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## **Effect of regional geology and mining activity on water quality: studies in the eMalahleni (Witbank) and South Rand coalfields**

By

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#### DISSERTATION



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#### **Abstract**

Acidic drainage generated in mining environments has been a major concern for many years, especially since the acidic drainage leads to the deterioration of quality in water resources. South Africa is a waterscarce country, and solutions to try and counteract the spread of acidic drainage in mining environments are of major importance. Prediction of the potential for constituents to generate or neutralise acidity produced has become an integral part of the treatment and mitigation process employed in numerous industries. The use of modern methods in the determination of acid generation and neutralisation potential in earth moving environments is critical in the improvement of mitigation and treatment methods. Methods are frequently generated in order to improve on existing methods, assist existing methods, or change the way existing methods operate. In the process of creating new methods, complications are often encountered, leading to an extended time period in the creation process.

The current method focuses on the analyses of acid-generating and acid-neutralising elements with the use of Inductively-Coupled Plasma Optical Emissions Spectrometry (ICP-OES). The method aims to assist in the prediction of acid generation/neutralisation potential of samples and improve the efficiency by reducing the period it takes for successful prediction to be carried out and analysing an array of minerals considered to be involved in acid generation and neutralisation reactions.

Samples were subjected to nitric and hydrochloric acid as a means of leaching out sulphate and sulphide sulphur species, respectively. Subjecting the samples to acid also releases readily-dissolving elements (likely to be involved in acid-neutralising reactions) and compounds into the leachate. The content of elements that are constituents of acid-producing minerals (Fe, S) are compared to elements that constitute acid-neutralising minerals (Ca, Mg, Na, K). A balance between the respective minerals allows for the determination of the acid-generating and acid-neutralising potential as part of Acid Base Accounting (ABA) procedures.

The method allows for the repetitive analyses of samples since the analysed leachate is kept in storage, and this allows for easy validation of procedures when necessary. The use of the ICP-OES also allows for the analyses of an array of mineral constituents and using the method in conjunction with X-Ray Diffraction (XRD) allows for the identification of minerals phases that may be influential in acid producing/neutralising reactions beforehand, which is useful when selecting constituents of concern to be analysed. The method is, however, still under development, but its rapid and easy use makes it one to consider for future prediction and mitigation studies.

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#### <span id="page-7-0"></span>**1. Introduction**

South Africa is a water scarce country, with an average rainfall of about 495 mm per annum. This is quite low in comparison to the global land average of 1033 mm per year (Hedden and Cilliers, 2014). The impacts of mining on the environment cannot be ignored, especially since mining activities have led to the degradation of the water quality in the areas in which mines operate. According to McCarthy, (2011), mining activities tend to increase the rate of sulphide oxidation in places where it is already occurring and may also initiate the reaction of sulphides in places where the sulphides are not naturally exposed.

In South Africa, this is especially true in regions where coal and gold mining are currently taking or have taken place. Due to the association of gold and coal with sulphide minerals such as pyrite, mining these commodities has led to the exacerbation of the generation of Acid Rock Drainage (ARD) since the mining activities increase the exposure of the sulphides and thus speed up the oxidation process that leads to the formation of acid rock drainage (McCarthy, 2011). The generation of ARD is a major environmental concern, not only because of the acidity itself but also due to the high dissolved load of ions, many of them toxic, that occurs as a consequence of this.

Even though acidic drainage formation is a natural process, mining activities thus tend to exacerbate the reaction of acid generating minerals. An increase in the exposure of these minerals due to mining therefore leads to an increase in the production of acidic drainage (McCarthy, 2011).

#### <span id="page-7-1"></span>**1.1. Aims and objectives of the study**

The research project forms part of the Mine Water Atlas of South Africa developed by Golder Associates for the Water Research Commission (WRC). The Mine Water Atlas was designed to be an educational resource for water consumers, since it can be used as a tool by water management planners and as a reference for the effect that primary mining activities have on the groundwater and surface water resources in South Africa (Golder, 2014).

The contribution of this research project to the Mine Water Atlas will be in assisting in the possible creation of a prediction tool that can be used to assess the nature and severity of acidic drainage problems that may arise in a given area. This will help with present and future mining endeavours, as well as in the planning of water usage.

The water quality in coal and gold mining areas is usually poor due to the fact that these deposits contain sulphide minerals, pyrite in particular. These sulphide minerals react with the water, in the presence of oxygen, and this oxidation process leads to the generation of acidic drainage and the detrimental contamination of the surrounding water bodies, both surface and groundwater. Pyrite was one of the minerals found in a study conducted on the eMalahleni coalfield by Pinetown and Boer (2006), meaning that the coal has acid-producing potential. In the same study dolomite and calcite, which are known to be quite reactive and effective in neutralising acid produced, were found present in a majority of the samples studied. This then means that even though the coal might have acid-producing potential, acidneutralising minerals exist to counteract the effects of this reaction. The extent of such a counteractive measure is, however, not well determined.

A study conducted by Azzie (2002) looked at the extent to which the surrounding rock, with an emphasis on the coal and shales of the eMalahleni coalfields (one of South Africa's most prominent coal mining areas), affects the composition of the water, with an emphasis on the undisturbed groundwater in the coal-mining regions of South Africa. It was found that the composition of the water bodies in the South African coal mines was affected by interaction with the host rocks. The interactions were found to be useful for predicting whether acidification or neutralisation was likely to be the main process affecting the water. By looking at the mineralogical characteristics of the surrounding rock, predictions about the acid producing/neutralising potential of a given rock can be made, and since the surrounding rock interacts with the water, water quality can then therefore be extrapolated from these findings. According to Pinetown and Boer (2006), the quality and chemical nature of water bodies surrounding certain ore deposits may differ considerably to water where no such deposit exists. This means then that when considering water quality, the study area may need to be well defined, and be located as close as possible to the ore body of concern or the area of earth movement processes. This supports the resolution to conduct case studies on the different operating and non-operating coal mines.

The methodology of the study is twofold:

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First, a desktop study was conducted on mines and water quality of the eMalahleni coalfield. The aim of this was to create a groundwater risk map relating to the coal mines of this coalfield.

Second, two mines in the eMalahleni coalfield and one in the South Rand coalfield were investigated as case studies, which included acid-base accounting analyses on samples collected. To accomplish this, a new approach using inductively coupled plasma optical emission spectroscopy (ICP-OES) was developed, which holds considerable promise.

## <span id="page-8-0"></span>**2. Coal: Geological background of the coal deposits of South Africa**

#### <span id="page-8-1"></span>**2.1. Geological perspective of South African coal**

All the coal resources of South Africa are hosted in the Karoo Supergroup (Johnson *et al.*, 2006), with most of the large deposits occurring as layers within the sedimentary rocks of the Vryheid Formation (or its stratigraphic equivalents-see below) (Hancox and Goetz, 2014) that forms part of the Ecca Group (Johnson *et al*., 2006). Seams do, however, occur locally in beds of the Molteno Formation and Beaufort Group (Stratten, 1986). Bituminous coal is the dominant coal type, forming the core of the country's resources and reserves. (Azzie, 2002).

#### <span id="page-9-0"></span>**2.2. A brief summary of the Karoo Supergroup**

The Karoo Supergroup is discussed as a means of offering a geological perspective for South African coal deposits. The Karoo Supergroup is found on the Main Karoo Basin (Figure 1). The Main Karoo basin is discussed in the context of this study as the stratigraphic units that were deposited from the Late Carboniferous to Middle Jurassic in South Africa because most of the lithologies that contain coal in South Africa are Permian in age, and are assigned to the Karoo Supergroup (Cairncross, 2001; Pone *et al.*, 2007). Karoo aged strata also occurs to the north of the Main Karoo Basin in South Africa, namely the Tuli Basin, Botswana Kalahari Basin, Ellisras Basin, Tshipise Basin, Aranos Basin and Karasburg Basin, just to name a few (Johnson *et al.*, 2006), but only rocks found within the Main Karoo Basin in South Africa will be discussed (Figure 1).



<span id="page-9-1"></span>Figure 1: The distribution of the Karoo basins in South-central Africa. Modified from Catuneanu *et al.* (2005). The Main Karoo Basin and Karoo-aged equivalents shown are below the equator.

The Main Karoo Basin covers an area of about 700 000 km<sup>2</sup> and attains a maximum thickness of 12 km, but it was more extensive during deposition (Johnson *et al*., 2006). The Karoo Supergroup strata are underlain to the north, central and north-east by the Kaapvaal craton and the Namaqua-Natal metamorphic belt, and towards the south they are bounded by the Cape Fold Belt (Johnson *et al*., 1997; Johnson *et al*., 2006).

The Karoo Supergroup can be divided into four lithostratigraphic units (Figure 2), namely the basal Dwyka Group, Ecca Group, Beaufort and Stormberg Group (Molteno, Elliot and Clarens Formations). These sedimentary successions are capped by the basaltic lavas of the Drakensberg Group (Hancox and Goetz, 2014).

#### <span id="page-10-0"></span>**2.3.1. The Dwyka Group**

The Dwyka Group is up to 800m thick in the Main Karoo basin and consists of various rock types displaying features that are correlated to a glacial or glacial-related origin (diamictite, conglomerate, rhythmite, mudrock with dropstones, and fluvioglacial pebbly sandstone) (Johnson *et al.*, 1996). The Dwyka Group was deposited on Precambrian bedrock surfaces at the northern basin margin, while in the south it unconformably overlies rocks of the Cape Supergroup and at the eastern edge, rocks of the Natal Group (Johnson *et al.*, 2006).

The rocks of the Karoo Supergroup lying between the Dwyka Group and the aeolian sandstone beds underlying the lavas at the top of the succession, can be broadly subdivided into two zones that can be recognised in all Southern African basins. The lower interval is composed of dark-coloured shales with scattered siltstones, sandstones and occasional coal seams. In terms of stratigraphy, it is represented by the Ecca Group and the lowermost part of the Beaufort Group in the Main Basin and their correlates towards the north. The upper interval consists of lighter-coloured mudrocks, sandstones and occasional conglomerates. Palaeontologically, it is represented by terrestrial vertebrate fossils rather than plant fossils, as found in the lower zone. The bulk of the Beaufort Group, Molteno, Elliot and Clarens Formations in the Main Basin, as well as equivalent formations in the northern basins, represent the upper zone (Johnson *et al.*, 1996).

#### <span id="page-10-1"></span>**2.3.2. The Ecca Group**

The Permian Ecca Group is essentially a clastic sequence of mudstones, sandstone, siltstone and some minor conglomerate and coal (Catuneanu *et al.,* 2005) that contains a total of 16 formations (Johnson *et al*., 2006), but only the Vryheid Formation, which forms the lowermost Ecca Group, will be considered for the purpose of this study. This is because the Vryheid formation contains the coal-bearing sedimentary rocks of the Ecca Group, located in the northern portion of the Main Karoo basin (Grodner and Cairncross, 2003; Hancox and Goetz, 2014). Coal is by far the main economic deposit found in the Ecca Group (Catuneanu *et al.*, 2005).

#### *2.3.2.1 Vryheid Formation*

The Vryheid Formation consists primarily of sandstone, shale, carbonaceous siltstone, minor conglomerate and several coal seams (Cairncross, 2001), all of which make up upward-fining cycles, that are known to be of fluvial origin. It is these fluvial successions that host most of the economically important coal seams (Johnson *et al*., 2006; Hancox and Goetz, 2014). These coal seams can be traced laterally over the entire area of occurrence of the Vryheid Formation in the Karoo Basin of South Africa (Hancox and Goetz, 2014).

#### <span id="page-11-0"></span>**2.3.3 The Beaufort Group**

The Beaufort Group is made up of a lower Adelaide and an upper Tarkastad Subgroup, both of which contain predominantly fluvial deposits (Johnson *et al.*, 2006), and according to Hancox and Goetz (2014), the Beaufort Group represents the transition from subaqueous deposition, associated with the Ecca Group, to fully subaerial deposition, where sedimentation is dominantly fluvial in origin (Hancox and Goetz, 2014).

#### <span id="page-11-1"></span>**2.3.4 The Stormberg Group (Molteno, Elliot and Clarens Formations)**

The Molteno Formation forms the basal part of the Stormberg Group (Hancox and Gotz, 2014) and contains alternating medium- to coarse-grained sandstones and grey mudstones. Coal seams are present in the Molteno Formation, although only a minor portion of these is considered to be economic (Hancox and Goetz, 2014).

The Elliot Formation is typically a "red bed" type fluvial deposit, comprising an alternating sequence of mudrock and subordinate fine- to medium-grained sandstone (Johnson *et al.*, 2006). No coal deposits occur within the Elliot Formation (Hancox and Goetz, 2014).

The Clarens Formation is dominantly a sandstone succession that represents an aeolian depositional system, with minor fluvial input (Hancox and Goetz, 2014; Catuneanu *et al.*, 2005).

#### <span id="page-11-2"></span>**2.3.5 The Drakensberg Group**

An episode of volcanism that preceded the breakup of Gondwana can now be observed as flood basalt remnants that are referred to as the Drakensberg Group (Johnson *et al.*, 1997). The Drakensberg Group forms part of the Karoo Igneous Province, together with the Lebombo Group. Basal lavas of the Karoo Igneous Province are considered to be conformable on the Clarens Formation although evidence of erosion of sandstones, creating topographic relief before the volcanic eruptions, has been observed in some places (Johnson *et al.*, 2006). Numerous feeder dykes and sills are associated with the basaltic lavas of the Drakensberg Group (Hancox and Goetz, 2014). A generalised stratigraphic sequence for the Karoo Supergroup on the north-eastern section of the Main Karoo Basin was reported by Johnson *et al*., (1996) and is shown in Figure 3.

#### <span id="page-11-3"></span>**2.4. The formation of Coal**

In order to understand the chemical and morphological makeup of coal, it is important to consider the formation process of coal. Coal is a naturally occurring hydrocarbon (Williams *et al.*, 2000) that originates from the accumulation of vegetable debris in a specialised environment of deposition (Thomas, 2013), such as swampy environments, known as mires. Mires contain the conditions necessary to allow peat, which is the initial matter in coalification, to collect and form beds that are then converted to coal in a complex and long process (Schweinfurth, 2009). The peat forms in a watersaturated environment from dead mosses, twigs, leaves and other parts of trees that do not decompose completely (Major, 1990). During coalification, the plant matter changes into a denser, drier, more carbon-rich, and harder material (Schweinfurth, 2009).



<span id="page-12-0"></span>Figure 2: Distribution of the Karoo Supergroup stratigraphy in the Main Karoo Basin of South Africa. Modified from Johnson et al. (2006)

These accumulations may be affected by different syn-sedimentary and post-sedimentary processes, to produce coals of different rank and structural complexity (Thomas, 2013). Coal rank is related to the coal quality, which is linked to coalification (Schweinfurth, 2009). Coal is divided into four ranks, namely (in decreasing order) anthracite, bituminous coal, sub-bituminous coal and lignite (Bowen and Irwin, 2008; Schweinfurth, 2009). The percentage of fixed carbon, volatile matter, and calorific value determine the rank of the coal, this is after the content of mineral matter and sulphur have been subtracted from the total constituents of the coal (Schweinfurth, 2009). The sulphur content of coal is derived from the sulphur content from the plant material that accumulates to form the peat. Some sulphur was also discovered to have been derived from the depositional environment (Calkins, 1994).

