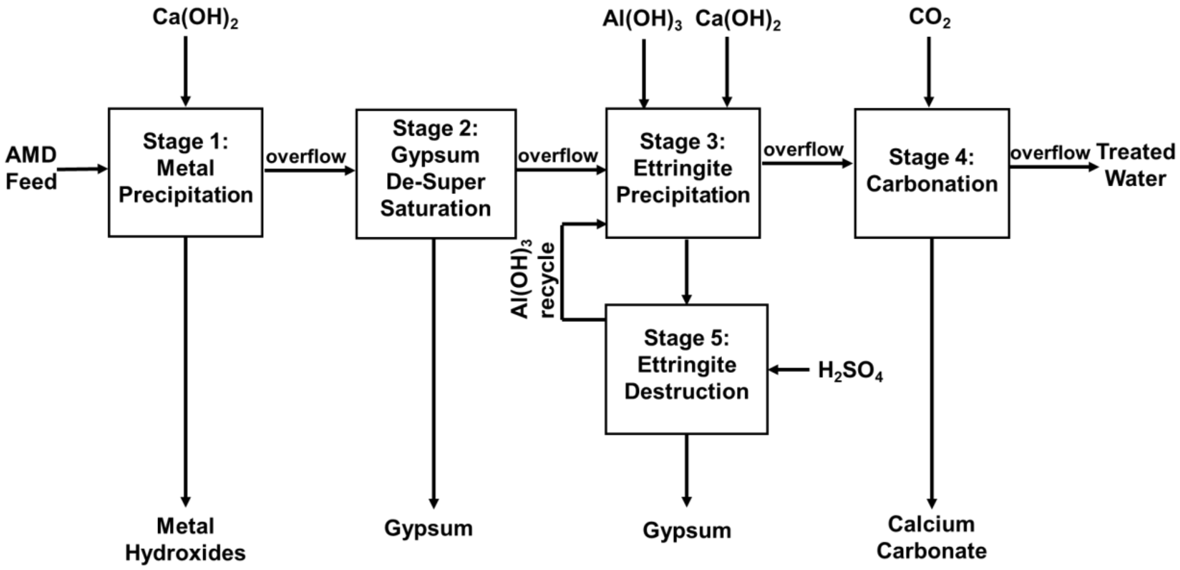

Figure 2.4: Savmin process flow sheet from Smit, 1999

Summary

The different technologies that are used in the treatment of AMD can be divided into the chemical treatment processes, the biological sulphate reduction and the physico-chemical treatment processes. These processes require a number of stages that result in high capital and maintenance costs, and produce large volumes of sludge that is difficult to thicken and filter. Furthermore, some of these processes use membranes and require a pre-neutralisation step to remove the bulk of the metals from solution prior to purification. The membranes are prone to scaling and require regular maintenance, which adds to the operating costs. The membranes also have a limited lifespan, which can further increase the operating costs. The energy requirement for some of these processes is also high. Therefore, it is necessary to search for an effective alternative low cost option for AMD treatment. AMD treatment with uncalcined waste coal is run at ambient temperature and pressure. It does not require multi-stages, therefore, the energy demand, capital and operating costs are very low compared to the conventional processes.

2.6. Coal characterisation and its application in the AMD treatment

2.6.1. Contribution of coal to the South African economy

Coal mining makes an important contribution to the South African economy. However, it creates severe environmental problems resulting from the generation of AMD (Netto *et al*., 2013). Approximately 93% of the country's electricity is produced by coal-fired stations (Prevost, 2014). The reason why coal has always been preferred to other energy sources is its cheap pithead price and the relative proximity of mines to users. Not only is coal cheap, but it is also, with small reserves of liquid fuels and natural gas, the only energy option (Prevost, 2014). Thus, South Africa is very dependent on coal.

Globally, 6.9 billion tons of coal is extracted by opencast or underground mining processes (World Coal Association, nd) (Mangena and Brent, 2006). Once mined, the coal is processed into useable materials, which also results in the generation of waste. The useable coal is a high carbon, high calorific value, low sulphur, low ash product and is desirable for export and applications. In general, South African coal has a comparatively medium ash content, which can be reduced by washing before sale. Higher grades of final product are delivered to export markets, with the lower grade product burned by Eskom's specially designed power station boiler hearths (Chamber of Mines, nd). The coal waste, on the other hand, is notably high in ash with a low calorific value and thus limiting its application. This coal waste is disposed on land as stockpiles and in some instance as backfill to cover opencast mining surfaces (Bian *et al*., 2007).

South Africa is the sixth largest holder of coal in the world with 31 billion tonnes of recoverable coal reserves, equivalent to 11 % of the world's total coal reserves. Prevost (2014) indicated that approximately 30% of the yearly saleable production is exported and this generates about 55% of the total revenue in the industry. Moreover, coal is the second largest mining income-earning commodity, beating gold (Prevost, 2014). Thus, coal plays an integral role in South Africa's domestic economy.

2.6.2. Coal characterisation

Lignite, sub-bituminous, bituminous and anthracite are types of coal formed underground from peat (Table 2.3). The main constituents of coal are C, O_2, hydrogen (H), N and S, which are thermally oxidized during coal combustion to produce electricity. Coal also contains trace elements such as As, Pb, Ni, Zn, selenium (Se), strontium (Sr), vanadium (V), Hg and boron (B) in association with different types of inorganic minerals such as aluminosilicates (clay minerals), carbonates (calcite and dolomite), sulphides (pyrites), and silica (quartz). The inorganic minerals make up 5 to 40 % of coal (Madzivire, 2009).

Table 2.3: Coal typical content (Bowen and Irwin, 2008)

Weight	**Anthracite**	**Bitminous**	**Sub-bitminous**	**Lignite**
Ash (%)	10 - 25	3 - 12	≤ 10	10 - 50
Fixed carbon (%)	85 - 98	45 - 85	35 - 45	25 - 35
Heat content (Btu/lb)	13000 - 15 000	11000 - 15000	8500 - 13000	4000 - 8300
Moisture (%)	< 15	2 - 15	10 - 45	30 - 60
Sulphur (%)	0.6 - 0.8	0.7 - 4.0	< 2	0.4 - 1.0

2.6.3. Alkalinity in coal

In countries such as the United Kingdom, some of the coal fields contain a significant amount of $CaCO_3$ (limestone) which neutralises much of the acidity, and therefore the term ‘mine water’ is more appropriate than ‘acid mine drainage’ in these situations (Sloss, 2013). However, in most situations, the pyrite oxidation adds significantly to the acidification of surface waters.

Coal is classified into various categories depending on criteria such as ash (or gangue) content of the coal; for example, semi-soft coking coal (10% w/w ash), metallurgical coal (15% w/w ash), power station coal (35% w/w ash) and waste coal (> 35% w/w ash). The ash consists of inorganic matter from the earth's crust and is an impurity that does not burn (Amcoal, nd) (Riley, nd). According to Prevost (2014), at least 20% of the coal mined in South Africa is discarded as waste (Prevost, 2014). Most coals contain mineral carbonates made up primarily of calcium carbonate and to a lesser extent ferrous and other metal carbonates (Riley, nd).

The compositions of a typical calcined and uncalcined coal are presented in Table 2.4 (Netto *et al.*, 2013; Amcoal, nd; Mubiayi, 2011). Although calcium carbonate appear to be low in a typical uncalcined coal material shown in Table 2.5, the material also contains silicate mineral (41% SiO_2) and metal oxide that can contribute to alkalinity (Novhe *et al.*, 2014). These metal oxides are known to be reactive under acidic conditions. Minerals that dissolve under acidic medium will be capable of raising the pH to the same levels as acid consumption with calcium carbonate, which under most circumstances should be above 7 (Day, nd). Francisconi *et al.*, (2013), Geremias *et al.*, (2008), Geremias *et al.*, (2012) and Netto *et al.*, (2013) studies have demonstrated the capability of the metal oxides to raise pH to above 7.

Table 2.4: Typical inorganic matter content in coal (Netto et al., 2013; Amcoal, nd; Mubiayi, 2011; Madzivire, 2009)

Constituent	**Formula**	**Typical South African coal (uncalcined)**	**Calcined coal**
		Composition (%)	
Silica	SiO_2	41	66
Aluminium oxide	Al_2O_3	26	23
Iron oxide	Fe_2O_3	6.7	5.3
Calcium oxide	CaO	11	4.63
Magnesium oxide	MgO	2.2	1.12
Potassium oxide	K_2O	0.24	0.78
Titanium oxide	TiO_2	1.5	1.79
Phosphorus pentoxide	P_2O_5	0.74	0.54
Ash		14.2-35.5	NS
Total sulphur	S	0.92	NS
Calcium carbonate	$CaCO_3$	3	0

**NS- Not specified*

Generally, waste coal has a good neutralising ability due to a relatively high ash content (> 35% w/w) containing inter alia carbonate-bearing gangue minerals, which consume acid (Amcoal, nd). The carbonate minerals will dissolve rapidly making them effective acid consumers and preferred neutralisation minerals (Salmon and Malström, 2014). The intention is to take advantage of this neutralising capacity to neutralise AMD. The alkaline content of waste coal determines whether there is enough inherent NP to counteract the acid generated from pyrite oxidation (Skousen *et al.*, 2000). Out of the many types of alkaline compounds present in rocks, only carbonates and clays are the most effective neutralising minerals because they have relatively high reactivity. diPretoro and Rauch (1988) found mine sites with NP above 3% as calcium carbonate equivalent in overburden produced alkaline drainages, while AMD resulted at NP less than 1%.

Brady and Hornberger (1989) suggest threshold values of NP greater than 3% and S less than 0.5% as guidelines for delineating alkaline-forming waste. This suggests that in order for waste coal to be suitable for AMD neutralisation, it must meet the criteria of NP above 3% and S less than 1%. Brady *et al*, (1994) showed that 3% net NP in a rock produced alkaline drainage while less than 1% net NP caused AMD from different mines. Brady and Hornberger (1990) concluded that NP from ABA shows the strongest relationship with actual post-mining water quality. NP must significantly exceed inherent acid generating potential (AP) in order to produce alkaline water. If NP and AP are similar, AMD will most likely result (Skousen, 2000). Therefore, uncalcined waste coal containing sufficient alkalinity and less S can neutralise AMD and remove contaminants. Waste coal can be used in the treatment of AMD, providing an economic use for the waste.

2.6.4. Treatment of AMD using calcined waste coal

Some studies (Francisconi *et al*, (2013), Geremias *et al*, (2008), Geremias *et al*, (2012) and Netto *et al*, (2013)) use calcined waste coal to treat AMD. This process does not take advantage of carbonate and clay minerals in waste to neutralise AMD because carbonates decompose at high temperature (near 700ºC) to give carbon dioxide and metal oxides (Mubiayi, 2011). The calcined waste coals however, contain free soluble alkaline components such as SiO_2, Al_2O_3, CaO and MgO, which neutralise AMD (Madzivire, 2009). The clay minerals transform into crystalline and non-crystalline (amorphous) aluminosilicates materials (Madzivire, 2009). Geremias *et al*, (2008) mixed calcined waste coal containing SiO_2 (66%) than Al_2O_3 (23%) and Fe_2O_3 (5.8%) with AMD in a rate of 1:25 (w/v) in Erlenmeyer flasks under magnetic stirring (200 rpm) at room temperature for 48 hours. After treatment, the pH and concentrations of Al, Fe, Mn, Cu, Cd and Zn were measured in order to evaluate the pH neutralization and the removal of metals in the solution (Geremias *et al*., 2008). The results obtained showed that the untreated AMD had low pH and high concentrations of Al, Fe, Mn and SO_4^{2-}. Treatment of AMD with calcined coal mining waste resulted in an increased pH with metal and SO_4^{2-}removal.

Calcined waste coal is characterised by fine, powdery particles that are spherical in shape. These fine, powdery particles can make the mixture of AMD and powdered calcined waste coal difficult to thicken and filter (Gitari *et al*., 2005). The process therefore requires mechanical mixing and thickeners, which may result in increased capital and operating costs. In contrast, AMD treatment with uncalcined waste coal utilises coarser particles which make filtration relatively easy, eliminating the use of mixers and thickeners that contribute to increased capital and operating costs. Furthermore, AMD treatment with calcined waste coal only relies on metal oxides present in a coal waste to neutralise AMD and does not make use of carbonate and clay minerals because they decompose at high temperatures. On the other hand, uncalcined waste coal does not only rely on oxide minerals but also utilises carbonate and clay minerals to treat AMD. The uncalcined waste coal is therefore, expected to provide higher alkalinity than calcined waste coal.

2.7. Column tests

Column tests are used extensively for the simulation of heap leaching (percolation process) (Robertson and Van Staden, 2009). It is proposed that the uncalcined waste coal samples be used to neutralise AMD by percolating the AMD solution over the waste coal stockpile and the neutralised solution be collected from the base of the pile in collection ponds. After completion, the waste coal residues may be returned to the open pit. This process will be simulated in the Mintek laboratory with column percolation tests. In order for the sample to be suitable for this process, the bed must also be permeable to the AMD solution. The permeability of the bed is a function of the fines content, and excessive slumping during column percolation indicates the potential of permeability restraints, which may become more pronounced on an actual pile (Guzman, 2008). The crush size of the solid material also plays a role in that a finer crush will generate more available reaction surface for neutralisation while at the same time, it may inhibit percolation. Percolation may be improved by agglomerating with a binder and by minimizing material compaction during stacking, for example, by using conveyors instead of trucks (Robertson and Van Staden, 2009).

2.8. South African water guidelines

As this project focuses on AMD neutralisation and removal of contaminants, the AMD constituents such as SO_4^{2-}, As, Pb, Cd, Cu, Zn, Fe, Co, Ni and Mn will be removed using uncalcined waste coal to meet the South African water guidelines as shown in Table 2.5. The extent of metal removal from AMD will be measured against these guidelines. In order to manage water reuse appropriately, the quality of the water to be reused must be correctly measured, monitored and assigned to appropriate uses, either by matching the quality to the most suitable activity or by treating the water to the quality required for the intended activity (Meyer, 2012).

Table 2.5: South African Water Guidelines for Different Uses (DWA, 2010)

Element	**Domestic use**	**Livestock drinking**	**Irrigation use**	**Industrial use**			
				User category			
				1	**2**	**3**	**4**
pH	6.0 - 9.0	-	6.5 - 8.4	7.0 - 8.0	6.5 - 8.0	6.5 - 8.0	5.0 - 10
SO_4^{2-} (ppm)	0 -200	0 -1 000	-	0 - 15	0 - 30	0 - 200	0 - 500
Ca (ppm)	0 - 32	0 -1 000	-	-	-	-	-
Mg (ppm)	0 - 30	0 -500	-	-	-	-	-
Cd (ppm)	0 - 0.005	0 - 0.01	< 0.01	-	-	-	-
Cr (ppm)	0 - 1	0 - 1	< 0.1	-	-	-	-
Co (ppm)	0 - 1	0 - 1	< 0.05	-	-	-	-
Fe (ppm)	0 - 0.1	0 - 10	< 0.2	0 - 0.1	0 - 0.2	0 - 0.3	0 - 10
Mn (ppm)	0 - 0.05	0 - 10	< 0.02	0 - 0.05	0 - 0.1	0 - 0.2	0 - 10

2.9. AMD prevention and waste coal management

Prevention of acid mine drainage formation mainly requires protection of sulphide minerals from air, water and bacteria. This can be done by several management techniques of waste rocks and tailings. Among the available management techniques, mine backfilling using a mixture of waste materials such as mixtures of mine tailings and soil, quarried and crushed aggregate, sand materials and cement, and other binders are used to minimize acid generation (Benzaazoua *et al*., 2002). Backfills are classified into dry, cemented, hydraulic and paste backfill. Backfilling and sealing of the mine waste is intended to prevent air reaching the rocks, thus limiting the oxidation of sulphides (Villain *et al*., 2013). Furthermore, Skousen *et al,* (2000) states that alkaline-rich materials, with significant sulphide concentrations, generally produce alkaline conditions in water (Skousen, 2000). It is proposed that acid base accounting (ABA) for acid-producing minerals and acid-neutralizing minerals be used to determine if a certain uncalcined waste coal material (after AMD treatment) will produce AMD or alkaline mine water. The waste coals that have propensity to produce alkaline mine water after AMD treatment could be backfilled to open pit mining without posing a risk to the environment and the backfilled waste can then be compacted in an open pit mining at conditions that will prevent the dissemination of air and water. This is a common practice in the coal mines (Spearing and

Kostecki, 2012). The waste with high sulphur content could be discharged into a lined pond, where the contact between discard, water and air is minimized to ensure minimum acid formation (Foundation for Water Research, 2004). The prevention of air flow in the waste coal can also reduce the risk of spontaneous combustion (Sloss, 2015).