Within each of the coal seams that are formed, the coal type is controlled by a range of local conditions, which can range from the local palaeoenvironment, the rate of accumulation, type of plant community and the nature and rate of plant degradation (Falcon, 1986). Sedimentary sequences that contain coal and some peat occur all around the globe and are thought to range in age from the Upper Palaeozoic to present. With the plants that are available to make up coals having evolved through time, different coal lithotypes have hence been produced at different times throughout Earth's history (Thomas, 2013).

Coal types can also be classified according to the organic debris (macerals), mostly to determine its best uses (Bowen and Irwin, 2008). Ward (2002) regards coal as consisting of two classes of materials, organic components (macerals) and mineral matter, which is a range of minerals and other inorganic constituents. The organic components are used in defining the nature of the coal i.e. rank and type. The maceral constituents play an important role in the benefits derived from coal, including its energy output on combustion, its potential as an alternative hydrocarbon source, its role in the metallurgical processing and its capacity for in-situ methane absorption.<br> $\bigcup_{i=1}^{\infty} \bigcup_{j=1}^{\infty} \bigcup_{j=1}^{\infty} \bigcap_{j=1}^{\infty}$ 

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<span id="page-14-0"></span>Figure 3: A generalised stratigraphic column of the Karoo Supergroup closest to the eMalahleni coalfields. The coalfield is located in the Vryheid Formation of the Karoo Supergroup in the Main Karoo Basin of South Africa. Modified from Johnson et al. (1996).

#### <span id="page-15-0"></span>**2.5. Coal mining in South Africa**

Many economies around the world depend extensively on coal for a significant part of their energy needs (Azzie, 2002). Even though coal use is a principal contributor to greenhouse gases that cause global warming (Thomas, 2013), it remains a primary source of energy in South Africa, with the largest proven coal reserves occurring in the north-west, north-east and to the north of the Main Karoo Basin in South Africa (Cairncross, 2001). Coal is a convenient fuel that is easy to extract, transport and use. It is also solid, has a high energy density and is relatively easy to break up (Williams *et al.*, 2000; Chabedi, 2013). Natural gas, renewable energy sources and nuclear energy have been forecast to contribute increasingly towards energy supply in the future, but coal still remains the major energy source for the near future since it is relatively abundant and cheap in South Africa (Jeffrey, 2005).

Coal has been mined for over a hundred and ten years from the Vryheid Formation in the eMalahleni area, South Africa (Grodner and Cairncross, 2003), with the first commercial coal mining practices having started in 1857 (Hancox and Goetz, 2014). Most of the coal is used locally for power generation although some is also exported to overseas markets (Catuneanu *et al*., 2005). Coal is also used in the metallurgical industry (titanium, ferromanganese, steel and ferrochrome industries) (Hancox and Goetz, 2014), where it is used as a reducing agent in iron and steel manufacturing, and also as a major feedstock for the chemical industry (Azzie, 2002).

Extraction of the coal is by underground or opencast mining techniques (McCarthy, 2011). In the main coal-mining regions (Witbank- Emalahleni, Highveld and KwaZulu Natal coalfields), opencast mining techniques are used to extract the shallow coals and underground operations are used for the deeper coal seams, usually not deeper than 200m (Cairncross, 2001). According to the Global Energy Statistical Yearbook of 2016, found from the Enerdata webpage, South Africa is the  $7<sup>th</sup>$  largest coal producer in the world (Figure 4), and the largest coal producer on the African continent.



<span id="page-16-1"></span>Figure 4: Graph showing top coal producing countries. Coal resources of South Africa are compared to the rest of the world. Modified from Enerdata (2017)

#### <span id="page-16-0"></span>**2.6. Problems associated with coal mining**

Coal mining usually results in the exposure of coal to air and moisture, which can then result in the ignition of the coal through the processes of chemisorption, oxidation, and spontaneous combustion. The ignition of coal, amongst other impacts, is a global concern since burning coal may lead to significant environmental degradation problems (Pone *et al.*, 2007). Another problem that can arise is the formation of Acid Rock Drainage (Banks, 2004).

Coal mining contributes significantly to the deterioration of water quality because the removal of coal from the earth exposes impurities in the coal, which then react to form acidic drainage, a major water pollutant. Impurities in coal occur in the form of sulphur (sulphate, sulphide and organic sulphur compounds) and mineral matter (Mketo *et al*., 2016). Sulphide mineralisation is common to mined ore deposits. Mineral deposits that are likely to be mined are formed beneath the Earth's surface under relatively reduced conditions out of contact with atmospheric oxygen (Plumlee, 1999). In the coal, these impurities are formed during coal genesis under a long microbiological and geological process (Mketo, *et al*., 2016; Alam, *et al*., 2012). Exposure of these minerals by erosion or mining in the presence of atmospheric oxygen or oxygenated ground waters is well known as the cause of acid-rock drainage since these minerals tend to be unstable under such conditions (Plumlee, 1999). As a result, sulphidemineral oxidation within mining wastes is one of the most significant environmental challenges faced by the mining industry globally. This issue is largely attributed to storage of mining and mineral processing residues in sub-aerial deposits, where sulphide minerals are thermodynamically unstable (Lindsay *et al*., 2015) Sulphide sulphur was found by many authors to be the main sulphur species of concern since it readily oxidizes in the presence of water and oxygen to form acidic drainage (McCarthy, 2011; Mokoena, 2012).

The term Acid Rock Drainage (ARD) (INAP, 2009) rather than Acid Mine Drainage (AMD) is adopted for this report since acidic drainage can also be produced from other activities not necessarily related to mining. According to Blowes *et al.*, (2005), ARD is not necessarily limited to sites where there is an excavation of sulphide-bearing metalliferous ore deposits and sulphide-rich coal as it can also occur wherever there is exposure of sulphide minerals to atmospheric oxygen due to other reasons (Blowes *et al.*, 2005). This includes places where natural erosion is rapid, road cuts, excavations, and also tunnels that contain sulphide mineralisation (INAP, 2009). Sediments deposited in reducing marine environments, such as deltas, may also produce acidic drainage. In these environments, sulphide minerals are precipitated and the subsequent exposure of this material to subaerial weathering leads to acid rock drainage and the release of metals (Eby, 2004). This then means that for the purpose of being inclusive of every environment in which acid drainage may occur, the term Acid Rock Drainage will be used.

#### <span id="page-17-0"></span>**2.6.1. Acid Rock Drainage (ARD)**

Acid Rock Drainage (ARD) forms primarily when sulphide minerals are oxidised in the presence of air and water. Even though ARD formation can be considered to be a natural process, the activities that involve the excavation of rock material that contains sulphide minerals, mining is an example, accelerate the process by exposing sulphide minerals to air, water, and microorganisms. The resultant drainage produced may be neutral to acidic, and the amount of dissolved heavy metals can vary greatly, but it always contains sulphate (INAP, 2009). The degree to which mine water contamination occurs is dependent on the physical and mineralogical nature and abundance of sulphide minerals, physical and mineralogical nature and abundance of neutralising minerals, water flow paths and contact times with sulphide and neutralising minerals, the presence of relevant catalysing bacteria, the levels of available oxygen and the generation and transport of heat (DWAF, 2008). The impact of ARD is highly dependent on the geomorphology, the climate and the distributional extent of the ARD-generating deposits (McCarthy, 2011). The acid generating or acid neutralising potential for a given rock is determined by its mineralogical composition. This includes the quantitative mineralogical composition, mineral grain size, shape, texture and the spatial relationship with other mineral grains (Repinga, 2010).

The character of acidic drainage reflects both the source and other factors that the water encounters along its flow path. The local geology, type of alteration present in the deposit host rocks, the morphological character of the ore body, the reactivity of both the acid-generating and acid-neutralising minerals and the content of pyrite and other iron sulphides (Plumlee *et al*., 1999) can have a major impact on a body of water; therefore, it is also important to determine the extent to which all these factors will influence the water bodies they come into contact with. This can assist in the determination of whether acidification or neutralisation will be the primary process affecting the water, and also the time period associated with such a process (Azzie, 2002).

If the dominant reaction in the water-rock interaction is sulphide oxidation, the water will be characterised by a low pH, high concentration of metals, and elevated sulphate concentrations (Banks, 2004). The oxidation rate of the sulphur is dependent on the temperature, pH, chemical composition of the pore water, concentration of oxygen and microbial population (Azzie, 2002; Pinetown and Boer, 2006). Bacterial action plays an important role since it can control mineral solubility and surface reactivity of sulphide minerals, and this can then have a significant impact on the reaction rate of sulphide minerals in oxidative dissolution. Solutions rich in sulphuric acid and metal-enriched waters have been found to be linked with microbial activity. This is especially true in areas with mining activities (Blowes *et al.*, 2005).

Common sulphide minerals that are known to generate acidity with oxygen being the oxidising reagent include: pyrite (FeS<sub>2</sub>), marcasite (FeS<sub>2</sub>), pyrrhotite (Fe<sub>1-x</sub>S), bornite (Cu<sub>5</sub>FeS<sub>4</sub>), arsenopyrite (FeAsS), enargite/famatinite  $(Cu_3AsS_4/Cu_3SbS_4)$ , tennantite/tetrahedrite  $((Cu,Fe,Zn)_{12}As_4S_{13}/$  $(Cu,Fe, Zn)_{12}Sb_4S_{13}$ , realgar (AsS), orpiment (As<sub>2</sub>S<sub>3</sub>), and stibnite (Sb<sub>2</sub>S<sub>3</sub>) (Plumlee *et al.*, 1999; INAP, 2009).

Sulphide minerals likely to oxidise and produce acidity with ferric iron as the oxidant are the minerals listed above and sphalerite (ZnS), galena (PbS), chalcopyrite (CuFeS<sub>2</sub>), covellite (CuS), cinnabar (HgS), millerite (NiS), pentlandite ((Fe,Ni)<sub>9</sub>S<sub>8</sub>), and greenockite (CdS) (Plumlee, 1999; Dold, 2017; INAP, 2009).

Sulphide oxidation will continue (or even accelerate) until one or more of the reactants runs out or is no longer available for reaction. For example, contaminated drainage from mining can continue to be produced for decades or even centuries after the mining has ceased. If proper prevention of ARD (for mining projects) is to be achieved, then planning should start during exploration and continue throughout the mine-life cycle (INAP, 2009).

Neutral mine drainage (NMD) and Saline Drainage (SD) may form, instead of ARD, from the oxidation process where acid-neutralising minerals are present in sufficient quantities to neutralise the ARD (Figure 5). NMD contains high metal content in solution at near neutral pH, whereas SD is characterised by high levels of sulphate at neutral pH without significant metal concentrations. Saline drainage's principal constituents are sulphate, magnesium, and calcium ions (INAP, 2009; Nordstrom, Blowes and Ptacek, 2015). Although the acid and saline drainages are two of the most serious threats posed to the environment by the coal mining, some of this water can be re-used in agriculture (irrigation) and industry (steam generation, cooling and processing). At times this water can also be good enough to be used for domestic and recreational purposes. The quality of the water can be improved through appropriate treatment procedures (Azzie, 2002).



<span id="page-19-0"></span>Figure 5: The relation between Acid Rock Drainage, Neutral Mine Drainage and Saline Drainage. Acquired from Nordstrom, Blowes and Ptacek (2015).

#### *2.6.1.1. The chemistry of ARD*

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The chemical quality of ARD can be highly variable since it is influenced by the physical, chemical, mineralogical and microbiological properties of each site (Kuyucak, 2002). The chemistry of ARD generation may be simple but the final product is highly dependent on the temperature and geology of the region that is being excavated and the availability of micro-organisms, water and oxygen. Since these factors are highly variable from one area to the next, the prediction, prevention, containment and treatment of ARD should be treated with great consideration and a high level of specificity (CSIR, 2009).

The most common acid-generating reaction occurs when the minerals pyrite  $(Fes<sub>2</sub>)$  and marcasite ( $Fes<sub>2</sub>$ ) are in contact with oxygenated water (McCarthy, 2011), although many other sulphide minerals such as chalcopyrite (CuFeS<sub>2</sub>), arsenopyrite (FeAsS) and enargite (Cu<sub>3</sub>AsS<sub>4</sub>) also have acid-producing potential (Aphane, 2014). Pyrite/marcasite oxidation is a normal process and the rate of oxidation under normal circumstances is slow, such that neutralisation processes readily remove the acid produced. According to Lindsay *et al*. (2015), pyrite is the most common sulphide in the Earth's crust and is a major concern since it is known to be the most influential sulphide mineral in ARD production and prediction. Pyrite is a common constituent in South African coal and gold deposits (McCarthy, 2011).

#### *2.6.1.2. The oxidation of pyrite:*

Step one: Sulphide in the pyrite oxidises upon contact with air and water; pyrite is decomposed  $2FeS_2 + 7O_2 + 2H_2O = 4SO_4^2 + 2Fe^{2+} + 4H^+$  $FeS_2 + 14Fe^{3+} + 8H_2O = 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ 

Step two: Iron (II) is oxidised to iron (III)  $4Fe^{2+} + O_2 + 4H^+ = 4Fe^{3+} + 2H_2O$ 

Step three: Precipitation occurs with ferric iron to ferric hydroxide  $Fe^{3+} + 3H_2O = Fe(OH)_3 + 3H^+$ 

Thus, the overall reaction can be written as:  $4FeS_2 + 15O_2 + 14H_2O = 16H^+ + 8SO_4^2 + 4Fe(OH)_3$  (Pinetown and Boer, 2006; Eby, 2004).

The oxidation of pyrite, in the presence of an oxidant and water, occurs when the mineral surface is exposed, in a complex process that can involve chemical, biochemical and electrochemical reactions. A number of mineral catalysts, dissolved oxygen and  $Fe<sup>3+</sup>$  can interact with the pyrite in this complex reaction that involves a variety of pathways (Blowes *et al.*, 2005). The reaction with Fe<sup>3+</sup> is considerably faster (2 to 3 orders of magnitude) than the reaction with oxygen and generates substantially more acidity per mole of pyrite oxidised but it is limited to conditions in which significant amounts of dissolved ferric iron occur. This means that the oxidation of pyrite by oxygen is more likely to occur at circum-neutral or higher pH, and as the pH lowers and becomes more acidic, the oxidation with ferric iron can be realised (INAP, 2009)

The colour of the drainage is usually observed in the surface environment because groundwater and underground mine water generally do not contain sufficient oxygen for step two (above), the oxidation of  $Fe^{2+}$  to  $Fe^{3+}$ , to proceed as long as there is still pyrite in the system. Therefore, this Fe oxidation and the precipitation of Fe-hydroxides will be confined to the surface weathering environment (Eby, 2004).

Other metal sulphides besides pyrite may occur in base metal deposits; this includes minerals such as galena (PbS), sphalerite (ZnS), chalcopyrite (CuFeS<sub>2</sub>), covellite (CuS), and chalcocite (Cu<sub>2</sub>S). MS minerals differ significantly from  $MS_2$  sulphide minerals during oxidation. The oxidation of  $MS_2$ sulphide minerals (such as pyrite (FeS<sub>2</sub>)) leads to the release of the H<sup>+</sup>ion in solution, and this is not the case for the MS sulphide minerals. This then means that, even though there might be a release of the  $H^+$ ions into solution during hydrolysis reactions of MS sulphide minerals, the impact on overall acidity is much less than that due to the oxidation of  $MS<sub>2</sub>$  sulphide minerals. MS minerals can still, however, generate enough acidity when oxidised by ferric iron (Eby, 2004; Plumlee *et al*., 1999).

Neutralisation reactions are important in the compositional makeup of drainage originating from sulphide oxidation. Generic reactions for consumption of acid related to the dissolution of carbonate minerals and reaction of silicate minerals, can be written as:

 $MeCO<sub>3</sub> + H<sup>+</sup> = Me<sup>2+</sup> + HCO<sub>3</sub>;$ 

where Me represents a divalent cation (Ca and Mg) but not iron or manganese because these release acidity after subsequent hydrolysis/precipitation. Effective neutralisation reactions are, therefore, generally directly related to the abundance of non-Fe/Mn carbonate minerals (INAP, 2009).

#### *2.6.1.3. ARD in mining*

Even though ARD formation is in essence a naturally occurring process (INAP, 2009), the concern arises when the rock mass is extensively fragmented during mining and other excavation processes, hence increasing the surface area exposed and consequently the rate of acid production (McCarthy, 2011). Earth moving processes, mining included, accelerate the weathering process of reactive sulphides because they create conditions that facilitate the movement of air and water, increase the surface area of the reactive material by exposing large volumes of the material, and create the opportunity for colonisation by microorganisms that catalyse the oxidation process in acidic conditions (INAP, 2009).

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When mines and spoil tip environments have oxidation reactions dominating over acid-base (neutralisation) reactions, the phenomenon of acid rock drainage (ARD), also known as acid mine drainage (AMD), is the result (Banks, 2004). ARD is regarded as the most notable form of pollution from the coal mining industry (Pinetown and Boer, 2006; Sahoo *et al.*, 2014). In coal mines, pyrite and marcasite are mostly responsible for the ARD problems (Pinetown and Boer, 2006). The sulphur in South African coals occurs as sulphide, sulphate or organic sulphur. The two main sulphur minerals found in South African coal are pyrite  $(FeS_2)$  and marcasite  $(FeS_2)$  (Hancox and Goetz, 2014). In the case of coal mines, the pyrite that causes ARD can be found in the host rocks as well as in the coal, but it tends to be more abundant in the coal (McCarthy, 2011).

Acid drainage production in mines is excessive because when mines are dug, circulation of oxygen and water are rapidly introduced into the deep geosphere, in zones where the concentrations of oxidisable minerals such as sulphides are high. This is the same when mine waste tips are created, because this brings deep sulphide-rich geosphere up into the atmosphere, where there is often excellent access to circulating water and oxygen (Banks, 2004). In the mining industry, the major sources of acidic drainage are underground mine shafts, runoff and discharge from open pits and mine waste dumps, tailings and ore stockpiles. A combination of these sources makes up about 88% of all waste produced in South Africa (CSIR, 2009).

Due to the inherent geochemical nature of their wastes, not all mines will produce ARD. Some mines are located in very arid regions, and as such will tend to produce little or no ARD, unlike those located in temperate or tropical climates with high rainfall (INAP, 2009; Plumlee *et al*., 1999ou). The severity of environmentally degrading impacts is also dependent on whether the mine is working or abandoned, the methods used in the mining process, the geological conditions (Bell *et al.,* 2000), and the area, size and purpose of infrastructure used during mining (Azzie, 2002). The severity also relates to the geomorphology, and the extent and distribution of such an environmentally-degrading deposit (McCarthy, 2011), the ore-deposit type, and the waste-disposal strategy (INAP, 2009).

ARD can also form from spoils from the material that was extracted during mining and from tailings produced in plants where the ores are processed, especially if they contain a significant amount of pyrite (Pinetown and Boer, 2006; Eby, 2004). Even though the primary sulphide minerals found in mine wastes are pyrite and pyrrhotite  $(F\epsilon_7S_8)$ , other sulphide minerals can also be subjected to oxidation reactions which may lead to the release of elements such as arsenic, aluminium, cadmium, cobalt, copper, lead, mercury, nickel and zinc into the mine water flowing through the mine waste. Oxidation products transported from the mine wastes can be transported to lakes, streams and oceans. Even though acid neutralisation can occur in some of the waste material, the water from waste material from the mines will likely contain increased concentrations of dissolved constituents (Blowes *et al.*, 2005)

Another way in which acidic drainage can form is through groundwater emerging from abandoned mines that contain sulphuric acid and other metal salts (Pinetown and Boer, 2006). This water can interact with the sulphide minerals in the mineral deposit that was being mined when the mine was still operative (Eby, 2004). When the water has been affected by the sulphide oxidation it can be displaced back to the underlying geology or it can also be discharged to adjacent surface water systems (McCarthy, 2011; Eby, 2004). The water affected by sulphide oxidation reactions can be neutral or strongly acidic but is always loaded with (in part toxic) metals and sulphate salts (Pinetown and Boer, 2006). Releasing this affected water into surrounding water resources can render the water useless, if not treated, for consumption, industrial and agricultural purposes (Mokoena, 2012).

Not only does the mining impact the surface and groundwater resources, the acidic drainage produced by mines can also have a negative impact on the soil quality, aquatic habitats and also the release of toxic metals to the surrounding environment can add to the degradation. This kind of environmental degradation can persist for a long time even after mine closure, with the situation compromising the health and the safety of nearby communities that are affected (CSIR, 2010; Ochieng, *et al*., 2010).

Acidic drainage is not the only problem that is associated with coal mining, poisoning from fluorine which may be contained in the coal is another form of contamination that can have adverse effects, especially on human health. Potentially harmful toxic elements such as arsenic, fluorine, mercury, thallium and antimony are introduced to the coal through mineralisation processes. If the coal is mined and burnt, the burning volatilises the toxic elements and exposes the individuals involved in the burning to the toxic elements in the emissions (Finkelman, *et al*., 1999; Robertson *et al.*, 1994). Even though fluorine is considered to be essential for both plants and animals, high concentrations of this element can be toxic (Dressler *et al.*, 2003). The health problems associated with fluorine during domestic coal use have been known to be even more extensive than those caused by arsenic (Finkelman, *et al*., 1999).

#### *2.6.1.4. Metal leaching and ARD*

The solubility of iron and other metals in solution increases with decreasing pH. At low pH (acidic conditions) these metals do not get adsorbed by oxyhydroxides and mineral particles but rather stay in solution. This can then result in acid rock drainage containing elevated amounts of the dissolved metals (Eby, 2004). This is because low-pH conditions promote the dissolution of metal-bearing compounds and also desorption of metals from solid surfaces (CSIR, 2010). An increase in the pH can lead to a reversal of these conditions, and a subsequent decline in the concentrations of dissolved metals that were released from the mine wastes (Blowes *et al.*, 2005). **HANNESBURG** 

## A dissolution of carbonate minerals leads to the release of magnesium, calcium, iron and other cations that may be present as impurities or solid-solution substitutions. The dissolution has the potential to raise the pH of the affected water by increasing the alkalinity of the water. Dissolution of carbonate minerals forms part of acid-neutralisation reactions which can lead to an increase in the pH conditions (Blowes *et al.*, 2005). If an increase of pH occurs, the solubility of metals is decreased and the formation of oxyhydroxides takes place. The net result is the removal of metals from the solution to the sediments, resulting in metal-rich sediments which are also a potential environmental hazard (Eby, 2004).

The combined process of the release of metals from minerals and their removal from solution and precipitation is known as metal leaching (INAP, 2009). Even though metal leaching problems can occur over the entire range of pH conditions; they are most commonly associated with ARD. The level of impact of metal leaching/ARD is dependent on their magnitude, the sensitivity of the receiving environment and the degree of neutralisation, dilution or attenuation. Metal leaching is enhanced by rapidly-weathering metal-containing minerals, drainage conditions that are favourable to increased metal solubility and a high flow rate through contaminant materials (Price and Errington, 1998).

Acid generation and metal leaching essentially result from the reaction of the surrounding rocks with the environment; therefore, a combination of field observations, laboratory tests and predictive modelling is needed before a proper identification, assessment and characterisation of an ARD problem can be made (Bowell, Rees and Parshley, 2000). Metal leaching and ARD have led to significant environmental and ecological damage, loss of aquatic life resulting from contaminated rivers and other water bodies, and elevated clean-up costs for industry and government (Price and Errington, 1998).

Iron-rich mine drainage waters typically have a yellow to orange to red discolouration at surface. The colours result from the presence of dispersed Fe(OH)<sub>3</sub> particles or dissolved Fe<sup>3+</sup>. These colours, and many other colours of the drainage encountered may be used to relate the metal precipitate to the colour of the drainage formed. Precipitates include jarosite and iron oxyhydroxides (appearance is a yellow to red colour), aluminium hydroxides (white colour), metal salts that can be pink (cobalt), green (nickel), deep blue (molybdenum), bluish-green (copper), and red (lead) (Bowell, Rees and Parshley, 2000).

Crystallisation of secondary minerals can occur *in situ* as a result of the oxidation of primary sulphide minerals. This can happen during temporary storage or after final discharge of the waste material from the mine. Tertiary minerals can also form when the material dries upon removal from the disposal site. These tertiary minerals are predominantly water-soluble solids that crystallise during the evaporation of pore water (Blowes *et al.*, 2005). JIVERSITY

#### *2.6.1.5. ARD treatment and mitigation options*

In order to find a solution for dealing with acid generation from coal mining, the nature of the coal (minerals, macerals, moisture content, fixed carbon content etc.) and the extent to which the coal has interacted with the environment should be determined. This is because water-rock interactions form the basis of the pollution-generating reactions. Thus, the building blocks of the rock which interacts with the water are essential in understanding acid-generating processes (Pinetown and Boer, 2006). An understanding of the waste rock mineralogy and morphology of sulphide minerals therefore plays a key role in the prediction of ARD generation because these factors strongly influence sulphide oxidation (Sahoo *et al.*, 2014). Treatment of the pollution is necessary since the water can cause serious pollution problems in public streams if it were to be re-used or released without treatment (Maree *et al.*, 2004).

The ease and rapidity with which the acid-neutralising minerals can react with acid produced varies considerably. Acid neutralising minerals include dissolving minerals calcite  $(CaCO<sub>3</sub>)$ , dolomite  $(MgCa(CO<sub>3</sub>)<sub>2</sub>)$ , ankerite  $(CaFé (CO<sub>3</sub>)<sub>2</sub>)$ , and magnesite  $(MgCO<sub>3</sub>)$ . Calc-silicate minerals such as diopside (CaMgSi<sub>2</sub>O<sub>6</sub>), wollastonite (CaSiO<sub>3</sub>), and garnets can similarly react to consume acid, as can rhodonite (MnSiO3), a metal silicate common in some types of sulphide-bearing mineral deposits. A number of other metal-compounds such as malachite  $(Cu_2CO_3(OH)_2)$ , gibbsite  $(A(OH)_3)$ , may also be effective in consuming acid produced (Plumlee, 1999; Dold, 2017). Dissolution of silicates such as plagioclase (anorthite) can also neutralize acid, but the rate of dissolution is slower than that of the carbonate minerals (Azzie, 2002).

In the South African coalfields, the acid-generating minerals co-exist with calcite and dolomite which can neutralise the acid generated (Vermeulen, *et al*., 2009). As the carbonate content dissolves, the pH rises to near neutral. Calcite is the first to be depleted, followed by dolomite-ankerite, and then siderite. The solubility products for the dissolution of the different carbonate minerals differ, with the most soluble minerals proceeding first, followed by the dissolution of the next most soluble mineral (Blowes *et al.*, 2005). The relative contribution of acid-neutralising minerals to the neutralisation of acidity is dependent on their abundance and reactivity. Laboratory studies of carbonate dissolution in sulphide waste rock have revealed that grain size, shape, texture, spatial relationship with other minerals and surface area are important controls on acid neutralisation (Lindsay *et al*., 2015; Mills, 1997).

Apart from the naturally-occurring neutralising minerals, the most cost-effective strategy for treating and mitigating ARD would be to control it at the source. The best way to achieve this would be to remove one or more of the principal ingredients of the ARD-generation process. Limiting the oxygen and water in contact with the sulphide minerals and/or increasing the neutralising minerals in the mine waste are control factors that may work (Kuyucak, 2002). Preventing water ingress into mine voids and also controlling the placement of acid-generating mine waste are other feasible prevention methods (CSIR, 2010).

The science and engineering of preventing and managing ARD are continuously evolving. This means that prevention and mitigation proceedings should be taken with due consideration of the uncertainties and risks that may arise in order to achieve the desired outcomes (INAP, 2009).

If the prevention of ARD cannot be achieved, then treatment by means of chemical and/or biological processes to eliminate or minimise the impact on the environment can be deployed. Treatment and mitigation of acidic generation is usually done to comply with regulated water standards (Kuyucak, 2002). The dilution of acidic waters with unaffected surface waters may provide substantial mitigation of the acidic water without any special addition of reagents (Plumlee and Lodgson, 1999).

Active acidic drainage treatment options include neutralisation (which often involves metal precipitation, metals removal and chemical precipitation), aeration, membrane processes, ion exchange and biological sulphate removal (INAP, 2009).

Lime neutralisation is the most common low-cost active treatment method used for treating ARD within the mining industry. Lime neutralisation can be quite effective, especially when treating ARD in large quantities due to its high abundance and reactivity, even though it does have its disadvantages. In the lime neutralisation process, the lime is used as CaO or Ca(OH)2, and is added to precipitate metals and sulphate (SO4) as sludge (Kuyucak, 2002; Banks, 2004). This treatment process raises the pH of the waters and removes the metals into a sludge, which can then be separated physically by settling (Plumlee and Lodgson, 1999).

A disadvantage of the lime neutralisation process could be that it produces a large volume of sludge and may be inefficient in removing some metal ions to low levels (Kuyucak, 2002). These active treatment options require active maintenance and mechanical devices to mix the reagents with the water (Plumlee and Lodgson, 1999).

Passive treatment procedures have been proven to be feasible alternatives to lime neutralisation/precipitation and sulphide precipitation methods (Kuyucak, 2002). Passive systems are advantageous since they require little or no input of reagents, active maintenance or mechanical devices (Plumlee and Lodgson, 1999; INAP, 2009). These treatment systems are particularly ideal for decommissioned sites and the treatment of seepage where the temperature, chemical composition and the flow rate are relatively optimal and do not fluctuate all year round. When these passive systems are functioning properly, they can produce compliance level effluents with no additional costs apart from the initial construction and limited periodical maintenance. Some sites might require supplementary chemical treatment to meet effluent limits, but this too can be done in a cost-effective manner (Kuyucak, 2002).

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The most common passive treatment systems are bisorption, anoxic limestone drains, and constructed aerobic and anaerobic wetlands. The performance of the individual systems is highly dependent on the quality and quantity of the raw acidic drainage. Influent flow rate, pH, the concentration of the contaminants and alkalinity/acidity are important factors that are important in the performance of passive systems (Kuyucak, 2002).

Soil and water covers have also been used on the mine waste to mitigate the impact of acidic drainage on the environment. Using soil covers may not be economically feasible sometimes, but water covers have been shown to be an economical alternative to dry covers. Water has a low oxygen diffusion rate with respect to air, and this makes water covers an effective long-term control method for acid generation. Water covers are, however, restricted to site conditions such as hydrology of the area, topography and the presence of a water source in the vicinity. Even though water covers may be effective in decreasing the rate of acid generation, the concentrations of some metals can still increase (Kuyucak, 2002). Discard dumps are therefore to be designed in a way that would ensure minimum acid formation by limiting contact with water and air (Maree *et al.*, 2004).