2.10 Other waste coal applications

Other waste coal applications include (1) Construction (production of cement and soil stabilisers (2) Environment (monitoring of harmful compounds associated with coal waste) and (3) Energy (fuel source).

2.10.1 Construction

In Iran ~1.5 million tons of waste coal is available for re-use and a possible application of this waste is the addition to recycled pavement material. Recycled pavement material (RAP) or asphalt is material extracted from existing pavements or roads, which is crushed and reused as construction material (Modarres and Ayar, 2014). The use of recycled material and looking at alternative additives can provide sustainable resources for the construction of pavements, roads and highways. Furthermore, the use of an additive to enhance the properties of RAP is advantageous as the recycled material could possibly be of a lower grade due to degradation (Modarres and Ayar, 2014). This application was investigated by Modarres and Ayar (2014) whose research objective was to develop a cement product from coal waste (CW) and RAP, and to evaluate the properties of the blended material.

In a related study, Modarres and Nosoudy (2015) aimed to reduce the use of lime as a stabilising agent by investigating the use of coal waste as an additive to clay soil for its use as filler material in the construction of pavements and roads.

2.10.2 Environment

In China, ~4.5 billion tons of CW is stockpiled (Hu and Xia, 2017). This waste can and has been applied for the manufacturing of bricks for use in building construction (Zhou *et al.*, 2014; Taha *et al.*, 2017). However, the brick making process is intensive and can have negative impacts. Thus, Zhou *et al.* (2014) aimed to assess radioactive nuclides and heavy metals associated with the CW-brick manufacturing process to provide evidence of the implications selected processes have from coal waste re-use.

In Poland, approximately 0.6 - 0.7 tons of coal waste is generated per ton of coal mined (Ciesielczuk *et al.*, 2014). The effect of self-heating and ignition, as well as a spontaneous oxidation process occurring at coal waste discard sites or stockpiles is also of concern due to the release of toxic substances (Fabianska *et al.*, 2013). Fabianska *et al.* (2016) undertook the task to determine the potential of soil and plants as carriers of harmful chemical compounds emitted from stockpiles.

2.10.3 Energy

The use of coal for domestic purposes is widespread, especially in the South African rural communities, where it is a source of fuel for heat and cooking. Coal in the form of briquettes is an example of the type of fuel or energy source used for domestic necessities. An estimated one million households in South Africa depend on coal briquettes (Mangena and de Korte, 2005). The production of coal briquettes is not a novel technology, the concern is the burning of these briquettes, which causes air pollution and in turn health risks due to prolonged smoke inhalation. For this reason, the CSIR in conjunction with CoalTech aimed to improve the quality of briquettes.

In the United Kingdom, the potential of coal mine tailings (CMT) for pellitisation or briquetting was considered a novel application as CMT are not usually applied for this process. In addition to the CMT, the use of biomass can also contribute desirable properties for pellet or briquette products. One such example of biomass for pellet production is spent mushroom compost (SMC). SMC is an agricultural waste or residue generated from the harvesting of mushrooms. The initial mushroom compost is a combination of straw, manure and gypsum which is mixed with spores for a period of 5 weeks, after which the compost is removed and disposed of as SMC (Ryu *et al.,* 2008). Ryu *et al.* (2008), aimed to produce an environmentally safe biomass-CW pellet with the objective to evaluate the physical attributes of the CMT-SMC pellets.

Summary

The oxidation of pyrite uncovered during coal and gold mining leads to AMD formation. A typical AMD solution has low pH and elevated levels of Ca, Cd, Fe, Mg, Mn and SO_4^{2-}. This quality of water is therefore, not suitable for livestock drinking, irrigation and industrial use, according to the South African water quality standards, as shown in Table 2.5. Richards *et al.* (1993) state that in any situation, both sulphide minerals and acid-consuming minerals are likely to be present in the coal material. The relative amounts of these types of minerals will determine whether long term formation of AMD will result. The use of calcined waste coal in the AMD treatment is energy intensive and results in the leaching of toxic elements to the treated water. The literature reveals that a typical uncalcined coal material also contains carbonates, metal oxide and silicate minerals which can consume acid (Madzivire, 2009; Novhe *et al.*, 2014). The alkalinity in the uncalcined waste coal can be utilised to neutralise AMD by percolating the solution over a coal stockpile and collecting the treated solution from the base of the pile in ponds. This process will be simulated by column operation in the laboratory. According to Skousen *at al.* (2000), when sufficient alkalinity is added to AMD, metals are precipitated as metal salts such as carbonates, hydroxides or hydrogen carbonates. Since the type of waste coal material that will be in the AMD treatment will contain high amount of alkaline-rich minerals and less sulphur, there can be no long term AMD production that can be expected. The waste coal residues will be backfilled to open pit mining at conditions that will limit the dissemination of air and water in the back-filled waste coal bed.

Chapter 3

Materials and Methods

3.1. Sample receipt and preparation

Waste coal samples were obtained from Exxaro (EXX), Forzando (FOZ) and Vlakfontein (VLA) mines. AMD solution samples with a pH of 2.82 and 2.48 were obtained from Khwezela mine and Sibanye Gold mine respectively. Three batches from each of the Exxaro, Forzando and Vlakfontein samples were blended with a mechanical blender and crushed to -40 mm, - 12.5 mm and -6.3 mm using a jaw crusher. This sample preparation method is usually applied in percolation processes and was used in preliminary tests (Guzman, 2008).

The following was then performed on the head samples for all three crush sizes:

- The 100% passing 40 mm head (waste coal samples before AMD treatment) samples were dry screened (with ϕ 450 mm screens) separately at: 40 mm, 19 mm, 12.5 mm, 9.5 mm, 6.3 mm, 3.35 mm, 1.18 mm, 500 µm and 150 µm and the masses were recorded.
- The 100% passing 12.5 mm head samples were dry screened at: 12.5 mm, 9.5 mm, 6.3 mm, 3.35 mm, 1.18 mm, 500 µm and 150 µm, and the masses were recorded.
- The 100% passing 6.3 mm head samples were dry screened at: 6.3 mm, 3.35 mm, 1.18 mm, 500 µm and 150 µm, and the masses were recorded.
- The individual screen fractions were split with a riffle splitter into smaller portions and reconstituted to generate sub-samples of ~25 kg each. One 25 kg sub-sample from each waste coal sample was further crushed to 100% passing 1.7 mm using a jaw and cone crusher. The samples were then split with a rotary splitter into 200 g each. The 200 g sub-samples from each sample were pulverised by a pulveriser machine for chemical essays and mineralogy. The particle size distribution raw data is presented in Appendix A.

Residues (waste coal samples after AMD treatment) from 6 m columns (~150 kg each) were blended and were split into ~25 kg samples each. One 25 kg sub-sample from each 6 m and 1 m column residue (~25 kg each) was crushed separately to 1.7 mm with a jaw or cone crusher. The crushed material was further split with a rotary splitter into 200 g portions. The 200 g sub-samples were pulverised for chemical essays and mineralogy.

3.2. Analytical methods

Chemical analyses were performed by Mintek's Analytical Services Division. Representative sub-samples of waste coals (before and after AMD treatment) were pulverised and analysed by inductive coupled plasma optical emission spectroscopy (ICP-OES) for Ca, As, Cu, Co, Fe, Pb, Mn, Ni, Zn, Cd, chromium (Cr) and magnesium (Mg). The sulphide sulphur (S^{2-}) was analysed by a combustion technique. The NP in the form of calcium carbonate was determined by the ABA method. AMD (untreated) and accumulated drainages (treated solution) were analysed by ICP-OES for: Al, As, Ca, Cd, Cu, Co, Fe, Mn, Ni, Zn, Pb, Cd, Cr, Ca, S and Mg.

3.2.1. Determination of acid-base accounting

The modified ABA procedure, according to Lawrence and Wang (1997), was conducted on the waste coal head and residue samples. The ABA procedure is used to obtain an understanding of a material's potential to either neutralise or generate acid. A fizz test was done to determine the quantity of acid to be used for the ABA procedure. The test is subjective and requires a judgement by the test operator. The "fizz factor" was determined by dropping 25% HCl on 1 g of pulverised sample. Subsequently, 2 g of pulverised samples were weighed using a calibrated balance and placed in a 250 mL Schott bottle.

90 mL of de-ionised water was added to the bottle. At time t = 0, a volume of 0.1 M HCl determined based on "fizz factor" according to Table 3.1 was added to the bottle. The bottle was placed on a shaker and was shaken at approximately 120 rpm (or any speed at which all solids are in suspension). After 2 hours (at t = 2), another portion of 0.1 M HCl (as per Table 3.1) was added to the bottle. After 22 hours (t = 22), the pH was adjusted to reach a value between 2 and 2.5. The bottle was returned to the shaker and was shaken for another two hours, totalling 24 hours. A volume of de-ionised water was added to the bottle to obtain a final volume of 125 mL. The pH was measured again after addition of water, and adjusted to a value between 2 and 2.5. The content was then titrated to pH 8.3 using 0.1 M NaOH.

Table 3.1: Volume of HCl required at various fizz factors

Fizz rating	**Volume of 0.1M HCL (mL)**	
	AT t=0	AT t=2
None	10	10
Slight	20	10
Moderate	20	20
Strong	30	20

The NP, expressed as kg $CaCO_3$/t, was then calculated using the following equation:

$$NP = [(N_{HCl} \text{ x } V_{HCl}) - (N_{NaOH} \text{ x } V_{NaOH}) \text{ x } 50] \text{ /weight of sample (g)} \tag{17}$$

Where N is normality (Eq/L) of HCl and NaOH and V is volume (mL) HCl and NaOH. NP is expressed as calcium carbonate equivalent.

3.2.2. X-ray diffraction (XRD) analysis of waste coals

Representative sub-samples, before and after AMD neutralisation, were analysed by qualitative XRD to obtain the bulk mineralogical composition and mineralogical changes between heads and residues. A Bruker D8 Advance powder diffractometer, with Linxeye detector with Fe filtered Co-K alpha radiation was employed. The method makes use of the net intensity of the main peaks of the phases, and identification was based on the crystal structure of phases that occur in amounts of >3 mass %.

3.2.3. Determination of sulphide sulphur

An appropriate amount of sample was weighed out into a 250 mL beaker. It was then covered with a watch glass. Brominated carbon tetrachloride solution (10 mL) was added and was left for 15 minutes with occasional gentle swirling of the beaker. Concentrated nitric acid (15 mL) was added and allowed to stand for a further 15 minutes at room temperature. Approximately 1 g potassium chloride was added to convert any sulphuric acid to sulphate and thus avoid losses on baking. The beaker was placed on a steam bath, the watch glass was partially removed and the mixture evaporated to dryness. Approximately 5 ml HCl was added and the mixture was evaporated to dryness. This step was further repeated twice to ensure removal of all the nitrates. The dry residue was baked in an air oven at 110 °C for 1 hour to dehydrate the silica. Approximately 2 ml of HCl was added and then diluted to approximately 100 mL. It was then boiled for 5 minutes.

The sample was filtered through a Whatman's No 42 (12.5 cm) or equivalent filter paper and washed with hot 0.2 % HCl solution. The wash solution was collected in a 600 mL Phillips beaker. The solution was diluted to 300 mL, it was then heated to boil and ascorbic acid was added cautiously until all the ferric iron had been reduced to the ferrous state. Approximately 20 mL of 10% barium chloride solution was added drop by drop to the boiling solution. The solution was filtered through a Whatman's No 42 filter paper (or equivalent). The precipitate was washed approximately 5 times with 0.2 % HCl solution and finally with cold water until free of chlorides. The paper and precipitate were transferred to a clean tared porcelain crucible and the precipitate was dried and ignited in a muffle furnace by gradually increasing the temperature to 80 ^{0}C. It was then ignited for a further 15 minutes. The crucible was cooled in a desiccator and weighed as $BaSO_4$. A reagent blank determination was carried throughout the procedure.

$$\text{Calculation: } (A - B) \times 0.1374 \times 100 = \%S \qquad (18)$$

Where A = mass of $BaSO_4$ (g) and B = mass of blank determination (g).

3.2.4. Determination of ash content

The waste coal samples (before and after AMD treatment) were analysed for ash by proximate analyses as follows:

A clean silica dish was tared in a furnace at 110 °C for about 30 minutes. The dish was cooled in a desiccator for about 30 minutes and then weighed. Approximately 2 g of coal sample was accurately weighed into the dish. The sample was spread evenly over the base of the dish. The dish containing the sample was placed in a muffle furnace. The temperature was raised to 950°C for 16 hours. The dish was removed from the muffle and cooled in a desiccator for 30 minutes. The dish and residue were weighed.

$$\%\,\text{Ash} = \frac{(\text{mass of dish + residue after } 900\,^{\circ}\text{C - mass of dish})}{\text{mass of sample}} \times 100 \qquad (19)$$

3.2.5. Determination of elemental composition in waste coal by ICP-OES

Approximately 0.2 g of coal sample weighed into a zirconium crucible. The solid samples were ashed on the fusion apparatus machine on a high flame for 30 minutes and the zirconium crucible was cooled. Approximately 1.5 g sodium peroxide, and 0.7 g sodium carbonate were added and were mixed well with a spatula. The mixture was fused on an automatic fusion apparatus until a complete melt was achieved. The mixture was then cooled and leached in a 250 ml beaker containing 50 ml distilled water. When the reaction stopped, 40 ml concentrated HCl was added. The crucible was removed with a plastic rod and washed well with distilled water. Excess peroxide was boiled off by heating on a hot plate until no more small bubbles were seen. The solution was transferred into a 200ml volumetric flask containing 10 ml of 0.2g/L of Scandium (Sc). The sample was shaken well to mix. Excess pressure released by loosening the stopper. The samples was then analysed by ICP-OES machine for base metals. Data was collected.

3.2.6. Determination of elemental composition in solution by ICP-OES

An auto-dilutor was used to pipette 5 ml sample into 25 ml beaker. Approximately 4% nitric acid and 0.2 g/l Sc were added. Deionised water was added to make up the volume to 25 ml. The solution was then analysed by by ICP-OES machine for base metals. Data was collected.

3.3. Column tests

3.3.1 Test matrix

The experimental matrix is presented in Table 3.2 and the loading data is shown in Appendix B.

Phase 1 (Test 1) was performed on Forzando coal (-40 mm) in 1 m columns and irrigated at 0.4 mL/min (1.3 L/m^2/h) and 2.0 mL/min (6 L/m^2/h). The columns were irrigated with an AMD solution from Sibanye Gold mine (pH 2.48) and were stopped when the pH of the treated solutions dropped below 6.

Phase 2 (Test 2) was performed in 1 m and 6 m columns on both Exxaro and Vlakfontein material at 3 different crush sizes (-40 mm, -12.5 mm and -6.3 mm). These columns were irrigated at 0.44 mL/min. Phase 2 was irrigated with an AMD solution from the Khwezela mine (pH 2.82). Due to insufficient samples, Vlakfonein at a -6.3 mm crush size was only tested in 1 m columns.

3.3.2. Agglomeration

Representative sample splits of approximately 25 kg were placed on plastic sheets. AMD was added with a watering can while the samples were rolled on the sheet to form agglomerates. AMD was added until agglomeration was complete as judged by visual inspection.

3.3.3. Column operation

Tests were performed in 160 mm ID, 1 m or 6 m tall, water-jacketed polypropylene columns. The columns were charged with crushed waste coal and irrigated with AMD in open cycle, which was percolated downwards by gravity. The alkalinity in the waste coal resulted in an increase in the solution pH, with subsequent precipitation and removal of the metals. The volume of precipitates was expected to be small relative to the overall void volume in the column and was therefore not expected to inhibit percolation. Drainages were collected from the base of columns. The masses, volumes, specific gravity (SG) and pHs of the feed and the drainages were measured daily. The drainages were accumulated in a collection tank. The pH of the mixed solution in the accumulation tank was also measured daily. The drainage pH was initially high and the test was run until the pH in the accumulation tank decreased to below 6, at which point the irrigation was switched off. The columns were allowed to drain and the wet solids were discharged.