The high-density sludge (HDS) process is another frequently used treatment method that does not involve the direct contact of lime with ARD, but rather recycled sludge is brought into contact with lime slurry for neutralisation (Aubé, 2004). A newly developed technique that involves the precipitation of metal sulphides involves reaction of sulphide ions with metal ions to give an insoluble metal sulphide species. Advantages of this technique include the potential selective precipitation of metals, better settling properties and is potentially more advantageous since metal sulphide precipitates have a lower solubility than, for instance, sulphates (Nduna and Lewis, 2014).

Solutions to the ARD threat are unlikely to be truly successful in the short to medium term and might even take centuries. These solutions are also unlikely to be from a single intervention but will require the integrated implementation of a range of measures. Such measures include passive and active water treatment systems, controlled placement of acid-generating mine waste and prevention of water accumulation in mine voids. ARD pollution is so persistent that in the absence of any remediation, in many instances the contaminated sites may never completely reach restoration (CSIR, 2009).

#### <span id="page-27-0"></span>**2.7. The coalfields of South Africa**

Coal is found in 19 coalfields in South Africa (Jeffrey, 2005; Pone *et al.*, 2007), mainly located in Mpumalanga, KwaZulu Natal, Limpopo, and the Free State, with lesser amounts in the Eastern Cape, Gauteng and North West Province (Jeffrey, 2005) (Figure 6)

The coalfields are structurally quite simple, with beds being near horizontal. Exceptions do occur, with some coalfields located close to structurally complex areas showing considerable amounts of dip. The most common structural disturbances that have an effect on nearly all the coalfields are related to the doleritic dykes and sills associated with the Drakensberg volcanic event (Catuneanu *et al.*, 2005). They have led to varying degrees of devolatilisation of the nearby coal seams and have also displaced the strata over considerable areas (Smith and Whittaker, 1986).

In a generalised South African context, the best quality coals are located in the KwaZulu-Natal, Emalahleni, Soutpansberg and Pafuri (which is also sometimes included under the Soutpansberg coalfield) coalfields. The coals from these coalfields are considered to be of higher rank since they contain lower ash contents (Smith and Whittaker, 1986) than those from the Free State and Eastern Cape coalfields. The coal from the Springbok Flats coalfield is not mined as it is at a deep level and contains in part high concentrations of uranium. For the current study, only the eMalahleni and South Rand coalfields will be considered.

#### <span id="page-28-0"></span>**2.7.1. The eMalahleni (Witbank) coalfield**

#### *2.7.1.1. General description*

The eMalahleni coalfield is situated in the northern part of the Main Karoo Basin. It extends over a distance of approximately 180 km from east of the town of Springs in the west to Emakazeni in the east, Middelburg in the north, and Rietspruit in the south. Pre-Karoo basement, including units of the Bushveld Igneous Complex, forms the northern boundary of the coalfield (Hancox and Goetz, 2014). In 2006, Pinetown and Boer (2006) considered the eMalahleni coalfield as one of the most important coalfields in South Africa, supplying more than 50% of the country's saleable coal at the time.

Metallurgical and thermal coals are both produced from the eMalahleni coalfield for local as well as export markets, and many of the major power stations in South Africa are located in this coalfield. Exploration and exploitation of the eMalahleni coalfield is fairly mature, with new large resources unlikely to be identified in the future (Hancox and Goetz, 2014).





<span id="page-29-0"></span>Figure 6 The coalfields of South Africa and Swaziland. Most of the coalfields occur in the Main Karoo Basin of South Africa, even though some are found in Karoo-aged basins adjacent to the Main Karoo Basin of South Africa. Modified from Jeffrey (2005)

The basement to the Karoo Supergroup is variable across the coalfield. From west to east the basement rocks include metavolcanic, dolomitic and metasedimentary rocks of the Neoarchaean Transvaal Supergroup, metasedimentary and metavolcanic rocks of the Palaeoproterozoic Waterberg Group and granitic and felsitic intrusives of Bushveld Igneous Complex age. The coalfield contains five, sometimes six, coal seams within a 70 m thick succession of the Vryheid formation. The seams are numbered from No. 1 at the bottom to No. 5 at the top of the sequence (Hancox and Goetz, 2014).

Four of the five coal seams of the eMalahleni coalfield are consistently developed over the entire 180 km length (Pinetown and Boer, 2006), but coal seams are nevertheless generally discontinuous, some of them are absent over prominent palaeotopographic highs (Smith and Whittaker, 1986). A generalised stratigraphic sequence for the eMalahleni coalfield is shown in Figure 7.

The coal seams occur in strata consisting of sandstone with some minor mudstone, siltstone and shale. The rocks that overlie seam 5 are mainly arenaceous. The Karoo rocks in the eMalahleni coalfield have not been subjected to any major displacements, except in some places where they are intruded by Karoo doleritic dykes as discussed above (Smith and Whittaker, 1986). Of the six classically recognised coal seams within the eMalahleni coalfield (Smith and Whittaker, 1986; Pone *et al.*, 2007), the primary economically extracted seams have been the No. 2, No. 4 (upper and lower) and in some places the No. 5 seam (Exxaro, 2015).

Development of seam No. 1 is highly variable as it occurs mostly in palaeovalleys and the seam tends to pinch out against palaeohighs (Hancox and Goetz, 2014). The No. 1 seam is considered to be the least economically important one (Smith and Whittaker, 1986), developed in the northern and eastern part of the coalfield where it is about 1.5 m to 2 m thick. Where seam No. 1 is economically extracted, it consists mainly of lustrous to dull coal with locally-developed sandstone and shale partings capped off by a competent sandstone or grit roof (Pinetown and Boer, 2006). The coal is of poor quality and is usually not included as part of the resource base except in places where it is joined to and forms the basal part of the No. 2 seam (Hancox and Goetz, 2014).

The No. 2 seam of the eMalahleni coalfield is the most economically important resource (Chabedi, 2013), containing approximately 69% of some of the best quality coal. The average thickness of the seam is 6.5 m in the central part of the coalfield and the seam then thins to about 3 m to the west and east (Smith and Whittaker, 1986; Hancox and Goetz, 2014). The No. 2 seam is in some areas split by an intra-seam layer of clastic sediment into No. 2 Lower (2L) and No. 2 Upper (2U) seams (Hancox and Goetz, 2014). Up to six well defined coal zones are found in the seam. Steam coal for the export market is usually mined from the basal five zones and the top zone produces coal of lower quality that is mainly used for the local Eskom market (SRK Consulting, 2009).

The No. 3 seam is poorly developed, and where it is found, it has an average thickness of about 0.5 m. The coal contained within the seam is good in quality but is generally not extracted economically due to its thin development. In the far western sector, it is locally greater than 0.5 m and may represent a potential shallow resource for opencast mining, but it contains high sulphur values that are often not lowered by beneficiation processes (Hancox and Goetz, 2014).



<span id="page-31-0"></span>Figure 7 Generalised stratigraphic column of the eMalahleni coalfield. Modified from Hancox and Goetz (2014)

The No. 4 seam is the second most important source of coal in the eMalahleni coalfield, contributing about 26% of its total resources (Pone *et al.*, 2007; Smith and Whittaker, 1986), and containing a varying thickness of about 2.5 m in the central part to around 6.5 m in other places. In some places, the seam is divided into No. 4 Lower (4L), No. 4 Upper (4U) and No. 4A seams that are separated by sandstone and siltstone partings. The coal is a dull to dull-lustrous coal, and the quality is variable across the eMalahleni coalfield. In general, the No. 4 seam is poorer in quality than the No. 2 seam (Hancox and Goetz, 2014). The coal of the No. 4 seam is mainly used as a power station feedstock and for domestic steam coal (Pone *et al.*, 2007).

The No. 5 seam has been extensively eroded over large areas of the eMalahleni coalfield, seldom attaining a thickness of 2 m (Smith and Whittaker, 1986). The No. 5 seam is separated from the No. 4 seam by a thick succession of interbedded sandstones and siltstones that can be up to 25 m in thickness. The poor-quality floor of the No. 5 seam, which is composed of carbonaceous fines and claystones, has given rise to significant challenges with regards to the mining of the seam (Hancox and Goetz, 2014).

The seams in the eMalahleni coalfield and their bounding strata are generally flat lying except in places where they are found to be locally tilted by dolerite intrusions (Hancox and Goetz, 2014; Chabedi, 2013). The Ogies dyke is the most prominent dyke (Exxaro, 2015), which splits the coalfield into a northern portion and larger central-southern portion (Hancox and Goetz, 2014).

#### *2.7.1.2. AMD in the eMalahleni coalfield*

A study conducted by Azzie (2002) confirmed a bimodal occurrence in the pH related to the eMalahleni coalfield, with some collieries being acidic and others near-neutral. Very few of the samples had pH values between 4 and 5. The mining was found to have impacted on the groundwater, with the oxidation of pyrite having introduced acidic conditions in the waters. Near-neutral colliery waters were found to be supersaturated with respect to most carbonate minerals.

Azzie, (2002) found that the composition of the water bodies was affected by their interaction with host rocks found in the coal mines. The interactions were useful in the prediction of whether acidification or neutralisation reactions would be the likely primary process responsible for the characterisation of the water in the South African coal mines.

#### <span id="page-32-0"></span>**2.7.2. South Rand coalfield**

#### *2.7.2.1. General description*

The small South Rand coalfield occurs within a deep, southerly trending palaeovalley (Hancox and Goetz, 2014), stretching from Heidelberg in the north to the Vaal Dam in the south (Henderson, 1986). Palaeohighs of Ventersdorp and Witwatersrand Supergroups strata isolate the coalfield from the rest of the coal-bearing areas (Hancox and Goetz, 2014).

The sedimentary succession of the South Rand coalfield (Figure 8) is essentially comprised of varying proportions of sandstones, shales, and mudstones of the Vryheid Formation (Henderson, 1986). The total thickness of the strata above the coal zone may reach a maximum of 220 m, with 150 m of this attributed to a dolerite sill (Chabedi, 2013).

The coal quality is generally poor because the ash content is very high and the calorific values are resultantly low (Chabedi, 2013). One main coal zone is present in the area, ranging in thickness from subeconomic stringers less than a metre to a composite seam in excess of 20 m at the central part of the coalfield (Henderson, 1986). The composite seam is split into two or more thinner seams by partings of sandstone, shale, and conglomerate. The stratigraphy of seams is not fully consistent throughout the area, but Chabedi (2013) does mention that there are three main seams that do occur in the coalfield, and hence a seam nomenclature can be used for convenience (Henderson, 1986; Chabedi, 2013).



<span id="page-33-0"></span>Figure 8: Generalized stratigraphic column of the South Rand coalfield (Modified from Hancox and Goetz, 2014) Three main coal seams are found in the South Rand coalfield, as well as a poorly developed Ryder Seam (Hancox and Goetz, 2014).

The quality of the No. 1 seam is generally better than that of the other horizons, but *in situ* reserves are limited. The seam is composed of dull-lustrous coal with dark streaks and bands. The roof and floor is made up of competent sandstone (Henderson, 1986), and average thickness of the seam is about 2.8 m (Hancox and Goetz, 2014)

The No. 2 seam (Main Seam) has a variable thickness but it is found to have an average thickness of 10 m (Hancox and Goetz, 2014), and is the only regionally continuous mining horizon throughout the coalfield (Henderson, 1986). Due to the presence of a glauconitic sandstone marker above the seam, the No. 2 seam of the South Rand coalfield has been correlated with the No. 4 seam of the Witbank coalfield (Chabedi, 2013).

In many places the No. 2 and No. 3 seams combine, and when they are separated by a parting, this parting is usually too thin for the two coal seams to be mined independently (Henderson, 1986). A Ryder seam, with an average thickness of about 2.5 m, is also found irregularly developed (Jeffrey, 2005). The Ryder Seam is of inferior quality in comparison to the other seams and since it is coupled with poor mining conditions, the seam has been of low priority and was not mined historically (Hancox and Goetz, 2014).

The South Rand coalfield is structurally complex, due to a number of dolerite intrusions and faulting that occurs throughout the area. In addition to the major faulting associated with dolerite dyke and sill intrusions, there are numerous major and minor faults that have been encountered in areas where mining has been carried out (Henderson, 1986; Chabedi, 2013).



#### <span id="page-35-0"></span>**3. Methods and materials**

#### <span id="page-35-1"></span>**3.1. Introduction**

A groundwater risk map for the eMalahleni coalfield was created by assessing the mineralogy, groundwater quality already reported, whether the mine was still operational or mining had ceased, on the sulphur content, the outcomes of reported ABA results that had been conducted on samples from the respective mines, the availability of acid-generating and acid-neutralising minerals and their respective quantities, groundwater assessment results from the different mines and any other geochemical assessment that was conducted on the mine that would assist in the determination of whether that particular mine would have acid-generating or acid-neutralising conduct. Any information that could be of assistance in determining the likely impact of coal mining on the groundwater quality at a given area was used in the classification. The data was collected from a total of 51 coal mines that were then assessed and classified according to their acid generating/neutralising potential.

Three mines were chosen for specific case studies involving acid-base accounting via analyses of coal and interlayered sediments. Two were chosen from the eMalahleni coalfield and one from the South Rand coalfield. The two mines chosen in the eMalahleni coalfield i.e. Khutala coal mine and Inyanda coal mine, were already operational during the time of sample collection whereas samples were collected from drill core in the South Rand Heidelberg Project located in the South Rand coalfield.

#### <span id="page-35-2"></span>**3.2. Study methodology**

The study thus incorporates a review and compilation of existing analytical data on water and South African coal from the selected study areas, obtained from the Water Research Commission and other sources, mainly through Golder Associates who sponsored the project from WRC funding, for selected sites where climatic, geological, topographic control factors are well defined, detailed reviews of rock mineralogy and water quality were undertaken. The work done for the three case studies included collection and analyses of samples from the coal seams themselves as well as, in one case, from coarse and fine discard stockpiles, and the acid producing/neutralising potential was determined using the method described in Section 3.7

#### <span id="page-35-3"></span>**3.3. Sample collection**

A total of 116 samples were collected, 14 from the Inyanda coal mine, 26 from the South Rand Heidelberg Project, 42 samples from Seam 2 of the Khutala coal mine and 34 from Seam 4 of the Khutala coal mine. XRD and ABA analyses were conducted on all the samples collected from the different sites.

Samples from the South Rand Heidelberg Project were collected from drill core during a visit to the South Rand Heidelberg Project proposed mining area. Khutala coal samples were collected from the underground mining section in the Khutala coal mine (Section 4.2.2.1) during a mine visit and the
different lithology found at Inyanda coal mine were collected during a mine visit on the Inyanda opencast mine (Section 4.2.1.1).

# **3.4. Crushing and milling for powder**

Samples were crushed to less than cobble-sized grains and then milled with a Siebtechnik laboratory disc mill (Labor Scheibenschwingmühle TS 250 mit Einsatz) at the University of Johannesburg's rock preparation laboratory to fine powder  $\langle \langle 1 \mu \text{m} \rangle$ . The powder was used for mineralogical analysis by X-Ray Diffraction (XRD), and also for the Acid Base Accounting procedures.