Table 3.2: Test matrix

Sample ID	Units	FOZ 1	FOZ 2	EXX 1	EXX 2	EXX 5	VLA 1	VLA 2	VLA 5	EXX 3	EXX 4	EXX 6	VLA 3	VLA 4
Test		**Test 1**		**Test 2**										
Screen size	mm	-40	-40	-40	-12.5	-6.3	-40	-12.5	-6.3	-40	-12.5	-6.3	-40	-12.5
Column height	m	1	1	1	1	1	1	1	1	6	6	6	6	6
Column inner diameter	mm	160	160	160	160	160	160	160	160	160	160	160	160	160
Feed solution pH	-	2.48	2.48	2.82	2.82	2.82	2.82	2.82	2.82	2.82	2.82	2.82	2.82	2.82
Column temperature	°C	25	25	25	25	25	25	25	25	25	25	25	25	25
Irrigation flowrate	mL/min	0.44	2.01	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.44

An overview of the experimental procedures and schematic representation of 1 meter column test are shown in Figures 3.1 and 3.2 respectively. The schematic representation of 6 meter column test is shown in Appendix C and SHE Risks in Appendix D.

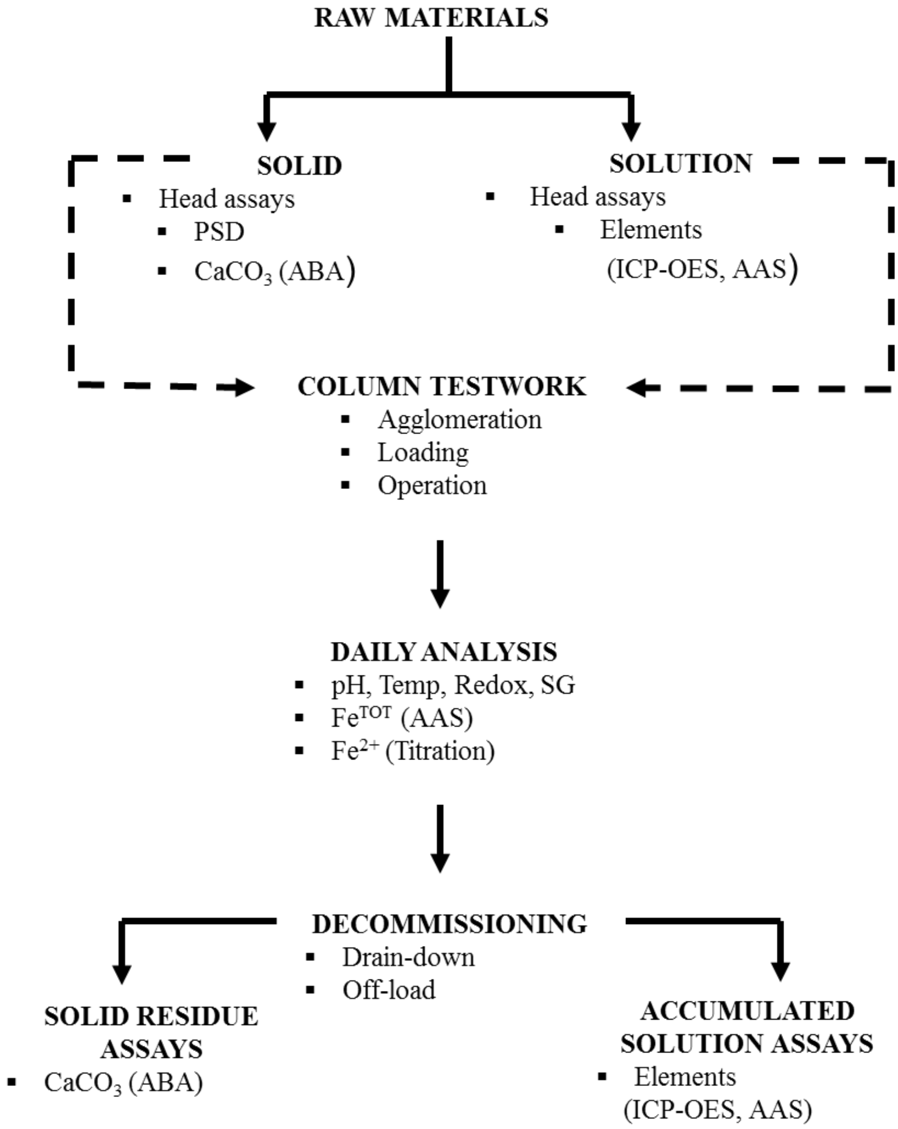

Figure 3.1: Experimental programme

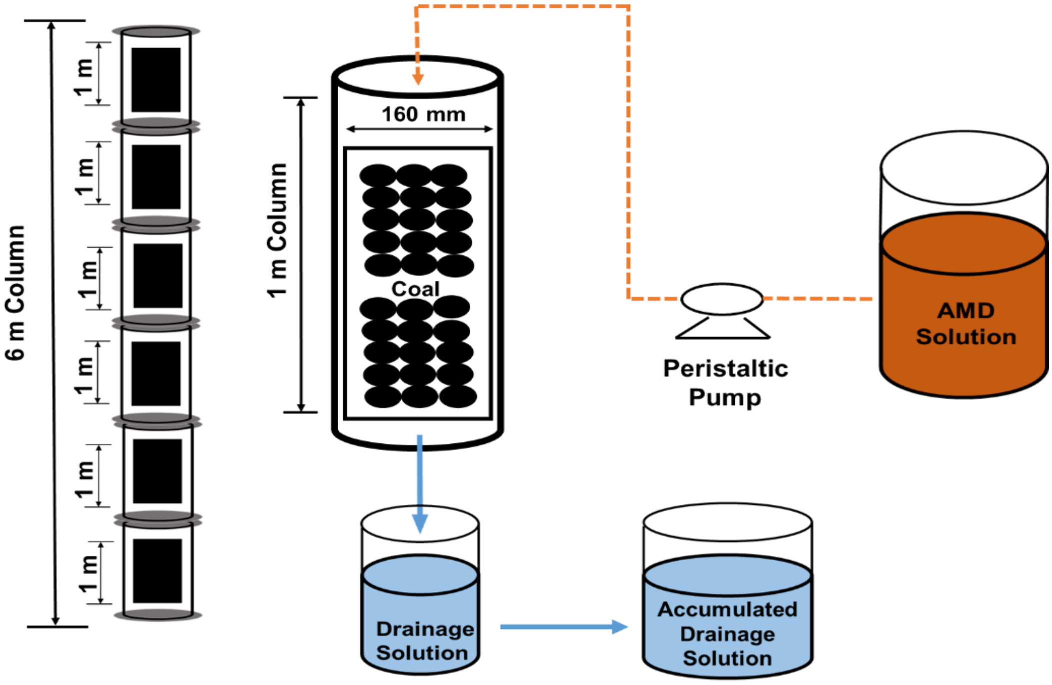

Figure 3.2: Schematic representation of column tests

3.4 Visual MINTEQ 3.1 Simulation

Geochemical modelling, Visual MINTEQ 3.1 Simulation was used to investigate the removal mechanism of dissolved metals. Visual MINTEQ is a free Windows version of MINTEQA2 ver 4.0, which was released by the United States Environmental Protection Agency (U.S. EPA) in 1999. It is the most widespread chemical equilibrium software in use that has thermodynamic data which can be used to estimate metal speciation, solubility, and equilibria of dissolved and solid phases in aqueous systems. This software has successfully been used by a number of researchers to model solution chemistry (Ma, 2012; Park, 2005). Visual MINTEQ 3.1 uses saturation index (SI) as a key parameter to evaluate the saturation states of thermodynamically probable precipitates. Theoretically, when $SI > 0$, the solution is supersaturated and precipitation occurs spontaneously; when $SI < 0$, the solution is undersaturated and no precipitation occurs; while $SI = 0$ implies the water and mineral are at chemical equilibrium.

Chapter 4

Results and Discussions

This chapter presents and discusses the results obtained from the experimental work conducted as explained in the previous chapter. This chapter also aims to examine the findings based on the literature stipulated in Chapter 2. The areas that will be studied are: the particle size distributions (PSD) of uncalcined waste coals, the composition of the waste coals and AMD before and after treatment. The effect of irrigation rate, type of waste coal and crush size on neutralisation capacity are also studied as well as the neutralising capacities of waste coals and the volume of the treated solutions.

4.1. Particle size distribution

Particle size distribution curves of the three head samples are presented in Figure 4.1 to 4.3, the PSD standard deviation is shown in Table 4.1 and the raw data is shown in Appendix A. The results showed that the trends of the PSD curves of all sub-samples in each crush size (-40 mm, -12.5 mm and -6.3 mm) were identical (the curves lie on top of each other), in all three waste coals (Exxaro, Vlakfontein and Forzando). This suggests that the samples tested were representative with respect to particle size. The fines (-1 mm) content increased from below 5% in the coarser crush size (- 40 mm) to above 20% in the finer (-6.3 mm) crush size. As the surface area required for chemical reaction increases with increasing fines content, it is expected that the finer crush sizes will have improved neutralising capacity. The Exxaro sample PSD is virtually the same sample as Vlakfontein sample PSD at -12.5 mm and -6.3 mm crush sizes. The standard deviation values are close to zero in all the samples. This suggest that the sub-samples were representative and the bulk samples were homogenous.

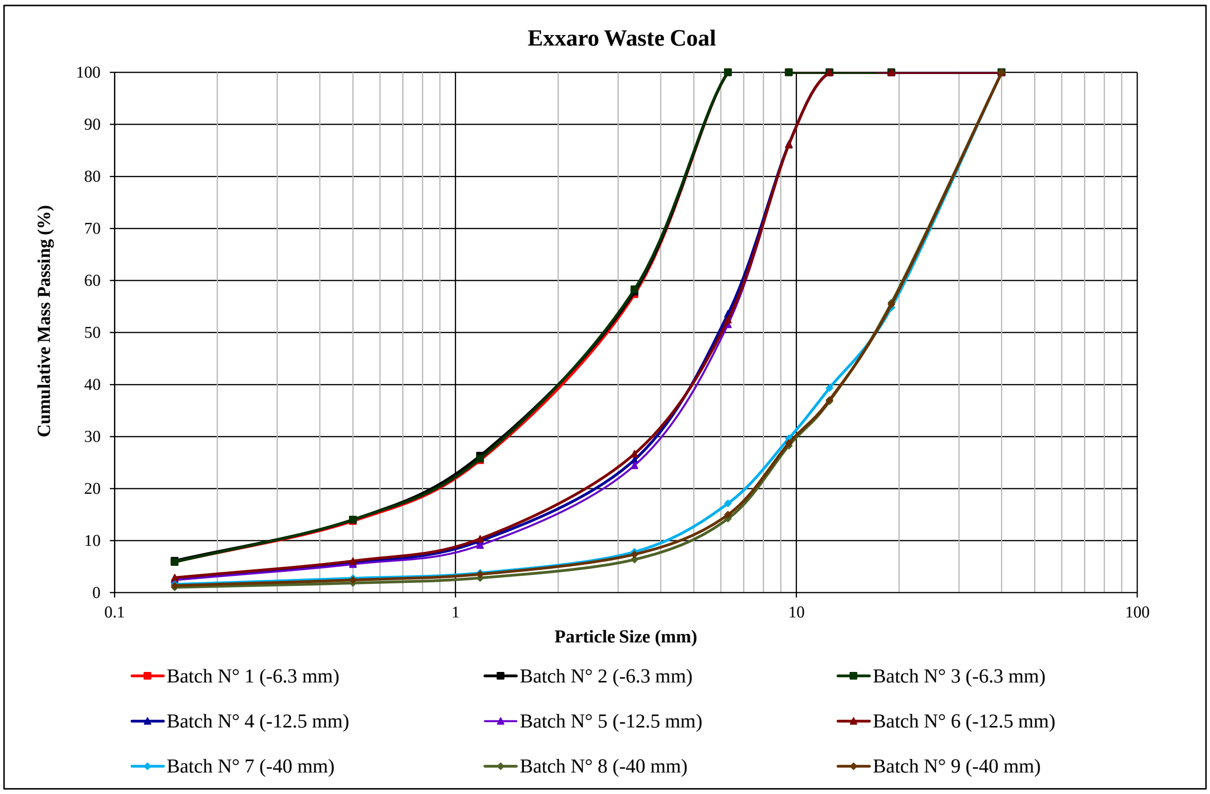

Figure 4.1: Particle size distributions of the Exxaro waste coal (head)

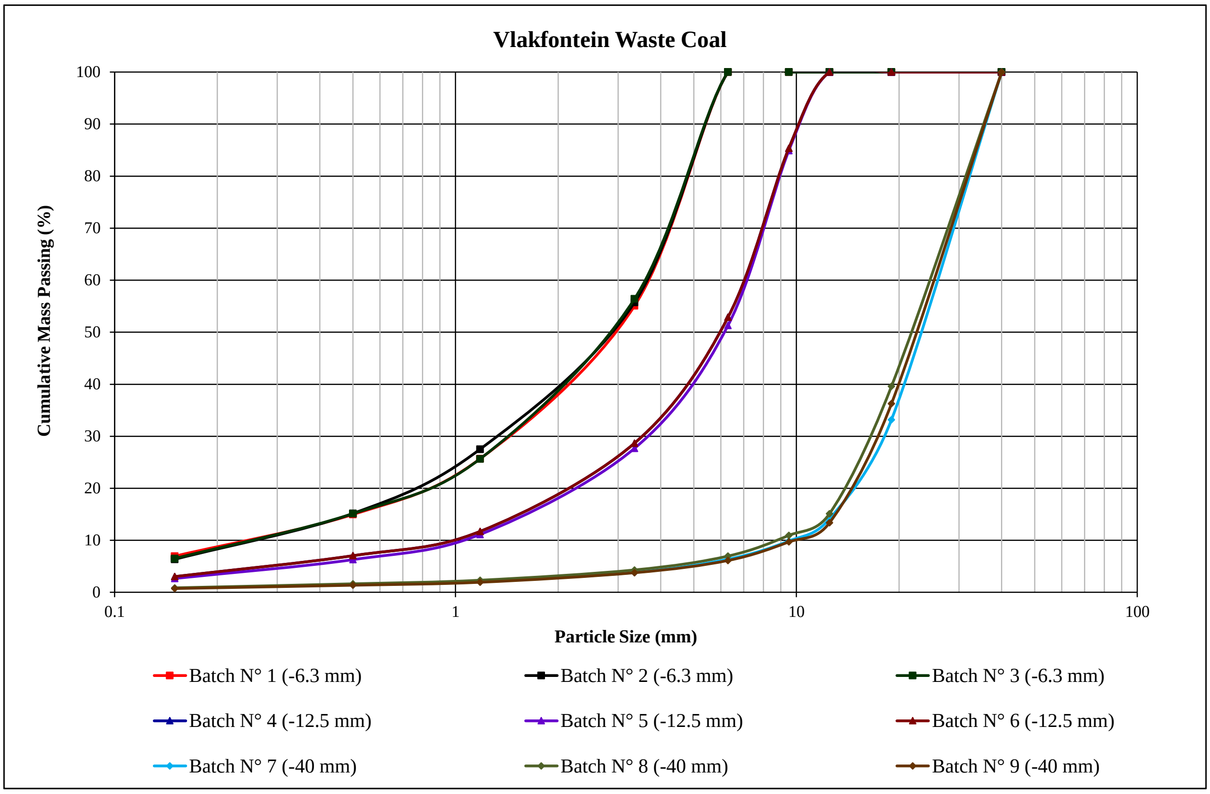

Figure 4.2: Particle size distributions of the Vlakfontein waste coal (head)