# **3.5. X-Ray Diffraction (XRD)**

The coal mineralogy from the sites chosen from the respective coalfields was investigated. The mineralogy of the rocks is considered to play a major role in the water quality of the water resources interacting with the different rock types and hence, in addition to Acid Base Accounting (ABA), X-Ray Diffraction (XRD) was used to identify the mineral composition of the samples collected. This work was carried out at the Spectrum laboratory, University of Johannesburg (UJ), using a Panalytical X'Pert diffractometer with an X'Celerator detector.

Quantitative X-ray Diffraction (QXRD) is a technique based on the principle that the peaks from a given mineral phase are related to the phase's abundance in a given mixture (Chipera and Bish, 2013), and it can be used to reveal structural information, crystal structure, crystal size, strain, layer thickness and preferred orientation of the analysed sample (PANalytical, 2016). For the purpose of the current study, however, the XRD method was used in a qualitative to semi-quantitative way to identify the mineral composition of the different rock types from the coal mines under study. The data obtained from the analysis was evaluated using High Score Plus Software. Table 1 shows the diffractometer settings. For the procedure used, the detection limit for most minerals is between 3 and 5 weight % (Dr C. Reinke, personal communication, 2016). Minerals identified are listed in Appendix C.



Table 1 Diffractometer settings



# **3.6. Acid Base Accounting (ABA) procedures**

Several techniques are available to assist in the prediction of acidity and metal content in acidic drainage. These methods are static and kinetic testing procedures. Static tests are low cost and are measured over a short period of time. These tests provide an estimate of a sample's ability to produce acid or neutralise acid produced. Static tests do not provide the rate at which acid-production or consumption occurs, but only provide the relative capacities for acid production or consumption. Static tests also assume all the acid-producing and acid-neutralising minerals available will react completely, and this is not always feasible since the particle size and morphology of the minerals involved is not taken into consideration (Azzie, 2002; White *et al*., 1999). These static tests should therefore be used in conjunction with other subsequent assessments such as kinetic tests to provide a more comprehensive characterisation (Lawrence and Wang, 1996).

A common static method is Acid-Base Accounting (ABA). In this procedure, the acid-generating minerals are measured and balanced against the measured contents of acid-neutralising minerals, after which the material can then be classified as acid-generating or non-acid generating based on this balance (Plumlee *et al*., 1999). Kinetic tests are measured over a long-term period (months or even years) and are used as means of confirming or reducing uncertainty in static test classification and to determine the rates and temporal variations in leachate water quality (Azzie, 2002; Hageman *et al*., 2015). According to Mills (1997) and Lawrence and Wang, (1996), ABA should be taken as a screening procedure since the procedure does not provide information on the speed (or kinetic rate) with which acid-generating or acid-neutralising reactions will occur.

The result of ABA analysis is always referred to as the "potential" since only a best-case scenario, in reference to the potential neutralisation capability, and the worst-case scenario, when taking the potential for acid generation into consideration, is taken into recognition. The potential for acidgeneration or acid-neutralisation still needs a detailed mineralogical analysis, combined with the ABA data, to reach the worst-case acid-generating potential scenario or a best-case acid-neutralisation potential (Mills, 1997).

Standard Acid Base Accounting procedures are carried out to determine the balance between acid producing and acid consuming components of a given sample. ABA procedures comprise of two measurements i.e. the determination of the neutralisation potential (NP) and the calculation of the acid producing potential (AP) of a sample. The traditional methods consists of sulphur assays, on separate subsamples, done by LECO furnace followed by titration: (1) an analysis without pre-treatment, representing total S content (sulphate, sulphide and organic); (2) an analysis after a leach with 12.5% HCl (which removes S hosted in sulphate); (3) an analysis after a leaching with  $7.5\%$  HNO<sub>3</sub> (which removes S hosted in sulphide). The difference between results (1) and (3) theoretically yields the acid producing potential.

NP represents the amount of acid-neutralising carbonate minerals present in a sample and is traditionally determined by a digestion titration procedure (Azzie, 2002). In this study NP and AP were determined by inductively coupled plasma optical emission spectrometry (ICP-OES) on the HCl-leach and the HNO3-leach respectively, which were carried out successively on the same sample aliquot. This procedure is described in detail in Section 3.7.

#### **3.6.1. Fizz test**

The fizz rating is a qualitative assessment of the effervescence resulting from the dissolution of acidsoluble carbonate minerals, and it is established by adding a few drops of 25% HCl to a given sample. A fizz test is traditionally carried out first as part of the determination of the neutralising potential by titration. The fizz rating is used to determine the volume and normality of HCl to be added to a 2 g sample in a 250 ml Erlenmeyer flask in the titration procedure. For a no fizz rating, 20 ml of the 0.1N HCl should be added, for a slight fizz, 40 ml of 0.1N HCl should be added, a moderate fizz would require 40 ml of 0.5N HCl to be added and a strong fizz, 80 ml of 0.5N HCl (Jambor, *et al*., 2006).

Although in this work the net neutralisation potential was not determined by titration, the test was nevertheless carried out because it is widely used and accepted as being a reliable way of checking the acid consuming potential relative to the acid producing potential of a given sample. It is very useful in determining the maximum amount of neutralisation and acid producing potential available in a sample. The method is relatively cheap, rapid and easy to perform. The method is also advantageous for use in screening a large number of samples for further selective and more detailed evaluation. It should also be noted that some samples with no carbonate minerals observed during XRD analysis also gave off a fizzy reaction when the HCL was added. This means that, for the purpose of studies such as the current study, the use of the fizz test as a means of quantifying neutralising capacity for samples may not be useful since acid-volatile material may also be present. Morse and Rickard (2004) regard volatile sulphides as a group of metastable iron sulphide minerals and dissolved sulphur species that, when exposed to HCl, form H2S, which can then be collected and analysed. The presence of such material would also lead to the over-quantification of the acid-generating/neutralising potential of a given sample.

For the fizz test (in the current study), about 2 g of samples was placed on aluminium foil, 6N hydrochloric acid was then added to each sample. Fizz ratings ranging from "None", "Slight", "Moderate" then "Strong" were observed and taken as an indication of the presence of carbonate minerals. A summary of the fizz test ratings for the respective samples is provided in Appendix A.

# **3.7. Analysis with Inductively Coupled Plasma- Optical Emission Spectroscopy (ICP-OES)**

Inductively coupled plasma/optical emission spectroscopy (ICP/OES) is a powerful tool used in the determination of trace elements in a variety of samples (Hou and Jones, 2000). The advantages of using the ICP over other analytical methods originate from its capability for efficient and reproducible simultaneous multi-element analysis via atomisation (in a nebuliser), excitation and ionisation (in an inductively coupled plasma torch) for a wide range of elements in various sample matrices. The high temperature (6000-7000 K) in the observation zone of the ICP makes it possible for the instrument to excite refractory elements whilst also making the ICP less prone to matrix interferences than for instance, atomic absorption spectrometry. The ICP is also an electrode-less source, meaning there is no contamination from impurities present in an electrode material (Ghosh *et al.*, 2013).

The analytical part of the ICP-OES instrumentation is optical and electronical. Photons emitted by the ICP are collected by a lens. The focusing optic forms an image of the ICP on the entrance slit aperture of a spectrometer containing a number of gratings. Arrays of charge-coupled devices (CCD's) convert the signals for each wavelength to electrical signals. These signals are amplified and processed by the detector electronics, after which the data is then displayed and stored by a computer (Hou and Jones, 2000).

The stock solutions of standards used for various elements analysed were commercially available solutions with concentrations very close to 10,000 mg/L (10 031 mg/L total sulphur, 10 000 mg/L magnesium, 10 025 mg/L calcium, 10 000 mg/L potassium, 10 000 mg/L iron and 10 000 mg/L sodium). From these, working standards were prepared by appropriate dilution (Kalenga *et al.*, 2011).

The elements analysed for this study were Ca, Fe, K, Mg, Na and S. Based on published concentrations of the elements of interest in coal and the dilution of the coal leaches, three mixed standard solutions of 4% HNO<sup>3</sup> were prepared, expected to cover the whole concentration range of sample solutions. The concentrations of these elements of concern are listed in Table 2. Concentrations listed are reported in  $\mu$ g/g or ppm. The nitric acid (65% HNO<sub>3</sub>) used in the preparation of the standards was of suprapur grade.

Analysis with ICP-OES was found to be easy and quick to use since a large number of samples could be analysed within a short space of time. The machine is automated and can be programmed to analyse the samples without having continuous physical contact with the samples. This limits contamination 1ANNEDDUKU and also saves time.



Table 2 Mixed standard solutions with concentrations of elements of concern to be analysed with the ICP-OES



## **3.7.1. Sample preparation for analysis with ICP-OES**

#### 3.7.1.1. Laboratory apparatus used

- i) Glass beakers
- ii) Aluminium foil
- iii) Funnels
- iv) Filter paper
- v) Erlenmeyer flasks
- vi) Hand-held pipette
- vii) Hot plate with adjustable temperature settings

#### *3.7.1.2. Reagents*

- i) 2 HCl:  $3 H<sub>2</sub>O$  acid solution  $(4.8 N)$
- ii) 1 HNO<sub>3</sub>: 7 H<sub>2</sub>O acid solution  $(2N)$

(All acid used for sample preparation was of analytical grade)

iii) Deionised water

A sequential leaching by first hydrochloric acid and then nitric acid was used as this method conforms to the leaching used in the traditional ABA method. Further, according to Mketo, *et al*., (2016), this would yield a combined recovery rate of close to about 100% for sulphur extraction in coal. Sulphide sulphur is the element of concern since, according to Eby (2004), sulphide oxidation leads to the production of acidic drainage in mine waters.

# **3.7.2. Sample preparation method**

- 1) 1 g of each sample was weighed in (see Appendix B)
- 2) The samples were placed on filter paper in a funnel and leached with 4.8N HCl in order to leach out the sulphate sulphur component as well as carbonates; the leachate was collected in a glass beaker. The amount of acid added to the different samples was hence variable since some samples required a larger volume of acid to be completely wet (see Appendix B)
- 3) The HCl solution was then washed off by adding deionised water to the samples and allowing it to filter through to the glass beaker as well.
- 4) The wet samples were then washed into an Erlenmeyer flask with  $2N HNO<sub>3</sub>$  acid solution. The amount required to wash off the samples into Erlenmeyer flask was also variable since some

samples needed a larger volume of acid in order to be washed off completely. The amount of nitric acid and hydrochloric acid used during the procedures was recorded.

- 5) The samples were allowed to stand overnight in the nitric acid. This was done to allow the sulphide sulphur content of the samples to be fully leached out. These samples were then filtered into a glass beaker to collect the leachate which would be analysed for sulphide sulphur and iron content. The leachates were diluted to 100 ml of 5% nitric acid solution and stored in polyethylene bottles.
- 6) The contents in the glass beakers with the hydrochloric acid were allowed to evaporate to dryness. 2 ml of the nitric acid solution was then added to the precipitates and evaporated again; this was done so as to convert the chlorides to nitrates. When the acid had evaporated and formed a precipitate at the bottom, 10 ml of the nitric acid solution was then added to dissolve the contents. This was then diluted to 100 ml of 5% nitric acid solution and stored in polyethylene bottles.

For analysis, 2 ml of the stored sample solutions were diluted to 10 ml of 2.5% HNO<sub>3</sub> solution in polycarbonate tubes

The calcium and magnesium contents of the first leach (HCl) were used as a proxy for the carbonate content (and therefore the neutralisation potential) whereas the sulphur and iron contents of the second (HNO3) leach were compared; in principle both could be used as proxies for the pyrite and marcasite content and thus for the acid-generating potential. However, frequent and interesting discrepancies were found, which are discussed in Section 3.8.2. FRSITY

# **3.8. ARD generation/neutralisation potential**

The iron sulphide minerals, pyrite and pyrrhotite, are most commonly associated with ARD formation. Oxidation of these minerals releases  $SO_4^2$ ,  $Fe^{2+}$ , and H<sup>+</sup> (Nordstrom, *et al.*, 2015). Since iron is considered an important component of acidic drainage, the iron content was also taken as an indicator of the amount of pyrite that was present in the sample. Pyrite was the dominant iron-containing mineral in the samples from analysis with XRD. The mineral pyrite contains Fe:S in the ratio 1:2. This means that, since sulphur is available as sulphide, sulphate and organic and native sulphur in the samples, the iron can be taken as a clear indicator of the amount of sulphide sulphur during the sulphur extraction procedures. This ratio of Fe:S therefore needs to be taken into account when considering the sulphide sulphur content of the samples. Other iron-rich minerals do exist, however, but these have low solubility rates and are not involved in acid-generating reactions.

Leachates B, obtained by adding nitric acid  $(HNO<sub>3</sub>)$  to the residue, were used for acid-producing  $(AP)$ categorisation of the samples. This is because the nitric acid leaches out the sulphide sulphur from the samples. Hydrochloric acid (HCl) was, however, added first to the sample in order to remove the sulphate sulphur constituent. The HCl also dissolves the carbonates from the samples, and since the carbonates under consideration (calcite and dolomite) are readily-dissolving (Azzie, 2002), the Mg and Ca contents of leachate A were used to determine the carbonate content instead of using a titration method. The iron and sulphide contents determined in leachates B were compared, whereby it was mostly found that the amount of sulphur exceeded the stoichiometry of pyrite  $(F \epsilon S_2)$ . This is discussed below in section 3.8.1. On the other hand, iron content may also be derived from the mineral siderite, and since Azzie (2002) mentions siderite as a slower dissolving carbonate mineral, this siderite-derived iron may occur in leachates B as well. In such cases the acid producing potential would be overestimated, and the neutralisation potential underestimated. Therefore, mineral assemblage as found from XRD analysis should also be taken into consideration.

Blowes *et al*., (2005) states calcium, magnesium, manganese, and iron (amongst others) as elements that are released during the dissolution of carbonates in acidic water, so these elements were chosen for analysis with the ICP-OES. Probable sources, from the minerals observed using XRD analysis, of the elements released during carbonate dissolution are calcite (calcium), dolomite (calcium and magnesium), siderite (iron).

After the easily-dissolving carbonate minerals are depleted, the pH of the solution falls until an equilibrium level is reached where the most soluble secondary hydroxide mineral is attained. During the dissolution of carbonate and hydroxide minerals, aluminosilicate minerals may also dissolve. Even though the dissolution of aluminosilicates is generally not rapid enough to buffer contaminated water to a specific pH, these reactions consume H<sup>+</sup> and, therefore, contribute to the overall acid-neutralisation potential of the rock material (Blowes *et al*., 2005). The aluminosilicates can therefore act as neutralising agents in ARD-rich environment. This deduction means that the true, or field, neutralising capacity can be underestimated if only the carbonate minerals are taken as the neutralising constituents (Mills, 1997). As has been reported by INAP (2009), minerals that were found from XRD analysis of the coal samples, which had neutralising potential include goethite, K-feldspar, albite, muscovite, and apatite. The study also takes the Na, K, Ca content of the leachates into consideration, as a means of accounting for these minerals.

# **3.8.1. Calculation of Acid Producing Potential (AP) and Neutralizing Potential (NP) from the analytical results.**

AP and NP are traditionally both expressed as kg  $CaCO<sub>3</sub>$  per tonne of coal or rock, which makes it easy to assess Net Neutralization Potential (NNP) as the difference between NP and AP.

From the summarised reaction for the oxidation of pyrite (Section 2.6.1.2):

 $4FeS_2 + 15O_2 + 14H_2O = 16H^+ + 8SO_4^2 + 4Fe(OH)_3$ 

or

$$
FeS_2 + 15/4O_2 + 7/2H_2O = Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \tag{1}
$$

2 moles of sulphur yield 4 moles of  $H^+$ . The ratio of S: $H^+$  is 1:2

And from the reactions:

$$
CaCO3 + 2H+ = Ca2+ + CO2 + H2O and
$$
  
\n
$$
CaMg(CO3)2 + 4H+ = Ca2+ + Mg2+ + 2CO2 + 2H2O
$$
\n(2)

1 mole of calcium or magnesium in carbonate neutralises 2 moles of H<sup>+</sup> .

This then means that acid generated by 1 mole of sulphur is neutralised by 1 mole of calcium or magnesium in calcite or dolomite. In the calculations below to derive the NNP, magnesium is not considered, nor is iron in siderite. The latter mineral was not detected as a major constituent by XRD and is likely to make only a minor contribution since it is a slow reactant in neutralisation (Azzie, 2002). While dolomite was detected by XRD in some samples, Mg/Ca ratios (by weight %, see Tables 7, 9 and 11) were generally found to be much smaller than the value given by stoichiometry of dolomite (0.606) and do not correlate at all with Ca content. Thus, the amount of dolomite is generally small. Further, it cannot be assessed from Mg contents of leaches, since Mg is also leached from other minerals such as clays. The neutralization potential derived as described below based on calcium in leaches A is therefore a conservative estimate.

Mass of sulphur =  $(32.065g$ .mol<sup>-1</sup> \* 1 mol = 32.065g)

Mass of Calcium carbonate =  $(100.0869g/mol^{-1} * 1mol = 100.0869)$ 

By mass, 1g of sulphur needs 3.12g of calcium carbonate to be neutralised, which is why for Maximum Acid-generating potential of sulphur, the sulphur is traditionally multiplied by a factor of 31.2

It was observed (see above and Section 3.8.2) that the amount of sulphur in the  $HNO<sub>3</sub>$  leach generally exceeds that expected from the stoichiometry of  $FeS<sub>2</sub>$  and  $Fe$  content in that leach by a variable amount. Clearly a significant amount of S located in the organic fraction of the coal is also leached out by HNO<sub>3</sub>, but this does not contribute to the AP. Thus, it appeared far more logical to use the Fe content as a proxy for pyrite and marcasite than S.

From equation (1), 1 mole of iron produces 4 moles of  $H^+$ , and from equation (2), 2 moles of  $H^+$  are neutralised by 1 mole of calcium or magnesium in calcite or dolomite. This then means that 2 moles of CaCO<sub>3</sub> are needed to neutralise 1 mole of Fe.

Therefore, 1 mole of Fe (is neutralised by) 2 moles of  $CaCO<sub>3</sub>$ .

Mass of iron =  $(55.845g$ .mol<sup>-1</sup> \* 1mol =  $55.845g$ )

Mass of calcium carbonate required to counter the iron =  $(100.0869g$ .mol<sup>-1</sup> \* 2mol = 200.1738g)

By mass, 1g of Fe is neutralised by 3.58g of CaCO<sub>3</sub>.

In this instance, to get Maximum Acid-generating potential by iron, Fe% is multiplied by 35.8. This is the Fe content from leachate B in which the pyritic sulphur was also leached.

From equation (2), 1 mole CaCO<sub>3</sub> contains 1 mole Ca<sup>2+</sup>

Mass of CaCO<sub>3</sub> = (100.0869g.mol<sup>-1</sup> \* 1mol = 100.0869g)

Mass of Ca<sup>2+</sup> from the calcium carbonate =  $(40.078g$  mol<sup>-1</sup> \* 1mol =  $40.078g$ )

1g of  $Ca^{2+}$  corresponds to 2.497g of  $CaCO<sub>3</sub>$ . This means that for the Maximum acid-neutralisation potential, as taken from considering calcium should be Ca%\*24.97. This is the Ca content from leachate A (HCl) in which the calcium carbonate is dissolved.

The samples were classified using the sulphur content (sulphide sulphur content), Net Neutralisation Potential (NNP), and Net Neutralisation Potential Ratio (NPR).

A cut-off of 0.3% was taken for the classification using the %S, as suggested by Price *et al*., (1997). This cut-off was found to be appropriate for most geological conditions.

Guidelines from Price et al. (1997) and *Soregaroli and Lawrence (1997)						
Sulphide sulphur	NP <b>NPR</b> (Bulk) (SAP)	Potential for <b>ARD</b>	Comments <b>NESBURG</b>			
$< 0.3\%$		None	No further ARD testing required provided there are no other metal leaching concerns. <i>Exceptions</i> : host rock with no basic minerals, sulphide minerals that are weakly acid soluble.			
$>0.3\%$	$<$ 1	Likely	Likely to be ARD generating.			
	$1-2$	Possibly	Possibly ARD generating if NP is insufficiently reactive or is depleted at a rate faster than that of sulphides.			
	$2 - 4$	Low	Not potentially ARD generating unless significant preferential exposure of sulphides occur along fractures or extremely reactive sulphides are present together with insufficiently reactive NP.			

Table 3 ARD Assessment guidelines



The classification using NPR was based on guidelines from Price *et al*., (1997). Values of NPR (NP:AP) <1 would indicate a likely ARD generation potential (PAG); values 1<NPR<2 would reflect an uncertain ARD generating potential if NP is insufficiently reactive or is depleted at a faster rate than sulphides; values 2<NPR<4 would reflect a low ARD generation potential unless there was significant preferential exposure of sulphides along fracture planes or extremely reactive sulphides with insufficiently reactive. Lastly, values of NPR>4 would indicate no ARD generation potential. A summary of the aforementioned is shown in Table 3.

For the classification using the Net Neutralisation Potential (NNP) there are two schemes. Following Fey (2003) a material would be considered to be non-acid producing if NNP> 20 kg/ton CaCO<sub>3</sub>. NNP< -20 kg/ton CaCO<sup>3</sup> means that the material is acid producing and material with -20<NNP<20 kg/ton CaCO<sup>3</sup> would have an uncertain acid producing capacity and kinetic tests might need to be carried out in order to confirm the acid producing/neutralising capacity of that material. On the other hand, Golder (2015) classified samples with NNP> 10 kg/ton  $CaCO<sub>3</sub>$  as non-acid producing, samples with - $10\le NNP < 10$  kg/ton CaCO<sub>3</sub> as having uncertain acid producing capacity and samples with NNP<-10  $kg/ton$  CaCO<sub>3</sub> as potentially acid generating. For the purpose of classification in this study, the classification used by Golder (2015) for NNP was used.

# **3.8.2. Analysis of Certified Reference Material (SARM 18)**

As a means of verifying the method described in Section 3.7, a coal sample used as Certified Reference Material (SARM 18) was co-analysed with the samples. The Certified Reference Material was obtained from Mintek (RSA) and was described as high-volatile, low rank bituminous coal which could be classified as vitrinite.

<b>Constituents</b>	$Ca\%$	Fe $%$	$K\%$	$Mg\%$	Na %	$S\%$
CRM A (from ICP-OES analysis)	0.0943	0.0325	0.0093	0.0203	0.0251	0.0377
<b>CRM B (from ICP-OES analysis)</b>	0.00694	0.0192	0.0028	0.0026	0.0026	0.0190
<b>Total for measured values</b>	0.1012	0.0517	0.0120	0.0229	0.0277	0.0568
<b>CRM (MINTEK values)</b>	0.1286	0.1014	0.0601	0.0663	0.013	0.0568
<b>Percentage Recovery</b>	78.68	50.98	19.97	34.54	(213)	100.0

Table 4 Analysis (OES) of the elements of interest in CRM SARM 18 coal, and recovery rates

Percentage recovery for the elements of interest in the CRM material were analysed (Table 4). Elements of interest include calcium (Ca), potassium (K), magnesium (Mg) and sodium (Na) for NP and iron (Fe) and sulphur (S) for the AP of the sample. The combined leaches yielded 100% recovery of S from this sample. This is in accord with Mketo, *et al*., (2016) who cited the pair of HNO3/HCl as having a high recovery rate (>95%) for targeted sulphur species. It should further be noted that values reported by MINTEK are total concentrations of the elements of interest. In contrast, the leaching method is expected to access only calcium from calcite and dolomite, magnesium from dolomite, sulphur from sulphates and sulphides, iron from pyrite and siderite, and potassium and sodium from sulphates and other salts. The S/Fe ratio of leach A converts to an atomic ratio of 2.018, conforming closely to the stoichiometry of pyrite (or marcasite), while that of leach B yields a lower atomic ratio (1.72) suggesting that Fe is also leached from another source. The leaching of pyrite or marcasite in leach A is unexpected and as sample analyses have shown (described in chapters below) is by no means the rule. The low overall recovery of Fe, K and Mg probably reflects a high proportion of these elements residing in silicate minerals. The large amount of Na recovered in leach A remains unexplained and could be due to contamination. This needs to be further investigated but is not a great concern in this study, since Na is not a component of important neutralizing phases.

The results of the leach ABA analyses on SARM 18 are shown in Table 4. It can be observed that this CRM has an uncertain potential to generate acidity when classified using the NNP; is low-PAG when the NPR (NPR<4) and non-PAG when the sulphur content (%S<0.3%) is considered.

<b>Sample</b>	S(%)	Ca (%)	Fe $(\%)$	AP	<b>NP</b>	<b>NPR</b>	<b>NNP</b>	<b>Classification</b>	<b>Classification</b>
				(using	(using			using Price et	using NNP
			ا ب	$Fe\%$	$Ca\%$		SBURG	al., (1997)	
<b>CRM A</b>	0.0377	0.094	0.0325	0.69	2.35	3.41	1.66	Non-PAG	Uncertain
CRM B	0.0190	0.007	0.0192						

Table 5: Acid producing/neutralising potential of CRM SARM 18 coal reference material.

NH

The CRM classifies as Non-PAG according to guidelines provided by Price *et al*., (1997). Since Acid-Base Accounting is a measure of how the acid-producing minerals compare to acid-consuming minerals in order to determine whether the material would be acid-generating or non-acid generating based on this balance (Plumlee *et al*., 1999), it is favourable that the recovery of the elements found in the minerals that are most likely to influence acid-generating and acid-consuming procedures was almost the same. Calcite (source of the calcium in leachate A) is recovered much more than the iron since ironcontaining compounds are less readily-dissolved during contact with acid during the leaching process. The method highlighted in this study for the leaching of sulphur species can then be taken to be valuable when it comes to determining the acid-generating versus acid-consuming potential of materials.

Lawrence and Wang (1996) have noted that using static tests (ABA is an example) can have many misinterpretations and related complications. This can occur even when the tests are carried out under very carefully controlled conditions. The most ideal situation would be to carry out the tests on many samples so that detailed care and attention are not given to individual samples. The largest discrepancies are related to the assessment of the neutralising potential of samples. The discrepancies arise due to mineralogical factors e.g. low carbonate content minerals will record high neutralisation potentials when very acidic digestions are utilised as part of the ABA procedure. Under such conditions, even minerals that would normally be insoluble (silicates) can dissolve and contribute to the NP of the sample. Under environmental conditions, such acidic conditions are unlikely to be encountered and effective NP values will be much lower.

# **4. Results and findings**

The results of the desk top study conducted for the groundwater risk assessment map of the eMalahleni coalfield and of the two case studies conducted in that coalfield as part of this work are presented and discussed in sections 4.1 and 4.2. The results of the case study in the South Rand coalfield are presented and discussed in section 4.3.

# **4.1. eMalahleni coalfield**

## **4.1.1. Groundwater risk assessment map for the eMalahleni coalfield**

The results of the desktop study for the groundwater risk assessment map of the eMalahleni coalfield are summarized in Appendix D. Figure 9 shows the risk assessment map as a schematic representation of these results, whereby the risk is classified in five categories. These categories are:

- Potential for acid-generation (PAG)- %S (Sulphide Sulphur)  $> 0.3$ %; the mineralogy of samples analysed from the mine was such that acidic drainage would be likely to be produced and the drainage would not be neutralised sufficiently; the mine had been reported in previous reports as having potential for acid generation.
- Potentially acid generating with Neutralisation potential: even though there is a potential for acidic drainage production there is enough neutralising capacity to counteract the acid produced.
- Uncertain: the sulphide content was not clearly stated; the mineralogical content of the samples was not well defined; ABA results are not available, or the acid generating/neutralising potential of the mine was not clearly defined.
- No potential for acid generation (No PAG): there was no evidence of acid-generating minerals in the sample analyses conducted, or there was enough neutralising capacity to counteract any acidic drainage that might be produced. The geology of the mined area or the mineralogical

composition of samples from the mine showed no evidence of minerals that had a potential to generate acidity.

 No data- there was no data found related to the mine that could be used for the purpose of the classification





Figure 9 A groundwater risk assessment map for coal mines in the eMalahleni coalfield (Modified from Barker 2014).

# **4.1.2. Summary of the findings**

- The majority of the coal mines in the eMalahleni coalfield were found to be potentially acid generating (PAG).
- Pyrite  $(F \in S_2)$  was found to be the main acid-producing mineral in the coalfield and the neutralising potential was provided mainly by calcite/aragonite (CaCO<sub>3</sub>) and dolomite  $(CaMg(CO<sub>3</sub>)<sub>2</sub>).$
- The south-western margin of the coalfield was found to have little or no acid-producing potential and this was attributed to the coal mineralogy of the area and the availability of sufficient neutralisation to counteract any acid that may be produced.
- Minerals containing sulphide sulphur were taken to be potentially acid-generating. Even though neutralising minerals were found in some of the samples analysed from the different mines, they were not always available in sufficient amounts to neutralise acidic drainage produced.
- Mineralogy was found to be very important in the determination of whether a mine would be considered to be having potentially acid generating/neutralising characteristics. Combination of the mineralogy and the ABA data was found to be the most reliable way of classifying the different coal mines for probable acid generation/neutralisation potential.

Overall, the findings confirm those of Azzie (2002) (see section 2.7.1.2) and are in accord with those published by Pinetown and Boer (2004), where they classified the coal of the eMalahleni coalfield as having acid-generating potential. This coincides with the findings as reported by Pinetown et al. (2007) where the AP>NP in coals of the Witbank coalfield, and the NNP (in a closed system)  $\langle$ -10 kg/t CaCO<sub>3</sub>. It is noted from Appendix D that there is no apparent correlation between which seams are being mined, or which mining method is used, and the acid-generating or neutralising potential of a given mine.

# **4.2. Case studies from the eMalahleni coalfield**

The Inyanda and Khutala coal mines were selected from the eMalahleni coalfield as subjects for case studies. The Khutala coal mine is situated centrally within the eMalahleni coalfield and the Inyanda coal mine lies just on the north-eastern periphery of the coalfield.

#### **4.2.1. Inyanda coal mine**

#### *4.2.1.1. Location of study area*

Inyanda coal mine (Figure 10) is situated approximately 14 km north of eMalahleni and about 46 km west of Middelburg in the Mpumalanga Province. The mine was an open pit operation situated on Portion 21 of the Kalbasfontein 284 JS farm (Golder, 2013; Exxaro, 2015).