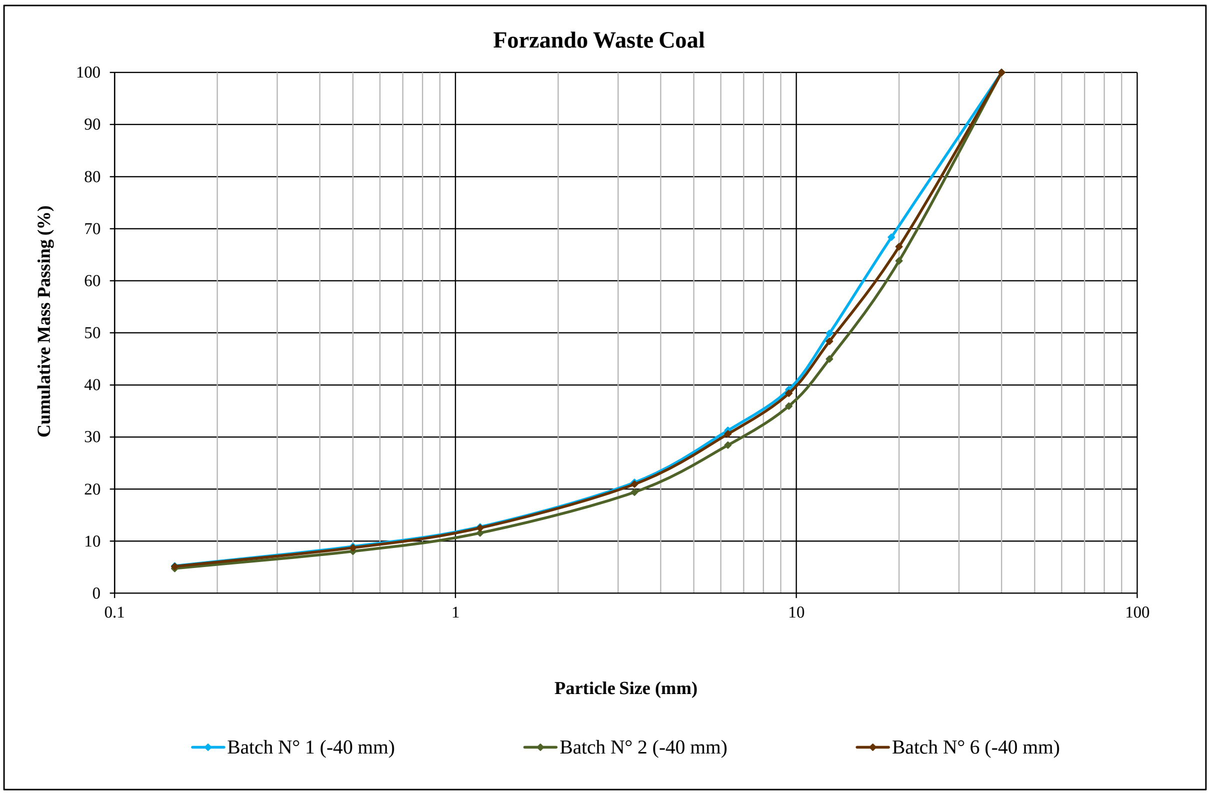

Figure 4.3: Particle size distributions of the Forzando waste coal (head)

Table 4.1 PSD standard deviations

Screen size	**Exxaro**			**Vlakfountein**			**Forzando**
mm	-40 mm	-12.5 mm	-6.3 mm	-40 mm	-12.5 mm	-6.3 mm	-40 mm
40							
19	0.116			0.731			0.23
12.5	0.46			0.626			0.54
9.5	0.184	0.018		0.072	0.057		0.196
6.3	0.203	0.236		0.057	0.143		0.189
3.35	0.229	0.277	0.128	0.035	0.077	0.021	0.0379
1.18	0.064	0.133	0.126	0.028	0.054	0.076	0.0500
0.5	0.017	0.089	0.058	0.014	0.021	0.058	0.0500
0.15	0.043	0.028	0.032	0.017	0.051	0.026	0.0058
-0.15	0.071	0.058	0.021	0.015	0.047	0.015	0.0115

4.2. Composition of the waste coal samples

The waste coal constituents are shown in Table 4.2. The results indicate that the Exxaro waste coal contained an alkalinity of 0.49 % NP as calcium carbonate equivalent, which is less than the alkalinity of Vlakfontein and Forzando waste coals. The alkalinity of Vlakfontein and Forzando waste coal were 2.32 % NP and 2.33 % NP as calcium carbonate equivalent, respectively. Silicon (Si) was the dominant element in all three waste coal samples, followed by Al, calcium (Ca) and then magnesium (Mg). This is a common characteristic of waste coal

(Modarres and Ayar, 2014, Vegas *et al.*, 2015). The Exxaro waste coal contained higher concentrations of Si and Al (22% Si and 9.9 % Al) than the Vlakfontein (5.2 % Si and 3.9 Al) and Forzando (9.5 % Si and 3.3 Al) waste coal. At this stage, it is expected that the Vlakfontein and Forzando waste coal will show better neutralisation capacity than the Exxaro waste coal.

The Exxaro waste coal contained 0.49 % NP and 1.2% S^{2-}. This therefore indicates that the acid generating species is higher than the neutralising potential in the Exxaro waste coal. This sample might therefore not be suitable for use in the AMD neutralisation. Brady *et al,* (1994) suggests that 3% net NP in the rock produces alkaline drainage while less than 1% net NP causes AMD. Skousen *et al*, (2000) states that the alkalinity (NP) must significantly exceed the inherent content of acid generation species in order to produce alkaline water. In both Forzando and Vlakfontein waste coals, the NP exceeded the acid generating species.

4.3. Composition of the AMD solutions

The concentration of elements in AMD solutions from Khwezela mine and Sibanye Gold mine are shown in Table 4.3. The results show that both the untreated AMD solutions contained high concentrations of sulphate, calcium, Al, Mn, Si, sodium (Na) and Zn, which is consistent with the literature (Scott, 1995). This quality of both solutions is not suitable for livestock drinking, irrigation and industrial use, according to the South African water quality standards specified by DWA (Table 2.5). The AMD from Khwezela mine contained higher concentrations of Al, Cu, Fe, Si and S than the AMD from Sibanye Gold mine. Both AMD solutions also contained low concentrations of Cd, Cr and Co.

Table 4.2: Waste coal constituents before AMD treatment (%)

Samples	Al	Ca	Co	Cr	Cu	Fe	Pb	Mg	Mn	Ni	Si	Ti	V	Zn	Sulphide S	NP ($CaCO_3$)**
Exxaro coal *	9.88	0.33	<0.05	<0.05	<0.05	1.78	<0.05	0.17	<0.05	<0.05	22	0.47	<0.05	<0.05	1.2	0.49
Vlakfontein *	3.71	1.31	<0.05	<0.05	<0.05	1.1	0.25	<0.05	<0.05	<0.05	5.6	0.26	<0.05	<0.05	1.1	2.32
Forzando *	3.32	1.21	<0.05	<0.05	<0.05	0.83	<0.05	0.18	<0.05	<0.05	9.5	0.20	<0.05	<0.05	0.6	2.33

*Waste coal sample

**Alkalinity expressed as equivalent $CaCO_3$ content

Table 4.3: AMD solutions

Source	Used	Al	Ca	Cu	Cd	Cr	Co	Fe	Mg	Mn	S	Si	Zn	SO_4^{2-} *
Sibanye Gold mine	Preliminary test	411	519	<2	<2	<2	3.9	4650	576	151	5060	37	13	15180
Khwezela mine	Treatment of Exxaro and Vlakfontein waste	424	492	10.9	<2	<2	<2	6325	494	103	6455	90.6	12.5	19365

*The concentration of SO_4^{2-} is calculated by multiplying the concentration of S^{2-} by a factor of 3 (it is assumed that the measured sulphur (S) in solution is SO_4^{2-}, hence the conversion of S to SO_4^{2-}.

4.4. Preliminary test

4.4.1 Effect of irrigation rate on waste coal neutralisation capacity

The preliminary neutralisation test was conducted on Forzando waste coal with Sibanye Gold mine acid mine drainage, with single pass to determine whether uncalcined waste coal can be able to neutralise AMD at -40 mm and -12.5 mm crush sizes.

The daily drainage solution (treated solutions collected daily from the columns) pH profiles for Forzando sample at 1 m and -40 mm crush size are shown in Figure 4.4. The Forzando sample at -40 mm crush size and 0.44 mL/min irrigation rate (FOZ 1) attained a pH above 7 within 24 hours and maintained this pH level for 19 days, while at 2.01 mL/min irrigation rate, at same crush size (FOZ 2) achieved a pH above 7 within 24 hours, which dropped after a day to pH 6.05. The higher irrigation rate therefore, resulted in a faster drop in the pH since the acid for reaction with the carbonate gangue was supplied faster. The Forzando sample at -40 mm crush size neutralised 10 litres of AMD at 0.44 mL/min irrigation rate, whereas at 2.01 mL/min irrigation rate, it only neutralised 3 litres of AMD solution. FOZ1 and FOZ 2 had neutralising capacities of 587 L/t and 393 L/t respectively. This suggests that reducing the flow rate for the same crush size increases the neutralising capacity. The preliminary test work therefore indicated that a lower irrigation rate (0.44 mL/min) provided more efficient solution utilisation and as a result, subsequent tests were performed at this irrigation rate.

The test work was used only as a preliminary test and no further investigations were conducted on the samples due to cost restrictions and insufficient samples. Uncalcined waste coal with sufficient alkalinity has shown to be capable of raising the AMD pH from Sibanye Gold. Therefore, it is probable that uncalcined waste coal will also be able to treat AMD from Khwezela mine since the contaminants that impacted the Sibanye Gold AMD are virtually the same as those that are found in Khwezela mine AMD (Table 4.3). Table 4.3 also shows that the levels of contaminants in Sibanye Gold AMD are almost equal (or in the same range) to the contaminants in Khwezela mine AMD.

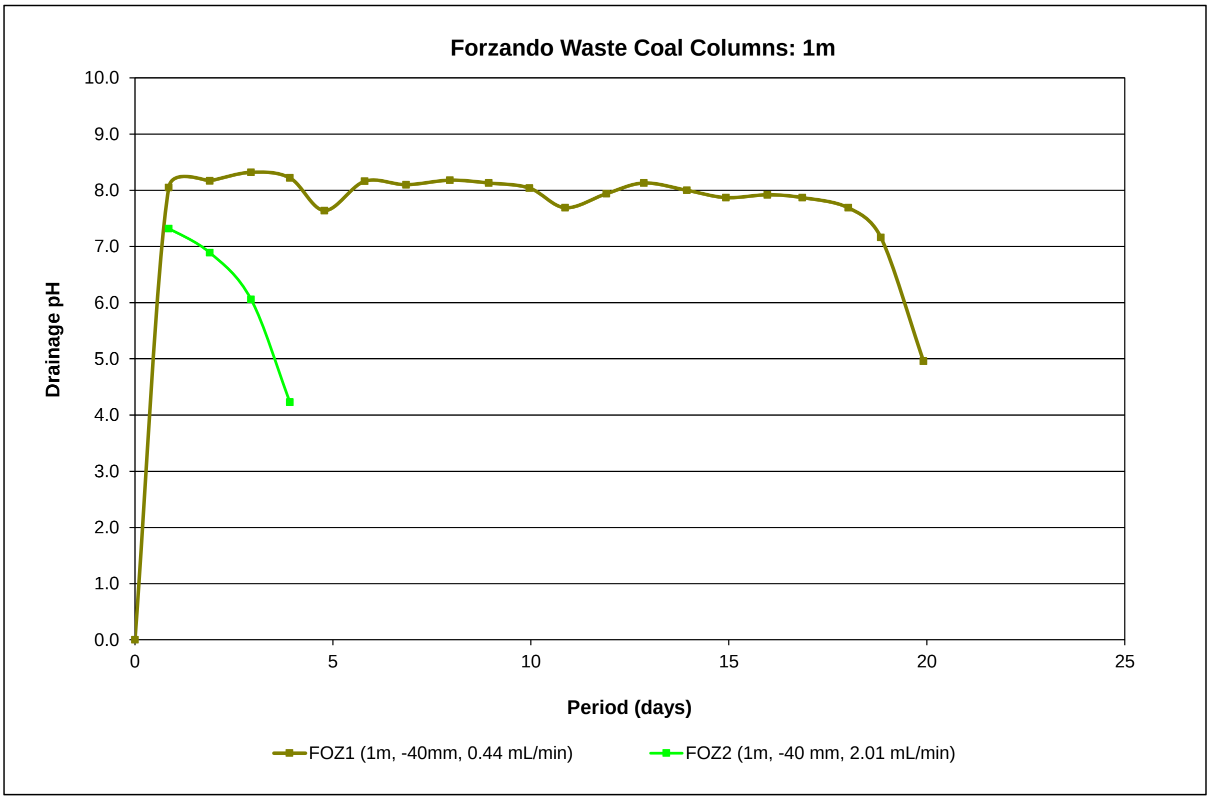

Figure 4.4: Drainage profiles: Forzando waste coal at 0.44 mL/min and 2.01 mL/min irrigation rates, 1 m height and -40 mm crush size

4.5. AMD treatment with Exxaro and Vlafontein waste coals

The AMD treatment with Exxaro and Vlafontein waste (which is the main focus of this research) was conducted on 1 m and 6 m columns, irrigated with Khwezela mine AMD, at single pass operational mode and 0.44 mL/min irrigation rate. The irrigation rate of 0.44 mL/min was chosen since the rate performed better in the preliminary test work. The Khwezela mine AMD was used instead of Sibanye Gold mine AMD since it was sourced in the same province as the waste coals and the chemistry of these AMD solutions is virtually the same. The proposed method will be used to treat AMD situated in close proximity to alkaline-rich waste coal to reduce transportation costs.

4.5.1. Effect of waste coal type and crush size on neutralisation capacity

Daily drainage pH profiles of the 1 m and 6 m columns are presented in Figure 4.5.

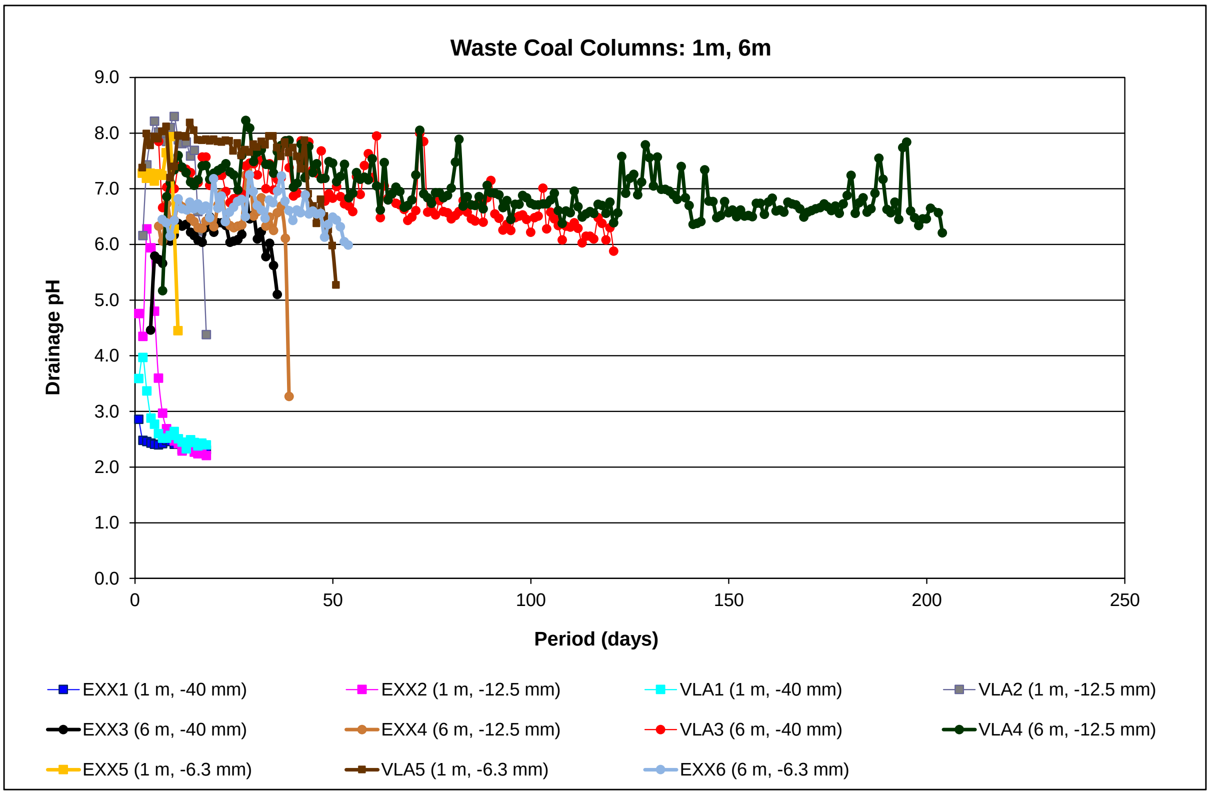

Figure 4.5: Drainage pH profiles

<u>1 m columns</u>

The Exxaro sample at the coarser crush sizes (-40 mm) did not achieve a neutral pH, whereas the -6.3 mm crush size achieved a pH above 7 on day 1 and maintained this level until day 10. The Exxaro sample at -12.5 mm exhibited a pH close to 7 on day 3 and started to drop immediately after day 3. The Vlakfontein sample at the coarse crush size (-40 mm) did not achieve a neutral pH, whereas the -12.5 mm crush size maintained a pH above 7 from day 2 to day 16 and the -6.3 mm crush size until day 45. The crush size therefore, has a marked effect on the neutralising capacity, with the Exxaro sample exhibiting the lower neutralising capacity due to the low neutralising potential (Table 4.2). Even though the sulphur species exceeded the NP in the Exxaro sample, the sample managed to neutralise AMD. The reason for this could be that the acid generating reaction was not instantaneous or faster than the neutralisation reaction. According to Antonio *et al*. (2014), the acid generation reaction (equation 1) is limited by the oxygen availability and its kinetics is dependent on the speed at which molecular oxygen reduces. Thus, no reaction takes place when the O_2 concentration in the medium is low. In this experiment, the neutralisation occurred under non-aerated conditions. Therefore, the O_2 concentration in the medium is expected to be low.

Although the Vlakfontein sample contained the same amount of alkalinity (NP) as the Forzando waste coal, the Vlakfontein sample could not neutralise AMD at -40 mm crush size, whereas the Forzando waste coal could neutralise AMD at the same crush size (-40 mm). The Vlakfontein sample was irrigated with the AMD solution from Khwezela mine, which contains elevated levels of aluminium and iron than the AMD from Sibanye Gold mine. The presence of these two metal species in high concentration may have decreased the effectiveness of the alkalinity in the Vlakfontein sample. According to Wolfe and Hedin (2010), the disadvantages of using $CaCO_3$ to treat AMD include slow reaction time and when exposed to AMD containing Al^{3+} and Fe^{3+}, solids quickly form. These solids foul limestone, decreasing its effectiveness.

Another notably difference between the Vlakfontein and Forzando waste coal at -40 mm crush size is their PSDs. The particle size distribution for Vlakfontein sample shows 80% passing 32 mm with 20% passing 15 mm and the particle size distribution for Forzando sample shows 80% passing 28 mm with 20% passing 3 mm, particle size distribution. This suggests that the Forzando sample contains more fine material (20% passing 3 mm) than the Vlakfontein sample (20% passing 15 mm). Neutralising capacity increases with the decrease in particle size. Thus, the difference in neutralising capacity between the samples (Vlakfontein and Forzando waste coal) can also be attributed to the difference in PSDs.

6 m Columns

On all 6 m columns, the first drainage came out on day 6 at pH between 6 and 7. All 6 columns exhibited positive outcomes with regards to AMD neutralisation. The Exxaro waste coal columns maintained a neutral pH for 38 days (-40 mm), 40 days (-12.5 mm) and 55 days (- 6.3 mm), respectively. It can be assumed that the alkaline minerals in coal were well liberated in finer particles than in coarse particles. Therefore, it can be speculated that higher neutralisation capacity exhibited by small crush size samples is due to the high degree of liberation of alkaline minerals in small crush size samples. Although the Exxaro sample showed a low neutralising capacity in 1 m columns, the neutralising capacity generally improves when a bigger mass, small crush size and a high stacking height is used. The Vlakfontein waste coal columns maintained a neutral pH for 121 days (-40 mm), and 204 days (-12.5 mm), respectively. The column tests were stopped when the pH of the daily drainage solutions dropped below 6. The drop in the pH of the daily drainage solutions is caused by the depletion of clay and carbonate minerals in the waste coal samples. Based on the pH profiles, neutralisation is dependent on the alkaline content and crush size.

4.5.2. Neutralising capacity and equivalent lime consumption

The neutralising capacity and equivalent lime consumption results are presented in Table 4.4.

Table 4.4: Neutralising capacity, volume of treated solutions and equivalent lime consumption

Samples	**Neutralisation capacity (L/t)**	**Vol of AMD neutralised (L)**	**Lime Equivalent (kg $Ca(OH)_2$ / t coal)***
EXX1 (1 m, -40 mm)	0	0	0.0
EXX2 (1 m, -12.5 mm)	79.1	1.7	1.0
EXX5 (1 m, -6.3 mm)	282.2	5.9	3.5
VLA1 (1 m, -40 mm)	0	0	0.0
VLA2 (1 m, -12.5 mm)	757.9	11.8	9.5
VLA5 (1 m, -6.3 mm)	2152.0	36.5	27.0
EXX3 (6 m, -40 mm)	158.2	23.7	2.0
EXX4 (6 m, -12.5 mm)	162.4	21.9	2.0
EXX6 (6 m, -6.3 mm)	283.6	37.0	3.6
VLA3 (6 m, -40 mm)	810.15	84.90	10.2
VLA4 (6 m, -12.5 mm)	1410.1	140.7	17.7

** Based on a lime consumption of 12.53 kg Ca $(OH)_2$ / m^3 AMD to neutralise AMD (Maree et al., 2013)*

1 m Columns

The results indicate that the Exxaro waste coal had no neutralising capacity at -40 mm crush size, whereas at -12.5 mm and -6.3 mm crush sizes, the neutralising capacities were 79 L/t and 282 L/t, respectively. The Vlakfontein waste coal at -40 mm, -12.5 mm and 6.3 mm crush sizes exhibited a neutralising capacity of 0; 758 L/t and 2152 L/t respectively. This indicates that the neutralising capacity of the waste coal increases with the decrease in crush size. The lime equivalents with the Exxaro sample ranged from 0 (-40 mm) to 3.5 kg $Ca(OH)_2$ / t coal (-6.3 mm). With the Vlakfontein sample, the lime equivalents were between 0 (-40 mm) and 27 kg $Ca(OH)_2$ / t coal (-6.3 mm).

6 m columns

The results indicate that the Exxaro waste coal had neutralising capacities of 158 L/t, 162 L/t and 284 L/t at -40 mm, -12.5 mm and -6.3 mm crush sizes, respectively. The Vlakfontein waste coal at -40 mm and -12.5 mm crush sizes exhibited a neutralising capacity of 810 L/t and 1410 L/t, respectively. The results also indicate that the neutralising capacity of the waste coal increases with the decrease in crush size. This is consistent with 1 m columns results. The lime equivalents with the Exxaro sample ranged from 2 kg $Ca(OH)_2$ / t coal (-40 mm) to 3.6 kg $Ca(OH)_2$ / t coal (-6.3 mm). The lime equivalents were between 10.2 kg $Ca(OH)_2$ t coal (-40 mm) and 17.7 kg $Ca(OH)_2$ / t coal (-12.5 mm) with the Vlakfontein sample.

The neutralisation capacity is generally higher in 6 m columns than in 1 m columns. This is thought to be the result of longer residence times and better solution contact achieved in the taller columns.

4.5.3. Volume of treated solutions

The volumes of treated solution are presented in Table 4.4. The volumes treated by the Exxaro samples were: 24 L (EXX3), 22 L (EXX4), 6 L (EXX5), 37 L (EXX6) in 33 days, 38 days, 10 days and 54 days, respectively. The volumes treated by the Vlakfontein waste coal samples were: 12 L (VLA2), 85 L (VLA3), 141 L (VLA4), 37 L (VLA5) in 18 days, 121 days, 204 days and 51 days, respectively. The results indicate that the Exxaro waste coal (0.49 % NP) neutralised a smaller amount of AMD compared to the Vlakfontein waste coal (2.32 % NP). Since the neutralising capacity increased with a finer crush size for both the Exxaro and Vlakfontein samples, it is therefore suggested that the alkaline minerals may not be as well liberated (exposed to the AMD solution) at coarser particle sizes as in the finer particle sizes. The substantial amount of AMD treated with Vlakfontein sample at small crush size suggests that the concept can be applied commercially.

4.5.4. Waste coal and AMD analysis before and after AMD treatment

Table 4.5 shows the proximate analysis of waste coal samples before and after AMD treatment. The Exxaro and Vlakfontein waste coal samples contained (before AMD treatment) ash contents of 70 % and 25 %, respectively. The results indicate that the ash component in all waste coal samples did not experience a significant change during AMD neutralisation.

Table 4.5: Proximate analysis of waste coals before and after AMD treatment

Waste coal	**Ash (%)**	**Fixed Carbon (%)**	**Moisture (%)**	**Volatile (%)**
Exxaro *	**70.0**	**14.4**	**1.47**	**14.5**
EXX 3 ** (6 m, -40 mm)	70.4	13.0	1.4	15.2
EXX 4 ** (6 m, -12.5 mm)	70.4	12.6	0.99	16.4
EXX 5 ** (1 m, -6.3 mm)	70.0	12.4	1.5	16.2
EXX 6 ** (6 m, -6.3 mm)	69.9	14.4	1.1	14.6
Vlakfontein *	**25.3**	**48.0**	**3.2**	**23.5**
VLA 2 ** (1 m, -12.5 mm)	25.3	47.6	3.6	23.6
VLA 3 ** (6 m, -40 mm)	25.0	45.7	3.7	22.9
VLA 4 ** (6 m, -12.5 mm)	24.9	46.2	5.6	23.6
VLA 5 ** (1 m, -6.3 mm)	25.0	47	3.9	20.6

* Before AMD treatment

** After AMD treatment

Table 4.6 presents X-ray diffraction (XRD) results of the Exxaro and Vlakfontein waste coals.

Table 4.6: XRD results

Phase	**Chemical formula**	**Vlakfontein waste coal**					**Exxaro waste coal**				
			Residue					**Residue**			
		Head	**VLA 2 (1 m, -12.5 mm)**	**VLA 3 (6 m, -40 mm)**	**VLA 4 (6 m, -12.5 mm)**	**VLA 5 (1 m, -6.3 mm)**	**Head**	**EXX 3 (6 m, -40 mm)**	**EXX 4 (6 m, -12.5 mm)**	**EXX 5 (1 m, -6.3 mm)**	**EXX 6 (6 m, -6.3 mm)**
Quartz	SiO_2	intermediate	intermediate	intermediate	intermediate	major	major	predominant	predominant	predominant	predominant
Kaolinite	$Al_2Si_2O_5(OH)_4$	predominant	intermediate	major	major	intermediate	major	intermediate	intermediate	intermediate	intermediate
Calcite	$CaCO_3$	minor	*	trace	*	*	*	*	*	*	*
Dolomite	$CaMg(CO_3)_2$	trace	trace	trace	trace	*	*	*	*	*	*
Pyrite	FeS_2	minor	trace	minor	trace	trace	*	trace	trace	trace	trace
Gypsum	$Ca(SO_4)•2(H_2O)$	*	minor	trace	intermediate	intermediate	minor	*	*	*	*
Mica	$KAl_3Si_3O_{10}(OH)_{1.8}F_{0.2}$	*	*	minor	*	*	minor	minor	intermediate	minor	minor

** not detected, <5% trace, 5-15% minor, 15-30% Intermediate, 30-50% major, >50% predominant*

Before AMD treatment, the Vlakfontein waste coal contained a significant amount of kaolinite (clay) mineral (>50%), minor amount of calcite (carbonate) mineral (5 to 15%) and a trace amount of dolomite (carbonate) mineral (<5%). It also contained a small amount (5 to 15%) of acid generating mineral (pyrite) and 15 to 30% amount of quartz. The results indicate that calcite and kaolinite experienced a decrease during AMD neutralisation in all the Vlakfontein samples, while dolomite only experience a decrease in the VLA 5 sample, where a smaller crush size was used (-6.3 mm). This suggests that the clay and carbonate minerals were involved in the neutralisation reaction. This is consistent with literature, which suggests that out of the many types of alkaline compounds present in rocks, only carbonates and clays are the most effective neutralising minerals (Skousen *et al*., 2000). Pyrite in all the Vlakfontein samples also experienced a decrease during neutralisation except in VLA 3 sample. In the Exxaro samples, the pyrite experienced an increase during AMD treatment. Pyrite is an acid generating mineral and could not have taken part in the pH increase during AMD neutralisation (Skousen *et al*., 2000). The presence of pyrite in the waste coals could not prevent a pH increase in AMD, this is consistent with literature, which suggests that alkaline-rich materials, even with significant sulphide concentrations, often produce alkaline conditions in water (Skousen *at al*., 2000).

The decrease in the pyrite in the Vlakfontein samples during AMD neutralisation suggests that the AMD generating potential is reduced due to the lower amount of pyrite now present in the residual material, and an increase in pyrite in the Exxaro samples imply that the acid generating potential has increased.

Gypsum experienced an increase during AMD neutralisation in all the Vlakfontein samples tested. This suggests that the neutralisation reactions resulted in the formation of gypsum. The formation of gypsum may have been influenced by the presence of $CaCO_3$ in the Vlakfontein waste coal as literature states that when $CaCO_3$ gets into contact with AMD, SO_4^{2-} precipitate as gypsum (Scott, 1995).

$$CaCO_3 + H^+ = Ca^{2+} + HCO_3^- \qquad (20)$$

$$Ca^{2+} + SO_4^{2-} \rightarrow CaSO_4.H_2O \qquad (21)$$

Before AMD treatment, the Exxaro waste coal contained elevated levels of kaolinite (30% to 50%) and quartz (30% to 50%), minor amounts of pyrite (5 to 15%) and mica minerals (5 to 15%). The sample was devoid of carbonate minerals such as calcite and dolomite, which are capable of raising the pH or were available in small quantities, less than 3% (detection limit > mass 3%). Kaolinite was the only alkaline mineral available in the Exxaro waste coal and it experienced a decrease during AMD treatment in all the Exxaro samples tested. Therefore, the pH increase with the Exxaro waste coal can be attributed largely to the presence of the kaolinite mineral in the sample.

The presence of calcite and dolomite in the Vlakfontein sample may have contributed to the high alkalinity (2.32 % NP) of this sample and their absence in the Exxaro waste coal may have resulted in the low alkalinity (0.49 % NP). The levels of the alkaline minerals in both the Exxaro and Vlakfontein samples are consistent with the neutralising capacities and drainage pH changes exhibited by these samples. Therefore, it can be concluded that calcite, dolomite and kaolinite minerals are the components in the waste coals responsible for AMD neutralisation. The alkaline minerals were not completely consumed during AMD neutralisation. This therefore suggests that the waste coal samples are not likely to produce AMD after use.

The chemical assays for the used waste coal samples (residues), relative to the head are shown in Table 4.7. The alkalinity of the waste coals tested decreased drastically during AMD neutralisation. This suggests that the alkaline minerals were consumed and were responsible for pH increase during AMD neutralisation. The concentrations of metal species did not significantly change during AMD neutralisation except VLA 5 which experienced an increase in aluminium and iron content. VLA 5 column operated for extended number of days than other 1 m columns. This may have led to a higher accumulation of aluminium and iron from AMD, which can precipitate during neutralisation when $CaCO_3$ is present (Wolfe and Hedin, 2010).

The concentrations of aluminium, iron, silicon, aluminium and sulphur remained high during AMD neutralisation. This suggests that these elements may contaminate clean water. The elevated concentrations of iron and sulphur that remain in coal samples after AMD neutralisation also indicate the presence of pyrite in the sample. The sulphur content ranged from 0.85 % to 1.2 % (after AMD neutralisation) and exceeded the alkaline content in all the Exxaro samples. This suggests that the solid residues could potentially cause AMD in the long term. These coal residues should be discharged into a lined pond to minimise the contact between waste coal, water and air to ensure minimum acid formation. This will also prevent metal leachate from polluting the underground water.

The concentration of elements in the drainage solution is shown in Table 4.8. The results demonstrate that the untreated AMD contained high concentrations of SO_4^{2-}, Fe, calcium (Ca), Al, Mn, Si, sodium (Na), Zn and Cu which is consistent with literature (Scott, 1995). AMD also contained low concentrations of Cd, Cr and Co. The results show that the treatment of AMD with waste coal resulted in an increase in pH and the extensive removal of metals such Al, Si, Fe, Na and SO_4^{2-}. However, the concentration of undesirable species in an AMD solution such as SO_4^{2-} and Mg remained above the minimum criteria of water for domestic, livestock drinking, aquatic ecosystem, irrigation and industrial use. Mg leached into solution. In addition, the pH is too low for Mg removal, which requires a solution pH of between 11.0 and 13.0 for precipitation (Madzivire *et al.*, 2011). Therefore, the treated solutions are not suitable for re-use unless a post-treatment step for Mg and SO_4^{2-} removal is added.

From the knowledge and information gathered during the course of this work, it is clear that the treated solutions need to be further treated, for instance, by use of biological systems, where the SO_4^{2-} concentration may be reduced to levels below the minimum criteria of water for irrigation use. Thus, an additional polishing step such as the Mintek SRB (sulphate reducing bacteria) process should be added to reduce Mg and SO_4^{2-} further to acceptable levels. The process has a potential of treating mine waters for re-use if a cheaper subsequent step to recover Mg and SO_4^{2-} in treated solution is added.