#### *4.2.1.2. Description of the geology of the study area*

The Inyanda Mine area lies within the eMalahleni coalfield, and the local geology comprises sediments of the Dwyka Group and the Vryheid Formation of the Ecca Group, all of which form part of the Karoo Supergroup. The coal seam topography and distribution is controlled by pre-Karoo topography, as well as the present-day surface topography due to erosion, leading to Seam 3, Seam 4 and Seam 5 being absent in the area. The average thicknesses of Seam 1 and Seam 2 were statistically determined as 4.7 m and 2.3 m respectively (Groundwater Square, 2014).

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Two economic seams occur at the Inyanda coal mine, the bottom coal seam being known as Inyanda No. 1 seam and the top coal seam as Inyanda No. 2 seam (Exxaro, 2015) (Figure 11), and these seams are separated by a feldspathic sandstone unit that varies in thickness from 0 to about 2 m. Even though Inyanda coal has previously been interpreted to result from diachronous sedimentation and was therefore considered to be an outlier of the main Witbank Basin, the Inyanda coal seams has recently been correlated to Seam 2 of the Witbank Basin using palynological analyses (Golder, 2015).

The coal seams are characterised by mainly dull coal that contains few bright laminae. The sub-outcrop is defined by weathering and erosion that has resulted in the top coal seam (Seam 2) occurring over a smaller area than the bottom seam (Seam 1). The area between the sub-outcrops of the top and bottom coal seams also contained some clay as the overburden (Exxaro, 2015).



Figure 10: Map showing location of Inyanda coal mine. Modified from Golder (2015)

The coal seams of the Inyanda coal mine form part of the Vryheid Formation (Golder, 2013). The coal bearing strata are underlain by shale and tillite of the Dwyka Group, as well as sandstone, shale and conglomerate of the Ecca Group.  $RSI$ Н.

The Inyanda coal mine consists of the Kalbasfontein Pit and the Pegasus South Pit. The Inyanda 1 and Inyanda 2 coal seams were mined at the Kalbasfontein Pit and Pegasus South Pit using the conventional truck and shovel mining method even though a large part of the Kalbasfontein pit was backfilled and rehabilitated already in the year 2015 (Golder, 2015). The two coal seams were mined separately across the deposit (Exxaro, 2015), with the mining carried out consecutively in strips from the east to the west, starting at the southern boundary moving towards the northern boundary of the ore body (Golder, 2013).





The coal occurs in two areas in the farm Kalbasfontein 284 JS. The southern area contained the majority of the coal reserves and the northern area overlaps the Kalbasfontein and neighbouring Geluk boundary. No coal occurs between the two areas. The No. 1 and No. 2 coal seams are both well developed in the southern area. The coal seams were found to be nearly horizontal with a gentle dip in a southerly direction. Structural disturbances such as folds and faults have not been encountered in the area. The only disturbance is by a sill, confirmed from airborne magnetic data and intersected in boreholes below the diamictite of the Dwyka Group. The sill is confined to the southern area and has had no negative effect on the volatile content of the coal (Exxaro, 2015).

The Pegasus North Pit is adjacent to and located to the north of the Pegasus South Pit of the Inyanda coal mine (Figure 14). The two pits are divided by a farm boundary, meaning that the geological character of Pegasus North Pit can be correlated between the pits.

# *4.2.1.3. Previous studies*

Since the Pegasus South Pit lies adjacent to Pegasus North Pit, separated by a farm boundary (Figure 14), the geology of the Pegasus North Pit, as described by Groundwater Square (2014), was found to be similar to the geology as observed in the Pegasus South Pit. The geochemical character of the rocks found in the two pits can therefore be assumed to be similar in character, and the outcomes of the study conducted on the Pegasus North Pit can therefore be considered valid for the Pegasus South pit also.

From geochemical analyses and interpretation conducted by Groundwater Square (2014) on 18 samples from Pegasus North Pit (6 sandstone samples, 7 shale samples and 5 coal samples), it was found that:

- Almost all of the sandstone samples (4 out of 6) had a %S higher than 0.3%. The neutralisation potential of the samples was also found to be very low. About 50% of the sandstone samples were found to have the potential to generate acidic drainage in the long term with a high salt load in the drainage.
- The shale samples had a low %S with only 2 out of the 7 samples having a %S that was higher than 0.3%. The shale samples were, however, found to have a very low neutralisation potential and were quantified as being likely to generate acidic drainage. Approximately 30% of the shale samples had a significant potential to generate long-term acidic drainage with a high salt load in the drainage.
- The 5 coal samples all had very high %S of above 1% and had null to very low neutralisation potential. The Acid Base Accounting (ABA) and net acid generation (NAG) results showed that the coal samples had a high potential of generating long-term acidic drainage.
- In summary, it was concluded that all the samples had significant potential to generate acidic drainage and those samples that did not produce any acidity had no potential to neutralise acidity form the other rocks.

A geochemical study conducted by Golder (2015) on discard, pit backfill and pit shell materials from the co-disposal facility, and other samples from the Kalbasfontein and Pegasus South pits at the Inyanda coal mine showed that:

- The total sulphur content of the fine discard material was 1.1%. The coarse discard material had a higher sulphur content ranging from 3.6- 3.8%. The fine discard material had equal proportions of sulphide and sulphate sulphur whereas the sulphur was mainly sulphide sulphur in the coarse discard material.
- The fine and coarse discard material from the co-disposal facility was considered to be acid generating per the guidelines of Morin and Hutt (2007) and MEND (2009). Classification using the guidelines of Price *et al*. (1997) and Soregaroli and Lawrence (1997) also showed that the fine and discard samples were likely to be acid generating.
- Backfill and pit shell samples from the Kalbasfontein pit at Inyanda were characterised by low sulphur content, with values of 0.11% and 0.07% respectively.
- Sulphur content of the backfill and pit shell samples from the Pegasus South pit were very low and consisted mainly of sulphide sulphur. Sulphur content of the backfill material was 0.07% and the pit shell samples had sulphur content of 0.05%.
- Classification of the ARD potential of the samples showed that the backfill and pit shell samples from the Kalbasfontein and Pegasus South pits were acid generating per the guidelines of Morin and Hutt (2007) and MEND (2009). Classification using the guidelines from Price *et al*. (1997) and Soregaroli and Lawrence (1997) showed that the samples had no acid generating potential due to the low total sulphur content. Total sulphur was used in the classification since it was considered to be conservative.
- Inyanda pit shell and backfill ABA results were found to be within the ranges of the Pegasus North ABA results.

## *4.2.1.4. Sample collection and analysis*

The samples were collected from the Slurry Paddocks and the fine and coarse discard stockpile at Inyanda coal mine (Figure 12) and also from both the Kalbasfontein Pit and Pegasus South Pit (Figure 13). Mining activity at the Pegasus South Pit was still at an early stage when the samples were collected, and no part of the pit had been backfilled. Coal samples were collected from Seam 1 and Seam 2 of the Pegasus South Pit (Figure 15) and also rock types that would eventually constitute backfill material i.e. sandstone, carbonaceous and non-carbonaceous clay, carbonaceous clay and shale (can be observed in Figure 16). The Kalbasfontein Pit was still operational at the time of sample collection, but the coal seams were nearing complete extraction and the pit was almost completely filled with backfill material apart from the small pit in which mining activity was still taking place.

The collected samples were then analysed at the Spectrum laboratory at the University of Johannesburg. Analysis was carried out using XRD- for mineral identification in the samples; and a combination of Acid Base Accounting procedures using analysis by ICP-OES as described in section 3.7 as a means of predicting the samples' potential for acid generation.

## *4.2.1.5. Sample compositing at Inyanda coal mine*

The compacted coarse discard samples from the slurry paddocks were composited to sample INYCO1 and the uncompacted coarse discard samples into sample INYCO2. INYCO4 is a composite sample consisting of Kalbasfontein backfill material. Discrete samples used for compositing are INY36, INY37, INY38 and INY39 (Figure 13) and the INYCO6 composite sample consists of Pegasus South backfill material with samples used for compositing are INY41, INY45, INY46 and INY47 (Figure 13).



Figure 12 Sample location points at the co-disposal and slurry paddocks facility of the Inyanda coal mine. Adopted from Golder (2015)



Figure 13: Sample location points at the Inyanda coal mine. Adopted from Golder (2015)



Figure 14 Location of Pegasus North Pit in relation to Pegasus South and Kalbasfontein Pits at Inyanda coal mine. The image is used as schematic presentation for the relative location of Pegasus South to Pegasus North Pit. Adopted from Golder (2015)



Figure 15: Inyanda Seam 1 and Seam 2 during mining at Pegasus South Pit



Figure 16: Pegasus South Pit during mining. Seam floor for Inyanda Seam 1 can be observed







# *4.2.1.6. Summary of mineralogy*

Dominant minerals found in the coal were quartz and kaolinite (Table 6). Potassium feldspar, nacrite, gypsum and brushite were also found as accessory minerals. The mineral pyrite was found in the coarse discards (un-compacted and compacted). No neutralising minerals were found in the coal, meaning that any acidity that may form has a low likelihood of being neutralised.

Quartz, kaolinite and muscovite were the dominant minerals found in the backfill material. Acidgenerating sulphide minerals and acid-neutralising carbonate minerals were not detected in the backfill material. The other rock types analysed from the area, which were likely to end up being part of the backfill material, also did not contain any acid-generating minerals at detectable levels, and the potentially acid-neutralising minerals found had low solubility rates.

Calcite and dolomite were not detected in any of the samples, even in the backfill material from the Pegasus and the Kalbasfontein pits. If the pyrite from the discard material were to oxidise and form acidic drainage, there would not be enough neutralising material from the mine to counteract the acid production. This could be detrimental in the future; especially if the coal is not completely recovered from the pits since no neutralising minerals were observed in the backfill material.

Noting that the detection limit of the XRD analysis method used is 3-5 weight % (see Section 3.5.), it should be borne in mind that this method can only detect acid generation or neutralizing potential in cases where the values are very high.

Table 7: Inyanda coal mine ABA analysis using ICP-OES





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#### *4.2.1.7. Summary of ABA results and acid generating potential*

A comparison of the results of the two classification schemes shows considerable consistency. The coarse discard samples (INYCO1 and INYCO2) classified as PAG in both classification schemes, whereas all other samples are non-PAG when classifying guidelines as provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997).

Backfill material from the Kalbasfontein Pit (sample INYC04) was found to be uncertain using NNP, and Non-PAG when using the NPR value, as per the classification guidelines from Price *et al*., 1997. The Pegasus South backfill material was also found to be unlikely to generate acidity. Low sulphur values, and the absence of acid-generating sulphide minerals are strong indications for this. Golder (2015) had reported low acid-generating likelihood when classifying using guidelines as reported by Price *et al.*, 1997. Figure 17 shows the classification of the samples using the %Sulphide- Sulphur vs Sulphide-NPR. It can be observed that a majority of samples collected are not likely to generate acidity, with the exception of coal coarse discard samples, which classified as having likely acid generating potential.



Figure 17: Graph showing results for %S vs SNPR for Inyanda coal mine samples

## **4.2.2. Khutala coal mine**

## *4.2.2.1. Location of study area*

The Khutala coal mine was located in the eMalahleni coalfield, some 55 km to the south west of eMalahleni and approximately 100 km to the east of Johannesburg (Figure 18) (Repinga, 2010). The operation comprises both underground (using the bord and pillar method) and surface mining sections (Lehasa, 2012).



Figure 18 Location of Khutala coal mine. Modified from Golder (2015)

# *4.2.2.2. Description of the geology of the study area*

The mine is underlain by Pre-Karoo rocks (mainly rocks associated with the Bushveld Complex). The coal is contained mainly in the Vryheid Formation that forms part of the Ecca Group. The Ecca Group is commonly found resting on tillites of the Dwyka Group, on a regional scale. Sandstone, shale, siltstone and coal are the predominant rocks types that are found in the Vryheid Formation at this locality (Golder, 2015).

Even though all 5 coal seams are present in the Khutala coal mine (Figure 19), only the No. 5, No. 4U and No. 2 seams are mined at present. The No. 4L, No. 1 and No. 3 coal seams are considered uneconomic to mine since they are found inconsistently developed, they are too thin, or are of too poor in quality (Golder, 2015).

Interburden and overburden consist of sandstone, carbonaceous shale and mudstone, as well as the unmined coal seams. Structural features that can be observed in the area include dolerite dykes (<2 m thick), sills, faults and a graben that divides the mine into a distinct northern and southern area. The graben is 100 m wide and has been down faulted by up to 20 m (Golder, 2015).





# *4.2.2.3. Previous studies*

Golder (2015) reported on results from studies that had been conducted previously on the Khutala coal mine. From studies conducted by different companies over a 15-year period, it was found that:

- Most of the samples from Seam 2 underground classified as having uncertain acid generating potential.
- Samples from Seam 2 in the opencast area had uncertain or acid-generating potential
- Seam 4 underground samples had an uncertain or acid-generating character
- Seam 4L and Seam 4U from the opencast workings were classified as uncertain or acid generating
- Samples from Seam 3 and Seam 5 of the opencast workings classified as acid-generating
- Other material found in the area, which included spoil material, material from dumps, mudstone, sandstone and carbonaceous shale, was mostly uncertain or acid generating. Spoils material had total sulphur content varying between 0.017% and 8.0% and the discard material had high sulphur content of about 7.8%.

Furthermore, Golder (2015) also reported on Acid Base Accounting tests that were conducted on spoils, coal and discard from the mine facilities in 2015. These are the findings from the analyses that were carried out:

- Spoils and overburden samples from the opencast pit indicated that sulphur was present as sulphide (0.21% to 0.61%), sulphate (0.021% to 0.52%) and organic (0.20% to 0.95%).
- Spoil materials were found to generally have insufficient buffering capacity, with 75% of the samples having (Total Acid-producing potential) TAP exceeding Bulk NP.
- Classification of ARD potential showed that all the spoils samples were acid generating to potentially acid generating as per the guidelines of Morin and Hutt (2007) and MEND (2009).
- Classification of the spoil material using guidelines of Price *et al*., (1997) and Soregaroli and Lawrence (1997) showed the spoils samples to be likely to generate acid.
- The total sulphur in the underground coal samples from the No. 2 and No. 4 Seams consisted of sulphide, sulphate and organic sulphur species.
- Average sulphide sulphur content in the No. 2 Seam  $(0.38\% 1.1\%)$  and No. 4 Seam  $(0.31\% 1.1\%)$ 1.0%) was considered to be generally high and similar in the coal samples. The sulphate sulphur was generally low  $\left($ <0.1%) in coal samples from both seams.
- The bulk NP was found to be higher in coal samples from the No. 2 Seam compared to coal samples from No. 4 Seam. Siderite was found to be the dominant carbonate mineral in the coal samples from both seams, causing the total-carbonate NP to be higher than the effective bulk NP.
- Excessive buffering capacity was found to be present in coal from the underground mine, with the bulk NP exceeding both the (total acid generating potential) TAP and (sulphuric acid generating potential) SAP in all the samples.

Golder (2017) reported that:

 The composite samples from underground mine workings had calcite and dolomite as the most ubiquitous carbonate minerals from the No. 2 and No.4 coal seams. Hence, the neutralisation potential in all the material types from the Khutala coal mine was expected to be provided by calcite and dolomite.