Table 4.7: Waste coal constituents (%)

Samples	Al	Ca	Co	Cr	Cu	Fe	Pb	Mg	Mn	Ni	Si	Ti	V	Zn	Sulphide S	NP ($CaCO_3$)
Exxaro coal *	9.88	0.33	<0.05	<0.05	<0.05	1.78	<0.05	0.17	<0.05	<0.05	21.6	0.47	<0.05	<0.05	1.2	0.49
EXX5 (1 m, -40 mm) **	9.88	0.27	<0.05	<0.05	<0.05	1.91	<0.05	0.28	<0.05	<0.05	22.4	0.49	<0.05	<0.05	0.98	<0.1
EXX3 (6 m, -40 mm) **	9.60	0.45	<0.05	<0.05	<0.05	2.15	<0.05	0.19	<0.05	<0.05	21.7	0.46	<0.05	<0.05	1.20	0.18
EXX4 (6 m, -12.5 mm) **	9.61	0.5	<0.05	<0.05	<0.05	2.02	<0.05	0.18	<0.05	<0.05	20.1	0.47	<0.05	<0.05	1.2	0.24
EXX6 (6 m, -6.3 mm) **	9.65	0.31	<0.05	<0.05	<0.05	1.75	<0.05	0.20	<0.05	<0.05	21.3	0.48	<0.05	<0.05	0.94	<0.1
Vlakfontein *	3.71	1.31	<0.05	<0.05	<0.05	1.1	0.25	<0.05	<0.05	<0.05	5.6	0.26	<0.05	<0.05	1.1	2.32
VLA2 (1 m, -12.5 mm) **	3.72	1.24	<0.05	<0.05	<0.05	1.29	0.18	<0.05	<0.05	<0.05	5.6	0.25	<0.05	<0.05	0.9	1.52
VLA5 (1 m, -6.3 mm) **	5.55	1.49	<0.05	<0.05	<0.05	3.43	0.16	<0.05	<0.05	<0.05	10.1	0.38	<0.05	<0.05	1.06	0.82
VLA3 (6 m, -40 mm) **	3.89	0.99	<0.05	<0.05	<0.05	1.24	0.17	<0.05	<0.05	<0.05	5.8	0.26	<0.05	<0.05	0.85	1.57
VLA4 (6 m, -12.5 mm) **	3.87	1.16	<0.05	<0.05	<0.05	1.69	<0.05	0.13	<0.05	<0.05	5.5	0.24	<0.05	<0.05	0.7	1.00

**Waste coal sample before AMD treatment*

***Waste coal sample after AMD treatment*

Table 4.8: Concentration of elements in AMD and treated solutions (accumulated drainages)

Sample	Al (ppm)	Ca (ppm)	Cu (ppm)	Cd (ppm)	Cr (ppm)	Co (ppm)	Fe (ppm)	Mg (ppm)	Mn (ppm)	S (ppm)	Si (ppm)	Zn (ppm)	SO_4^{2-}(ppm) **
Feed (AMD) Solution	423.5	492.3	10.85	<2	<2	<2	6325	493.8	103.3	6455	90.55	12.48	19365
EXX 5 *	<2	506.7	<2	<2	<2	<2	<2	1373.3	102	2393	<2	10.47	7179
Removal efficiency (%)	100	21	>86				100	-113	25	72	98	36	72
EXX 3 *	<2	549	<2	<2	<2	<2	<2	932.7	92.3	1800	4.603	2.09	5400
Removal efficiency (%)	100	9	>85				100	-54	27	77	96	86	77
EXX 4 *	<2	484.5	<2	<2	<2	<2	<2	910.5	72.2	1653	11.4	<2	4959
Removal efficiency (%)	100	32	>87				100	-28	51	82	91	89	82
EXX 6 *	8.33	472	<2	<2	<2	<2	<2	1387	46.6	2230	10.7	<2	6690
Removal efficiency (%)	98	25	>86				100	-120	65	73	91	87	
VLA 2 *	3.7	511.5	<2	<2	<2	<2	2.8	1360	70.3	2325	<2	<2	6975
Removal efficiency (%)	99	10	>84				100	-140	41	69	98	86	69
VLA 5 *	10	476	<2	<2	<2	<2	2.4	1265	91	1650	4.99	<2	7.023
Removal efficiency (%)	98	16	>84				100	-122	24	78	95	86	78
VLA 3 *	<2	468	<2	<2	<2	<2	<2	1255	15	1945	<2	<2	5835
Removal efficiency (%)	100	16	>84				100	-125	87	73	98	86	73
VLA 4 *	7.12	407	<2	<2	<2	<2	<2	1400	20.4	2140	<2	<2	6420
Removal efficiency (%)	99.6	15.7	>84				100.0	-125.5	87.1	73.3	98.0	85.8	73

*Treated solution

**$SO_4^{2-} = [S^{2-}] \times 3$

The comparison of AMD treated solutions with limestone and uncalcined waste coals (- 6.3 mm) is shown in Table 4.9.

Table 4.9: Comparison of treated solutions with limestone and uncalcined waste coals (-6.3 mm)

Sample	**Al (ppm)**	**Ca (ppm)**	**Fe (ppm)**	**Mg (ppm)**	**Mn (ppm)**	**SO_4^{2-}(ppm)**
Feed (AMD) Solution*	423.5	492.3	6325	493.8	103.3	19365
EXX 5 **	<2	506.7	<2	1373.3	102	7179
Removal efficiency (%)	100	21	100	-113	25	72
VLA 2 **	3.7	511.5	2.8	1360	70.3	6975
Removal efficiency (%)	99	10	100	-140	41	69
Feed (AMD) Solution***	6.8	40	2500	35	15.7	8342
Treated solution ****	7.3	682	56	45	21.8	1969
Removal efficiency (%)	-7	-1605	98	-29	-39	76

* AMD solution before treatment with uncalcined waste coals

**Treated solutions with uncalcined waste coals

***AMD solution before treatment with limestone (Maree *et al*., 2012)

**** Treated solution with limestone (Maree *et al*., 2012)

The AMD treatment with waste coals resulted in a high removal of metal species such as aluminium, iron and manganese, whereas AMD treated with limestone resulted in an increase in aluminium, iron and manganese. AMD treatment with limestone only achieved a pH of 6.6, while AMD treated with uncalcined waste coals attained pH values of up to 8.3. The poor removals efficiencies in the treatment of AMD with limestone can be attributed to the pH level of 6.6 which is not high enough to remove most elements as stated by Skousen *at al*. (2000). The pH required to precipitate most metals from AMD ranges from pH 6 to 9 (Skousen *at al*., 2000). According to Surender (2009), limestone is only capable of increasing the pH of AMD to neutral levels. One of the available AMD treatment options uses an integration of limestone and lime since limestone alone is not very effective in treating AMD (Surender, 2009). Therefore, this demonstrates that the use of uncalcined waste coals to treat AMD is effective and more robust in the removal of species such as of Al, Ca and Fe from AMD than limestone. However, limestone reduces SO_4^{2-} better than waste coal. Therefore, the results suggest that uncalcined waste coal is effective in the removal of certain elements but not all and the same applies to limestone.

In addition, the limestone utilised in the treatment of AMD needs to be mined and be transported over long distances, resulting in wear on infrastructure such as roads as well as pollution and environmental degradation in mining communities, whereas the uncalcined waste coal does not require further mining and is available in close proximity to the mine waters. In addition, the treatment plant can be built close to the mine and contaminated mine waters.

4.6 Prediction for metal removal using Geochemical Modelling

Geochemical modelling was used to investigate the removal mechanism of dissolved metals. It must be noted that this approach assumes precipitation or co-precipitation metal removal mechanism but does not rule out other mechanisms that may prevail such as adsorption. Precipitation is assumed to result in the formation of minerals in the columns due to the operating conditions, which could be inducive. XRD analysis, which could have aided significantly in the identification of the minerals, was not performed due to cost restrictions. The mineral phases that were likely to form during treatment of AMD in the columns were predicted using Visual MINTEQ Version 3. The saturation indices (SI) were used as an indication for possible mineral formation due to precipitation. It should be noted that geochemical calculations performed using computer codes do not prove the presence or absence of a phase, but provide an indication of the tendency for a reaction to occur (Madzivire *et al.*, 2011). The results of Visual MINTEQ are shown in the Table 4.10 below:

Table 4.10: Mineral and Saturation index

Mineral	**Saturation Index**
Al_2O_3(s)	8.3
Anhydrite	1.4
Al(OH)10SO_4(s)	17.87
Covellite	17.17
Ferrihydrite	8.45
Geothite	11.16
gypsum	0.29
Lepidocrocite	10.28
H-jarosite	9.77
Cupric ferrite	21.33

The removal efficiency of the metals after treatment with both waste coals were 100%, 100%, >86%, >25% and <25% for Al, Fe, Cu, Mn and Ca, respectively. Mg is the only metal that was not effectively removed, instead, it showed an increase which could be attributed to the dissolution of the waste coal. The simulation results show that the high removal of Al and Fe is a result of the formation of minerals such as Anhydrite, geothite, alumina and jarosite. Cupric ferrite and possibly covellite appear to be the only minerals responsible for the removal of Cu. The insignificant removal of Ca (<25%) can be explained by the low saturation index (0.29) of gypsum as it is the only mineral responsible for Ca removal. The high saturation indices, specially of Al(OH)10SO_4, Ferrihydrite, Geothite and Lepidocrocite suggest the possibility of the formation of these minerals as seen in Table 4.8 that Al and Fe were removed to concentrations below 3.7 ppm.

4.7 Economic model

A desktop costing model was developed to compare the cost of neutralising AMD with waste coal (in heaps) versus lime (in agitated vessels).

The stacking methodology for the coal heaps comprises an on-off pad, whereby a permanent pad is constructed and the ore is stacked (using either trucks or mechanical stacker) in a single 6 m lift. AMD is pumped over the heaps and a dripper or sprinkler irrigation system is used. Solution draining from the base of the heaps is collected in drainage pipes and solution ponds. Spent coal is removed with a front-end loader. The lime neutralisation plant consists of a series of agitated tanks with overhead motors, a clarifier and auxiliaries such as feed pumps and holding tanks.

The capital cost includes ground preparation, construction of a permanent pad of sufficient area to allow the stacking, equipping, percolation and drainage, de-equipping and removal operations. Adequate sustaining capital or alternative operating cost provision must be allowed for replacement of the gradually depleted drainage layer and blocked or damaged drainage piping. The operating costs include labour, pumping power, reagents and maintenance materials.

4.7.1 Costing model methodology

The model employs a method of factoring costs from the best available benchmark data, using the following sequence of steps:

1. Basic production criteria are specified (e.g. rate of AMD generation, coal neutralisation capacity, coal bulk density, heap stacking height, lime tank residence time, number of tanks and lime neutralising capacity).
2. Mass balance data is calculated (e.g. coal stacking rate, solution application rate, mass under percolation, area under percolation, pond volumes, tank volumes, pump sizes and lime addition rates).
3. Direct capital costs are calculated based on the mass balance and selected multipliers. Appropriate benchmark factors are selected for the calculation of the heap capital costs (e.g. cost / m^2 of pad area constructed, cost / m^3 of pond volume excavated, and cost / m^2 of plastic liner).
4. Uninstalled costs of capital items such as tanks and pumps are calculated from the Mintek equipment cost database (Ruhmer, 1996). Installed capital costs are calculated from the uninstalled capital costs by multiplying with an appropriate factor, e.g. civils, piping, instrumentation and electrical costs.
5. Indirect capital costs such as engineering, procurement and construction management (EPCM), owner’s cost, etc. are calculated from the total installed capital costs by multiplying with an appropriate factor.
6. Reagent consumptions are specified from experimental and published data. Reagent costs from published journals are used.
7. Total operating costs are calculated taking into account labour, power, reagents and maintenance.

4.7.2 Costing model data

The economic model was used to compare the costs of two proposed flowsheet options, as illustrated in Figure 4.6:

- Option 1: neutralisation with coal only
- Option 2: neutralisation with lime only

Table 4.11 provides a summary of the design criteria from the two flowsheet options. The model is based on an AMD production of 1750 m^3 / day (Maree *et al.*, 2013). A neutralising capacity of 1.4 m^3 AMD / t coal, a solids bulk density of 1 t / m^3 and a heap height of 6 m was specified from the experimental results from test VLA 4 (Table 4.4). A lime cost of R 2000 per tonne and a lime neutralising capacity of 12 kg $Ca(OH)_2$ / m^3 AMD was used from literature (Maree *et al.*, 2013).

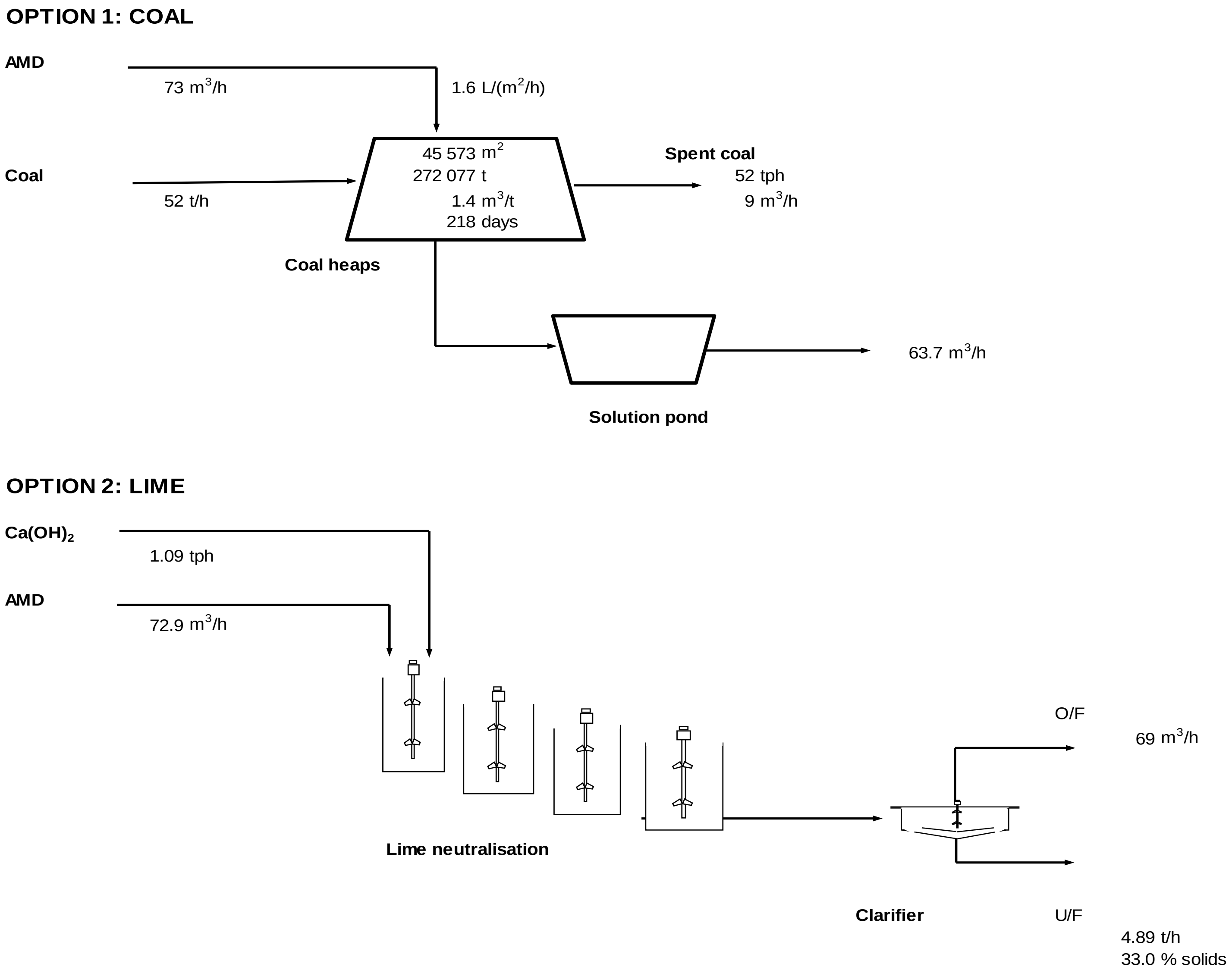

Figure 4.6: Flowsheet comparison

Table 4.11: Summary of design criteria

PLANT CAPACITY		**Option 1** **Coal**	**Option 2** **Lime**
AMD drainage	m^3 / annum	638,750	638,750
Coal (solid) feed	tpa	456,250	0
HEAPS		**Option 1** **Coal**	**Option 2** **Lime**
Temperature	°C	Ambient	-
Solution feed rate	m^3 / h	73	-
Solution irrigation rate	L / m^2 / h	1.6	-
Solids feed rate	tph	52	-
Stacked bulk density	t / m^3	1.0	-
Area under neutralisation	m^2	45,573	-
Mass under neutralisation	t	272,077	-
Lift height	m	6	-
Residence time	days	218	-
LIME NEUTRALISATION		**Option 1** **Coal**	**Option 2** **Lime**
Temperature	°C	-	Ambient
Terminal pH	pH	-	7-8
Feed tank volume	m^3	-	146
Feed flowrate	m^3 / h	-	73
Number of stages		-	4
Total residence time	h	-	5
Residence time per stage	h	-	1.3
Reaction tank volume	m^3	-	91
Power input per tank	kW	-	7.5
Clarifier area	m^2	-	0.0030
Clarifier diameter	m	-	0.062
O/F flowrate	m^3 / h	-	69
U/F solids	m^3 / h	-	4.89
U/F solid concentration	%	-	33

A summary of the capital costs is provided in Figure 4.7 and a summary of the operating costs is provided in Figure 4.8. Amortised capital is also included in the operating costs, based on a 10% annual interest and a 10 year payback period. South African electricity cost of 86 cents / kWh was used (Blom, 2017). The economic model does not include the costs of a post-treatment step. The transport cost was estimated to be R5 per tonne to transport waste coal over a distance of 5 km and R30 per tonne for lime over a distance of 30 km (Steyn, 2018).

Capital costs for lime neutralisation was estimated at R18 million versus R63 million for uncalcined waste coal neutralisation (Figure 4.7). Operating costs (including amortised capital) were approximately R25 million for lime neutralisation and R18 million for waste coal neutralisation (Figure 4.8). The owner's costs are all the costs required to bring a project to a commercially operable status, less the cost of the procurement and construction (EPC) contract (Dobre, 2017).The crushing cost is a biggest component of the capital costs of uncalcined waste coal neutralisation and it accounts for 43% of the total capital costs. The capital costs of uncalcined waste coal neutralisation would therefore be lesser if the waste cost was freely available at -6.3 mm crush size on site.

Even though the waste coal neutralisation exhibited exorbitant capital costs compared to the capital costs of lime neutralisation, the investment spent on capital costs (once off costs) of waste coal neutralisation could be recovered over time due to the option’s lower operating costs.

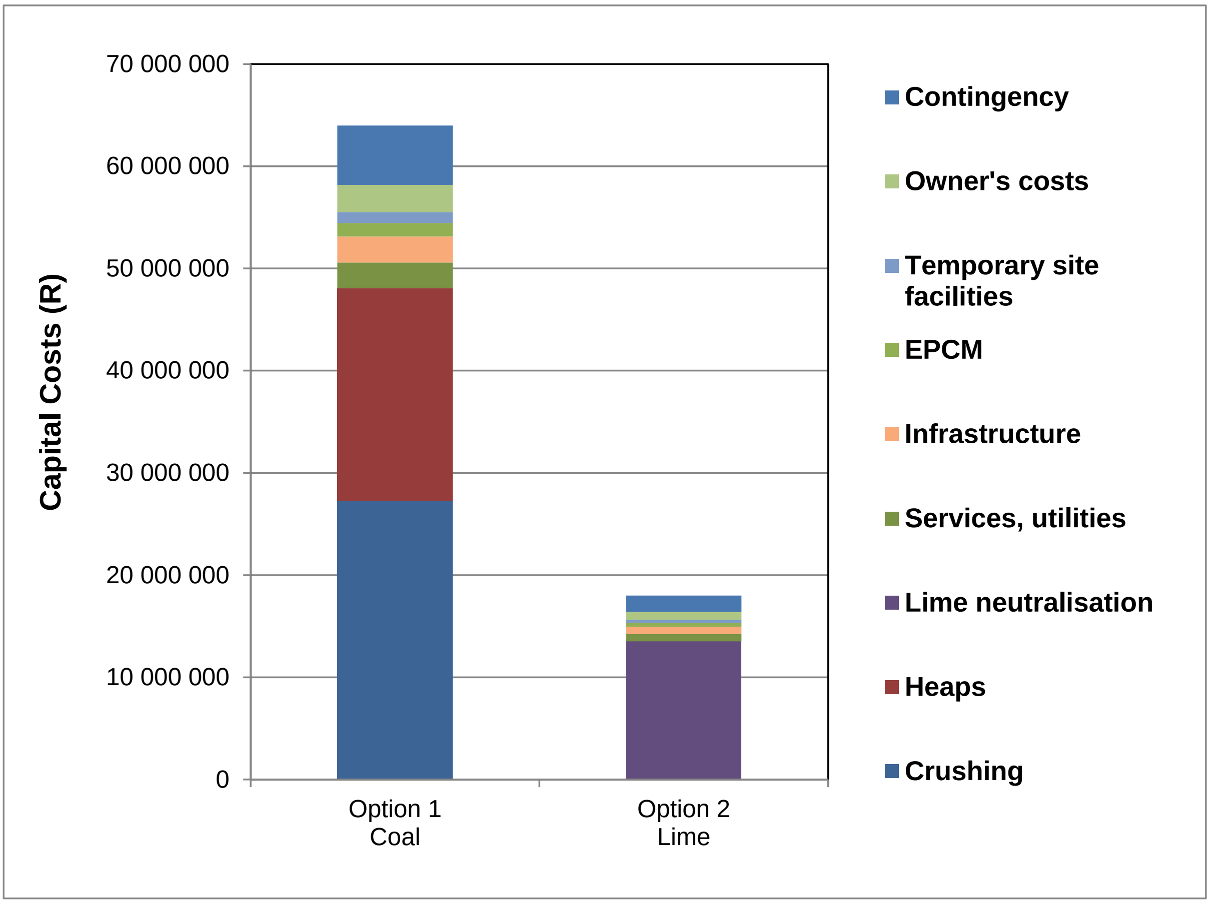

Figure 4.7: Summary of capital costs

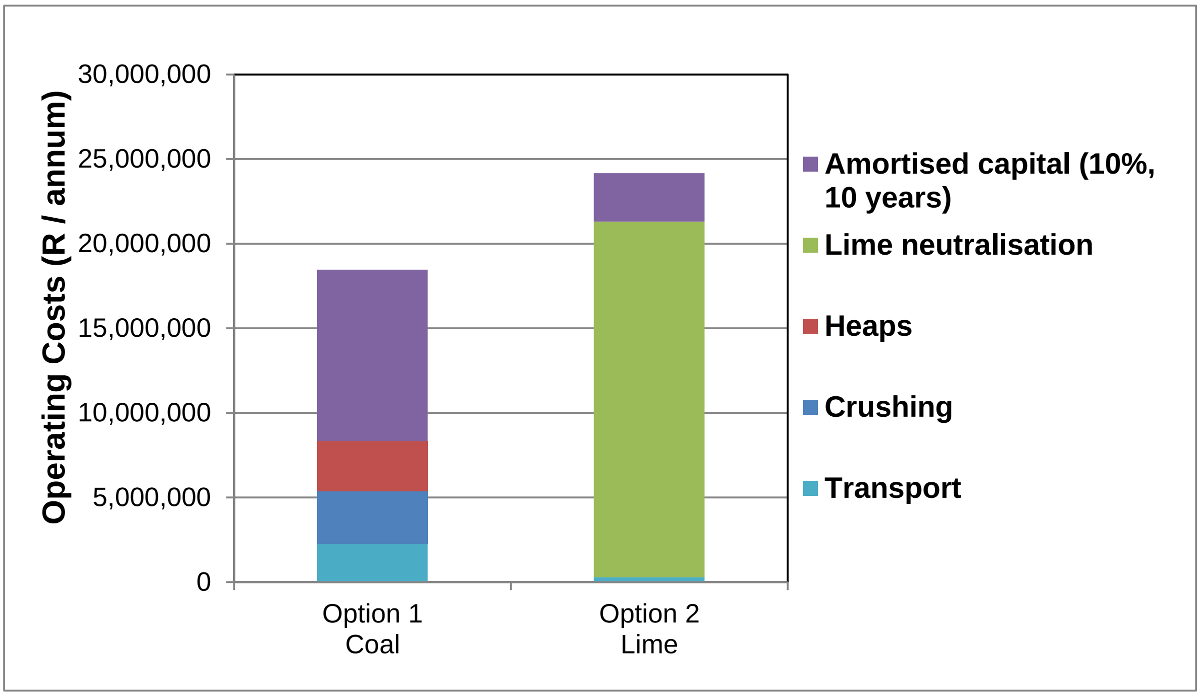

Figure 4.8: Summary of operating costs

Summary

The results revealed that the AMD was highly acidic and contaminated with both cations and anions. AMD was then percolated over 1 m and 6 m columns containing waste coal samples (Exxaro and Vlakfontein waste coals) with alkalinity of 0.48% NP and 2.32 % NP, respectively. This resulted in an increase in the AMD solution pH and an extensive removal of metals. The alkalinity of the waste coals also decreased during AMD neutralisation. This indicates that alkalinity was responsible for pH increase in AMD. The Vlakfontein and Exxaro coals achieved neutralising capacities of 2152 L/t and 282 L/t, respectively, at a -6.3 mm crush size. This is equivalent to lime consumptions of 27 kg and 3.5 kg $Ca(OH)_2$ per t coal, respectively. Lime consumption equivalents are based on a neutralising requirement of 12.53 kg $Ca(OH)_2$ per m^3 AMD. Chemical analysis of drainage solutions indicated high removal efficiencies for Al, Cu, Fe, Si and Zn. However, the concentration of undesirable species in AMD solution such as SO_4^{2-} and Mg remained above the minimum criteria of water for domestic, livestock drinking, aquatic ecosystem, irrigation and industrial use. Mg concentrations in solution increased during AMD neutralisation. Total sulphate removals were between 62% and 82%. The treated solutions with uncalcined waste coals would still not qualify to be disposed to the environment because the water disposal limits are lower than the maximum water limits for irrigation use, and contaminated water potentially has detrimental effects on the environment (DWA, 2010).

Although the results indicated high removal efficiencies for Al, Cu, Fe, Si and Zn and neutral pH values after AMD treatment with uncalcined waste coals, the treated solutions were still not suitable for re-use or disposal. Therefore, future work should be conducted focusing on integrating the AMD treatment using uncalcined waste coal with cheaper emerging neutralisation processes to reduce Mg and SO_4^{2-} in treated solutions. Moreover, the costs of this integration should be studied. Future work could also investigate if lime costs could be alleviated by pre-neutralisation or partial neutralisation of AMD with uncalcined waste coal before lime neutralisation. Lime also has a limited capability with respect to SO_4^{2-} removal (Surender, 2009). The integration of AMD treatment using uncalcined waste coal with lime neutralisation process could result in better removal efficiencies of SO_4^{2-} . It should be noted that uncalcined waste coal is capable of reducing up to 82% of SO_4^{2-} and lime can then remove the remaining SO_4^{2-}. The results therefore, indicate that the uncalcined waste coal samples are not suitable to be used as a neutralising agent for AMD solutions in order to reduce lime consumptions. However, the process has a potential of treating mine waters for re-use if a cheaper subsequent step to recover Mg and SO_4^{2-} in treated solution is added. Capital costs were estimated at R18 million for lime neutralisation, R63 million for waste coal neutralisation and operating costs were estimated at R 25 million for lime neutralisation and R13 million for waste coal neutralisation. Although the capital costs for waste coal neutralisation exceeded the capital costs for lime neutralisation, the operating costs of AMD treatment with waste coal are significantly lower than the operating costs of AMD treatment with lime. Therefore, the investment spent on capital costs for waste coal neutralisation could be recovered over time due to the saving in the operating costs (lower than the lime neutralisation operating costs) of this option.

Chapter 5

Conclusions and Recommendations

5.1 Conclusions

Mining may generate AMD solutions and mining solid waste which may negatively affect the environment. AMD is characterized by low pH and high concentrations of metals (aluminium, iron, manganese, nickel and cobalt) and sulphate. The main aim of this study was to evaluate experimentally, the efficacy and efficiency of treating AMD with uncalcined waste coal to meet the South African water quality standard for domestic, livestock drinking, irrigation and industrial use. In this study, AMD was treated with uncalcined waste coal samples from Exxaro, Forzando and Vlakfontein coal mines on 1 m and 6 tall columns of 16 cm diameter. The test work was conducted to determine the neutralising potential of the waste coal expressed in litres AMD per ton of waste coal, the removal efficiency of dissolved species such as Al, Fe and sulphate in AMD and to compare the economics of AMD neutralisation with uncalcined waste coal, with the economics of the traditional lime neutralisation process.

AMD treatment with Exxaro, Forzando and Vlakfontein uncalcined waste coal samples resulted in a rise in pH of the AMD. The Vlakfontein (2.32 % NP) and Forzando (2.33 % NP) waste coals exhibited higher neutralising potentials and neutralising capacities than the Exxaro waste coal (0.48 % NP). The neutralising capacities increased with a decrease in crush size, with the Vlakfontein material yielding neutralising capacities of between 804 L/t and 2118 L/t at the -40 mm and -6.3 mm crush sizes, respectively. It was assumed that the alkaline minerals in coal were more liberated in smaller particles than in coarse particles. Therefore the increase in neutralising capacities with a decrease in crush size may be due to higher degree of liberation of alkalinity in finer particles.

The alkalinity in the waste coals and concentrations of calcite, dolomite and kaolinite minerals in the waste coals decreased extensively during AMD neutralisation suggesting that the minerals were responsible for pH increase in AMD. For example, the Vlakfontein waste coal contained kaolinite (>50%), calcite (5 to 15%) and dolomite (<5%) minerals before AMD treatment. After AMD treatment, the levels were reduced to 15 - 30% (kaolinite), <3% (calcite) and <3% (dolomite), which proved that the minerals took part in the neutralisation reaction. This is consistent with literature, which suggests that out of the many types of alkaline compounds present in rocks, only carbonates and clays are the most effective neutralising minerals.

A decrease in the feed flowrate had a positive impact on the neutralisation of the AMD solution. For example, FOZ 1 was operated on 1 m column at 0.44 mL/min irrigation rate and exhibited a higher neutralising capacity (587 L/t) than FOZ 2 (234 L/t) which was operated at 2.01 mL/min irrigation rate. The higher irrigation rate resulted in a faster drop in the pH and in turn in lower neutralising capacity since the acid for reaction with the carbonate gangue was supplied faster.

The Exxaro waste coal neutralised a smaller amount of AMD compared to the Vlakfontein waste coal, with the Exxaro waste coal exhibiting lime equivalents of up to 3.6 kg $Ca(OH)_2$ / t coal and the Vlakfontein sample exhibiting lime equivalents of up to 27 kg $Ca(OH)_2$ / t coal. Initially, it was expected that the Vlakfontein waste coal will perform better than the Exxaro waste coal since the Vlakfontein waste coal contained elevated levels of neutralising potential than Exxaro waste coal. The results were therefore consistent with the postulation.

The treatment of AMD with uncalcined waste coal resulted in extensive removal of metals such as aluminium, silicon, iron and sodium. However, the concentration of undesirable species in AMD solution such as sulphate and magnesium remained above the minimum criteria of water for domestic, livestock drinking, aquatic ecosystem, irrigation and industrial use. Magnesium requires a solution pH of between 11.0 and 13.0 for precipitation and the solution pH in the columns was less than pH 11, hence the element could not be removed.

Although the AMD treatment with uncalcined waste coal resulted in high removal efficiencies for aluminium, copper, silicon, iron and zinc, and neutral pH values, the treated solutions were still not suitable for re-use or disposal. Therefore, more work should be conducted to explore the possibility of integrating the AMD treatment using uncalcined waste coal with cheaper emerging neutralisation processes, such the Mintek SRB process to name but a few, with the aim of reducing magnesium, sulphate and other contaminants to acceptable levels for re-use. The cost of this integration should be determined. Future work should also investigate if lime costs could be alleviated by pre-neutralisation or partial neutralisation of AMD with uncalcined waste coal before lime neutralisation.

The uncalcined waste coal samples are not suitable to be used as a neutralising agent for AMD solutions in order to reduce lime consumptions. However, the process has a potential of treating mine waters for reuse if a cheaper subsequent step to recover magnesium and sulphate in treated solution is added.

A desktop economic model was developed to compare AMD neutralisation with coal in heaps versus lime in stirred tanks. The model was based on an AMD production of 1750 m^3/day, a neutralising capacity of 1.4 m^3 AMD / t coal, a solids bulk density of 1 t/m^3 and a heap height of 6 m. A lime cost of R2000 per tonne and a lime neutralising capacity of 12 kg $Ca(OH)_2$ / m^3 AMD was used, as well as electricity costs of 86 cents / kWh.

Capital costs were estimated at R18 million for lime neutralisation, R63 million for waste coal neutralisation and operating costs were estimated at R 25 million for lime neutralisation and R13 million for waste coal neutralisation. Although the capital costs for waste coal neutralisation exceeded the capital costs for lime neutralisation, the operating costs of AMD treatment with waste coal are significantly lower than the operating costs of AMD treatment with lime. Therefore, the investment spent on capital costs for waste coal neutralisation could be recovered over time due to the saving in the operating costs (lower than the lime neutralisation operating costs) of this option.

5.2 Recommendations

This study has proven that uncalcined waste coal can be used to neutralise AMD and it removes most of the contaminants from an AMD solution. However, magnesium leaches into the solution from waste coal during neutralisation and sulphate remains high. The process requires a post-treatment of the solution in order to lower the sulphate and magnesium content so as to meet the South African water quality standard for domestic, livestock drinking, irrigation and industrial use. I therefore recommend that a costing of a post-treatment stage for magnesium and sulphate removal be conducted. If the costs of adding a post-treatment step are high, the possibility of applying this study, including a post-treatment step for sulphate and magnesium should only be considered when the prices of lime are very high. Costing of a post-treatment step was not included in this study due to cost constraints.

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APPENDIX A: PSD DATA

Table A1: Exxaro PSD data (100% passing 6.3 mm)

EXXARO (-6.3 mm)									
Screen Size (mm)	Mass (kg)			cum. Mass (kg)			cum. Passing (%)		
	Batch N^{o}1	Batch N^{o}2	Batch N^{o}3	Batch N^{o}1	Batch N^{o}2	Batch N^{o}3	Batch N^{o}1	Batch N^{o}2	Batch N^{o}3
40	0.0	0.0	0.0	21	21	21	100	100	100
19	0.0	0.0	0.0	21	21	21	100	100	100
12.5	0.0	0.0	0.0	21	21	21	100	100	100
9.5	0.0	0.0	0.0	21	21	21	100	100	100
6.3	0.0	0.0	0.0	21	21	21	100	100	100
3.35	9.0	8.8	8.7	12	12	12	57	58	58
1.18	6.7	6.6	6.8	5	5	5	25	26	26
0.5	2.5	2.6	2.5	3	3	3	14	14	14
0.15	1.7	1.6	1.7	1	1	1	6	6	6
-0.15	1.2	1.3	1.2	0	0	0	0	0	0

Table A2: Exxaro waste coal PSD data (100% passing 12.5 mm)

EXXARO (-12.5 mm)									
Screen Size (mm)	**Mass (kg)**			**cum. Mass (kg)**			**cum. Passing (%)**		
	Batch N^{o}4	**Batch N^{o}5**	**Batch N^{o}6**	**Batch N^{o}4**	**Batch N^{o}5**	**Batch N^{o}6**	**Batch N^{o}4**	**Batch N^{o}5**	**Batch N^{o}6**
40	0.0	0.0	0.0	25	25	25	100	100	100
19	0.0	0.0	0.0	25	25	25	100	100	100
12.5	0.0	0.0	0.0	25	25	25	100	100	100
9.5	3.4	3.4	3.4	21	21	21	86	86	86
6.3	8.1	8.6	8.4	13	13	13	54	52	52
3.35	7.0	6.7	6.4	6	6	7	26	24	27
1.18	3.9	3.8	4.1	2	2	3	10	9	10
0.5	1.1	0.9	1.1	1	1	2	6	5	6
0.15	0.7	0.8	0.8	1	1	1	3	2	3
-0.15	0.7	0.6	0.7	0	0	0	0	0	0

Table A3: Exxaro waste coal PSD data (100% passing 40 mm)

EXXARO (-40 mm)									
Screen Size (mm)	**Mass (kg)**			**cum. Mass (kg)**			**cum. Passing (%)**		
	Batch N^{o}7	**Batch N^{o}8**	**Batch N^{o}9**	**Batch N^{o}7**	**Batch N^{o}8**	**Batch N^{o}9**	**Batch N^{o}7**	**Batch N^{o}8**	**Batch N^{o}9**
40	0	0	0	25	25	25	100	100	100
19	11.2	11.0	11.1	14	14	14	55	56	55
12.5	3.8	4.7	4.6	10	9	9	39	37	37
9.5	2.4	2.1	2.1	7	7	7	30	28	29
6.3	3.1	3.5	3.4	4	4	4	17	14	15
3.35	2.3	2.0	1.9	2	2	2	8	6	7
1.18	1.0	0.9	1.0	1	1	1	4	3	4
0.5	0.3	0.2	0.3	1	0	1	3	2	2
0.15	0.3	0.2	0.3	0	0	0	2	1	1
-0.15	0.4	0.3	0.3	0	0	0	0	0	0

Table A4. Vlakfontein waste coal PSD data (100% Passing 6.3mm)

VLAKFONTEIN (-6.3 mm)									
Screen Size (mm)	**Mass (kg)**			**cum. Mass (kg)**			**cum. Passing (%)**		
	Batch N^{o}1	**Batch N^{o}2**	**Batch N^{o}3**	**Batch N^{o}1**	**Batch N^{o}2**	**Batch N^{o}3**	**Batch N^{o}1**	**Batch N^{o}2**	**Batch N^{o}3**
40	0.0	0.0	0.0	6	6	6	100	100	100
19	0.0	0.0	0.0	6	6	6	100	100	100
12.5	0.0	0.0	0.0	6	6	6	100	100	100
9.5	0.0	0.0	0.0	6	6	6	100	100	100
6.3	0.0	0.0	0.0	6	6	6	100	100	100
3.35	2.5	2.5	2.5	3	3	3	55	56	56
1.18	1.7	1.6	1.8	1	2	1	26	28	26
0.5	0.6	0.7	0.6	1	1	1	15	15	15
0.15	0.5	0.5	0.5	0	0	0	7	6	7
-0.15	0.4	0.4	0.4	0	0	0	0	0	0

Table A5. Vlakfontein waste coal PSD data (100% Passing 12.5 mm)

VLAKFONTEIN (-12.5 mm)									
Screen Size (mm)	**Mass (kg)**			**cum. Mass (kg)**			**cum. Passing (%)**		
	Batch N^{o}4	**Batch N^{o}5**	**Batch N^{o}6**	**Batch N^{o}4**	**Batch N^{o}5**	**Batch N^{o}6**	**Batch N^{o}4**	**Batch N^{o}5**	**Batch N^{o}6**
40	0.0	0.0	0.0	22	22	22	100	100	100
19	0.0	0.0	0.0	22	22	22	100	100	100
12.5	0.0	0.0	0.0	22	22	22	100	100	100
9.5	3.3	3.4	3.3	19	19	19	85	85	85
6.3	7.3	7.5	7.3	12	12	12	53	51	53
3.35	5.4	5.3	5.4	6	6	6	29	28	29
1.18	3.8	3.7	3.8	3	2	3	12	11	12
0.5	1.0	1.1	1.0	2	1	2	7	6	7
0.15	0.9	0.8	0.9	1	1	1	3	3	3
-0.15	0.7	0.6	0.7	0	0	0	0	0	0

Table A6. Vlakfontein waste coal PSD data (100% Passing 40mm)

VLAKFONTEIN (-40 mm)									
Screen Size (mm)	Mass (kg)			cum. Mass (kg)			cum. Passing (%)		
	Batch N^{o}7	Batch N^{o}8	Batch N^{o}9	Batch N^{o}7	Batch N^{o}8	Batch N^{o}9	Batch N^{o}7	Batch N^{o}8	Batch N^{o}9
40	0	0	0	23	22	22	100	100	100
19	15.0	13.6	14.3	7	9	8	33	40	36
12.5	4.3	5.5	5.2	3	3	3	14	15	13
9.5	1.0	0.9	0.8	2	2	2	10	11	10
6.3	0.8	0.9	0.8	1	2	1	6	7	6
3.35	0.6	0.6	0.5	1	1	1	4	4	4
1.18	0.4	0.4	0.4	0	1	0	2	2	2
0.5	0.1	0.2	0.1	0	0	0	1	2	1
0.15	0.1	0.2	0.1	0	0	0	1	1	1
-0.15	0.2	0.2	0.2	0	0	0	0	0	0

APPENDIX B: SOLUTION BALANCE AND LOADING DATA

Table B1: Solution balance

Column ID	Feed In (L)			Drainage Out (L)			Out/In (%)
	Cumulative Volume	Moisture Volume	Total	Cumulative Volume	Moisture Volume	Total	
EXX 3 (6m; -40mm)	29.0	7.8	36.8	23.7	8.2	31.9	86.8
EXX 4 (6m; -12.5mm)	31.6	7.0	38.5	21.9	7.9	29.8	77.4
EXX 5 (1m; -6.3mm)	8.6	1.1	9.7	6.6	1.5	8.1	83.1
EXX 6 (6m; -6.3mm)	44.7	6.9	51.6	35.0	16.1	51.1	99.0
VLA 2 (1m; -12.5mm)	13.5	0.8	14.3	11.8	1.4	13.2	92.1
VLA 3 (6m; -40mm)	95.7	5.4	101.1	84.9	6.2	91.1	90.1
VLA 4 (6m; -12.5mm)	158.0	7.1	165.1	140.7	9.7	150.4	91.1
VLA 5 (1m; -6.3mm)	42.2	0.9	43.0	36.5	2.2	38.7	90.0

Table B2: 1m columns loading data

Sample ID	Units	EXX1 (1 m, -40 mm)	EXX2 (1 m, -12.5 mm)	VLA1 (1 m, -40 mm)	VLA2 (1 m, -12.5 mm)	EXX5 (1 m, -6.3 mm)	VLA5 (1 m, -6.3 mm)
Column height	**mm**	**1**	**1**	**1**	**1**	**1**	**1**
Screen size	mm	-40	-12.5	-40	-12.5	-6.3	-6.3
Sample mass (dry)	kg	24.9	24.9	22.5	22.5	20.89	16.97
Moisture content required	%	5.0	5.0	5.0	5.0	5.0	5.0
Mass of liquid required to make 5% moisture	g	1311	1311	1184	1184	1099	893.16
Column loading	**Units**	**EXX1**	**EXX2**	**VLA1**	**VLA2**	**EXX5**	**VLA5**
Date loaded							
Total mass of wet agglomerates	kg	26.21	26.21	23.68	23.68	21.99	17.86
Total mass of wet agglomerates loaded	kg	23.81	22.19	17.91	16.36	21.99	17.86
Total mass of wet agglomerates remaining	kg	2.4	4.02	5.77	7.32	0.00	0.00
Total mass moisture loaded	kg	1.19	1.11	0.90	0.82	1.10	0.89
Total moisture volume	L	1.16	1.08	0.88	0.80	1.08	0.88

Table B3: 6m columns loading data

Sample ID	Units	EXX3 (6 m, -40 mm)	EXX4 (6 m, -12.5 mm)	VLA3 (6 m, -40 mm)	VLA4 (6 m, -12.5 mm)	EXX6 (6 m, -6.3 mm)
Column height	**mm**	**6**	**6**	**6**	**6**	6
Screen size	mm	-40	-12.5	-40	-12.5	-6.3
Sample mass (dry)	kg	150.0	150.0	135.0	135.0	132.6
Moisture content required	%	5.0	5.0	5.0	5.0	5.0
Mass of liquid required to make 5% moisture	g	7895	7895	7105	7105	6978.95
Column loading	**Units**	**EXX3**	**EXX4**	**VLA3**	**VLA4**	**EXX6**
Date loaded						
Total mass of wet agglomerates	kg	158	158	142	142	139.58
Total mass of wet agglomerates loaded	kg	158	142	110	105	139.58
Total mass of wet agglomerates remaining	kg	0	15.9	31.8	37.1	0.00
Total mass moisture loaded	kg	7.89	7.10	5.52	5.25	6.98
Total moisture volume	L	7.76	6.97	5.42	5.16	6.87
Total dry mass loaded	kg	150.00	134.90	104.79	99.76	132.6

APPENDIX C: SCHEMATIIC REPRESENTATION OF TESTWORK

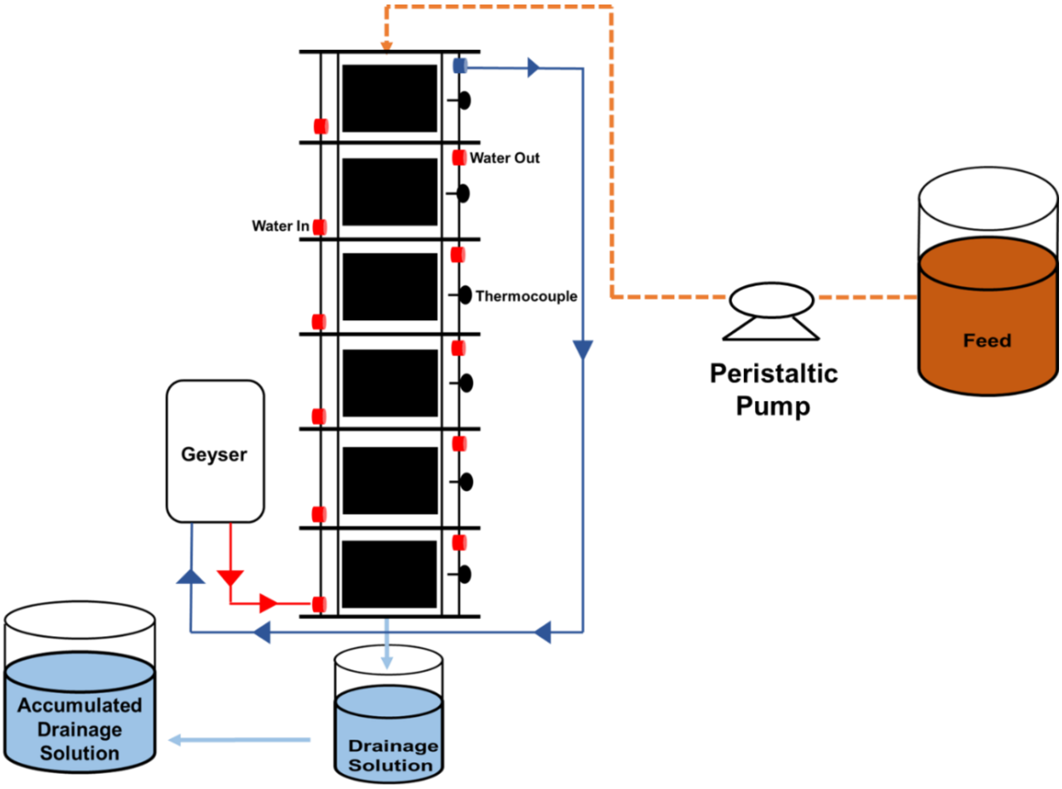

Figure C.1. Schematic representation of 6 m column test

APPENDIX D: SHE RISKS

Special care should be taken when handling dry coal samples and other hazardous materials used in the test work. Dust poses the biggest health hazard as it can be inhaled if proper elimination or mitigation measures are not in place. The dust, when inhaled, may become lodged in the lungs and may cause cancerous effects in the body over time. The following Personal Protection Equipment (PPE) was worn during execution of the aforementioned test work:

- Acid / alkaline resistant laboratory coats or overalls (laboratory and pilot bay) to mitigate potential chemical burns to the body;
- Hard hat (pilot bay) to mitigate potential injury to the head;
- Respirator with dust cartridges (pilot bay) to avoid inhalation of dust;
- Safety boots (laboratory and pilot bay) to mitigate potential injury to the feet;
- Safety glasses (laboratory and pilot bay) to mitigate potential chemical burns to the eyes;
- Safety gloves (laboratory and pilot bay) to prevent potential chemical burns to the hands, and
- Harnesses should be worn during loading and assembling of 6 m columns.

“Kindly note that all safety, health and environmental (“SHE”) risk information is given for information purposes only and does not constitute a risk assessment for any SHE purposes, nor does it substitute any statutory risk assessment that the client is required to undertake.