- Sulphide, sulphate and organic sulphur species were found to be present in the coal samples. The sulphide contents in the coal samples from seams No. 2  $(0.38-1.1\%)$  and No. 4  $(0.31-$ 1.0%) was such that high acid potential values were recorded for the coal samples.
- Classification of the ARD potential for coal samples based on the TNPR (Total Neutralisation Potential Ratio) showed that 80% of the coal samples from No.2 Seam and 50% of samples from No. 4 Seam in the underground mine workings classified as having an uncertain acidgenerating potential and the remaining 20% and 50% respectively, was classified as potentially acid generating.
- Classification using the guidelines from MEND (2009) and Morin and Hutt (2007) (paste pH vs NPR) showed that only 30% of the samples from the underground mine workings classified as potentially acid generating (PAG)
- Classification using the guidelines from Soregaroli and Lawrence (1997) and Price *et al*. (1997) (NPR vs %S) showed the samples from the underground mine workings as having low to possibly acid generating potential.
- The acid-generation potential of coal samples was found to be variable and the drainage from the underground mine workings was expected to vary from near-neutral, low metal drainage in the short term to acid rock drainage in the long term.

# *4.2.2.4. Sample collection and analyses*

Samples were collected from Seam 2 (Figure 20) and Seam 4 (Figure 21) where they were being mined in the underground mine workings of the Khutala coal mine. The samples were dominantly coal, and a total of 42 discrete samples were collected from Seam 2 and 34 discrete samples were collected from Seam 4. The samples were spatially distributed across the mining area in order to ensure a proper representation of the coal in the mining area.  $\Box \Box \Box$ 

The collected samples were then analysed at the Spectrum laboratory at the University of Johannesburg, using the same procedures as those used for the Inyanda samples (Section 4.2.1). The results of XRD analyses are summarized in Table 8, and those of the ABA analyses using ICP-OES are given in Table 8.



Figure 20 Khutala Seam 2 sample locations. Adopted from Golder (2015)



Figure 21 Khutala Seam 4 sample locations. Adopted from Golder (2015)



Table 8: Khutala coal mine- Results of XRD analyses.








# *4.2.2.5. Summary of mineralogy*

- The coal contained dominantly quartz (and other silicon oxide polymorphs) and kaolinite (Table 8). Although pyrite occurred in some samples above the detection limit, the presence of calcite and dolomite could indicate that there is enough neutralising potential in the coal to mitigate whatever acidic drainage that may result from the oxidation of pyrite.
- Tridymite  $(SiO<sub>2</sub>)$  was also found in some of the samples. This mineral is a polymorph of quartz, usually found in high-pressure environments where meteorites may have impacted. There is no evidence of any meteorite impact in the eMalahleni coalfield, so the only possibility is that it could have been eroded from elsewhere and is therefore detrital in nature. This is probably the case for minerals like microcline and muscovite as well.
- Acid-neutralising minerals kaolinite, augite, microcline, muscovite and siderite were also observed from XRD analysis. These minerals are not as readily-dissolving as dolomite and calcite but are nonetheless potentially acid-neutralising and can therefore assist in acidneutralising reactions in the long term.

 Accessory minerals were also detected from XRD analysis, with the most common of these being oxide minerals.



Table 9: Khutala coal mine ABA analysis using ICP-OES











#### *4.2.2.6. Summary of ABA results and acid generating potential*

The heterogeneity of the sample population in terms of S, Ca and Fe content, within single seams, is quite remarkable and illustrates the difficulty in assessing whether a coal mine as a whole would be acid-producing or not, in the future.

Of the 42 samples from Underground Seam 2, 9 (21.4%) classified as PAG when using guidelines as provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997). Classification using NNP values yielded 6 of the samples as being PAG. The sulphide sulphur content (from leachates B) was observed below 0.3% in a majority of the samples, which then lead to the classification of the samples as having low to no acid-generating potential. Of the 34 samples from Seam 4, only three were found to be PAG when classification was done using guidelines as provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997), and two of these three samples were found to be PAG when using NNP values. From these data, it appears that Seam 2 has slightly more net potential acid generating capacity than Seam 4.



Figure 22 Graph showing results for %S vs SNPR for Khutala coal mine samples

There is overall a good agreement between the Ca and Fe contents found in leaches A and B of the ABA procedure, and the results of the XRD analyses. From analysis with XRD, pyrite was found with acid-neutralising minerals in the majority of the samples. This could explain the high proportion of samples classified as Non-PAG. Some of the samples that classified as PAG also had acid-neutralising minerals, meaning that even though the potential for acid generation was identified, there was also potential for the acid produced to be neutralised. The agreement between classifications using the three different criteria in this sample set is much better than in the Inyanda samples. This is due to the higher concentrations of all three relevant elements, S, Ca and Fe, which causes the NPR classification, based on the AP:NP ratio rather than the difference, to be significant.

Acid-neutralising minerals such as calcite, dolomite, aragonite, and kaolinite were found to be ubiquitous in the samples from analysis with XRD. The carbonate and aluminosilicate minerals are likely to provide acid-neutralisation in the short and long term, respectively. Figure 22 shows the %S vs SNPR classification of the samples based on the ABA analysis. Most of the samples were found to be Non-PAG, but some still do classify as Low to likely-PAG.



# **4.3. Case study from the South Rand coalfield**

As part of the study, a site was chosen for investigation from the South Rand coalfield. The site forms part of Anglo American's South Rand Heidelberg Project, which is an exploration project for a proposed underground mine. The mine was not operational at the time of sample collection, and the samples were collected form drill core. A summary of the data from the case study is highlighted below:

# **4.3.1. Heidelberg South Rand Underground Mining Project**

## *4.3.1.1. Location of study area*

The Heidelberg South Rand Underground Mining Project is situated approximately 15 km south-west of Heidelberg, and 50 km south-east of Johannesburg (Figure 23) (Golder, 2015).



Figure 23 South Rand Heidelberg location. Modified from Golder 2015

### *4.3.1.2. Description of the geology of the study area*

The study area is wholly underlain by Karoo Supergroup sediments. The local geology comprises of sandstone, with interlayered shale layers and coal layers of the Vryheid Formation (Figure 24) (Golder, 2015). A 100 m thick dolerite sill and intrusive dolerite dykes are found in the central part of the area. (Golder, 2015).

The area falls within the South Rand coalfield. The five coal seams are present within this coalfield, i.e. No.1, No. 2 , No. 3, No. 4 and Ryder Seam, are near-horizontal. In general, the Vryheid Formation in this area comprises mudstone, rhythmite, siltstone and fine- to coarse-grained sandstone. This sandstone was found interlayered with shale (Golder, 2015). The Vryheid Formation stratigraphically overlies the Dwyka Group (Johnson *et al*., 2006).

The South Rand coalfield contains major east-west trending faults with displacements of up to 35 m. Host rocks for the dykes are usually fractured during and after displacement (Golder, 2015)



Figure 24 A generalised stratigraphic column of the study area. Modified from Golder (2015)

### *4.3.1.3. Previous studies on existing mines in the South Rand coalfield*

Static geochemical tests were carried out by Golder Associates in 2006 on 48 samples of waste rock material collected from 10 core boreholes. The drill cores were identified to be composed mainly of clays, carbonaceous shale, mudstone, siltstone and sandstone. The potential for acid generation was evaluated by using the screening criteria as described by Price *et al*. (1997). The following conclusions were reached from the geochemical tests:

- From the static geochemical tests, it was found that the majority of the samples had sulphide sulphur below 0.25%, and the maximum recorded total sulphur content was 3.07%.
- The siltstone, shale and carbonaceous shale were found to be "likely acid generating" due to the higher acid-generating potential (AP) of the material relative to the acid-neutralising potential (NP).
- The sandstone and the coaly shale material were found to be non-acid generating due to the higher NP of the material relative to the AP. The high NP in the coaly shale was attributed to a high carbonate percentage in the samples.
- Classification based on Soregaroli and Lawrence (1997), where the sulphur content and the NPR were taken into consideration, showed that there was generally insufficient sulphide available for ARD although a few samples had a higher %S and would then contribute to localised ARD production during mining (Golder, 2006).

Golder (2015) reported on a geochemical study carried out on underground drill core samples in 2008/2009. Acid Base Accounting procedures were carried out on 14 composite samples of coal and 158 discrete samples of waste rock materials from 19 boreholes. The discrete overburden and interburden samples consisted of dolerite, sandstone, siltstone and sandstone/siltstone. The Acid Base Accounting results showed that:

- The total sulphur content of the coal samples varied between 0.26% and 1.7% and that of the waste rock samples (including the interburden and overburden samples) ranged from 0.001% to 10%.
- Net neutralisation potential of the coal samples varied between 13 kg CaCO $_3$ /ton and 45 kg  $CaCO<sub>3</sub>/ton$  with an average NNP of 32 kg  $CaCO<sub>3</sub>/ton$ .
- The paste pH values  $(6.7 \text{ to } 8.2)$  suggested the availability of sufficient NP to neutralise acidity formed during the test procedure.
- Classification based on Morin and Hutt (2007) and MEND (2009), where the paste pH and neutralisation potential ratio (NPR) were considered, showed that 64% of the coal samples had uncertain ARD potential, 28% were potentially acid generating and the other 7% were not potentially acid generating.
- Classification using Price *et al*. (1997) and Soregaroli and Lawrence (1997), where the sulphur content and NPR were considered, showed that all but one of the coal samples (93%) were potentially to likely acid generating. The differences in classification is related to the differences in the parameters considered during the classification.
- Classification using the sulphur content and NPR of the waste rock samples (mainly siltstone, sandstone and sandstone/siltstone) showed that half of the rock samples were potentially acid generating and the other half had no potential of generating acidity due to the lower sulphur content found in those samples.

Another study reported by Golder (2015) was carried out as part of an Environmental Impact Assessment (EIA). Acid Base Accounting tests were carried out on 48 discrete and composite samples of coal, carbonaceous shale, siltstone, mudstone and sandstone. The ABA results indicated that:

- The total sulphur content of the coal samples varied between 0.04% and 0.38%. For the overburden, parting and roof materials, the sulphur content ranged from 0.03% to 3.1%.
- Classification based on the sulphur content and NPR indicated that 12.5% of the coal samples were potentially to likely acid generating
- Classification based on the paste pH and NPR indicated that all but one of the coal samples were either (potentially acid generating) PAG or had uncertain ARD potential.
- In summary, the previous studies showed that the sulphur distribution in the South Rand Heidelberg Project was highly variable, with lower sulphur values generally recorded in the opencast resources. A significant risk of acid generation was found to be in the underground mine, discard dump and the coal stockpiles.

It should be noted that all previous studies conducted were not in the study area where the current case study is located, part still form part of the South Rand coalfield.

### *4.3.1.4. Sample collection and analyses*

Drill core was collected from the proposed mining area. A detailed core log is given in Appendix E and an overview of the logged core is shown in Figure 25. The samples collected from the drill core include sandstone (different variants of the sandstone), coal, dolerite, mudstone, shale and siltstone. The lithology associated with the coal was assumed to be the material that would eventually form backfill when the coal had been extracted, and this material would then play a major role in the acid producing/neutralising potential of the mine in the future.

The collected samples were then analysed at the Spectrum Analytical Facility at the University of Johannesburg, using the same procedures as for the Iyanda and Khutala mines and as described in Section 3.7. The XRD results are presented together with macroscopic rock descriptions in Table 10, and the results of the ABA analyses are given in Table 11.



Figure 25 Stratigraphic column obtained during core logging at project site

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**ROCK TYPE FIELD/SAMPLE MINERAL CONTENT (from XRD analysis) DESCRIPTION** Sample no. Minerals list Sampling depth (m) **Carbonaceous** Very fine-grained. Cream to light GAA28GC-25 Kaolinite, Nitratine 140.51 mudstone brownish-cream in colour. Dark 141.11 brown variant was also observed. GAA28GC-26 Quartz, Kaolinite, 138.87- Rutile, Dolomite, 138.92 Anatase, Muscovite Dolerite/ Fine-grained. Aphanitic texture. GAA28GC-44 | Augite, Anorthite, 45.60- 45.96 Amygdaloidal Some faulting and fracturing Clinopyroxene, dolerite were observed. Greenish-brown Enstatite, Pigeonite in colour. Calcite veinlets (moderate) were obeserved in the non-fractured dolerite, abundance decreases towards the GAA28GC-45 Albite, Augite, 41.00 top. Amygdaloidal dolerite Anorthite, 41.30 contained moderately abundant Orthopyroxene, calcite veinlets. Some of the Lizardite dolerite was extremely fractured at some intervals. Β Sandstone Medium-grained sandstone, with GAA28GC-39 Quartz, Kaolinite, 94.25 some patches of coarse-grained Albite, Microcline 94.50 sandstone. Colour is light-grey to light grey-brown. The sandstone was intact- hardly fractured. Cross-bedding observed at some GAA28GC-40 Quartz, Kaolinite, 89.39 places although the sandstone Orthoclase, Albite, 89.68 was mostly massive. Glauconite Muscovite, was observed (pale green to Sanidine bluish-green). Baked contact observed where the sandstone GAA28GC-43 Quartz, Calcite, 46.62- Orthoclase, Albite, 46.80was in contact with the dolerite. Sanidine A brown sandstone variant was

Table 10: South Rand Heidelberg Project- Rock descriptions and mineral content.

also found. The brown sandstone





## *4.3.1.5. Summary of mineralogy*

- Pyrite was found in the coal samples during analysis with the XRD (Table 10) and was also observed macroscopically as blebs on the surface of the coal core. However, calcite and dolomite (readily dissolving acid-neutralising minerals) were also found in the coal samples, qualitatively suggesting the presence of neutralising potential.
- Other acid-neutralising minerals were also found in the pyrite-containing coal. These include muscovite, kaolinite, and feldspar. These minerals have slow reactivity rates.
- Carbonaceous sandstone and carbonaceous mudstone were other rock types that were found to contain dolomite. A quantitative assessment of acid-generating and neutralising potential of the coal and interbedded sediments is provided by the Acid Base Accounting results.





Table 11: South Rand Heidelberg Project ABA analysis using ICP-OES



#### *4.3.1.6. Summary of ABA results and acid generating potential*

Samples were classified according to guidelines as provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997), a summary is shown in Table 11. As in the cases of the Inyanda and Khutala samples, sulphur content is derived from leachate B where HNO<sub>3</sub> is added to the sample in order to leach out the sulphide sulphur. As commented in sections 4.2.1 and 4.2.2, sulphur from the organic fraction may also be partially leached out at this stage, leading to an overestimate of the targeted sulphur species and the acid generating potential using the sulphur content.



Figure 26 Graph showing %S vs SNPR values for samples collected at the SRHP

Pyrite was detected by XRD in three coal samples, which is surprising as the Fe content of these same samples would reflect pyrite contents below the XRD detection limit. Accordingly, all these coal samples were classified as Non-PAG using the NNP and guidelines provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997). They also showed low sulphide-hosted sulphur content, leading to a non-PAG classification following that criterion. Calcite and dolomite were also found in the pyritecontaining samples. The acid-buffering minerals provided the neutralisation potential which was found to be more than the acid-producing potential in all three samples in which pyrite was detected. Two coal samples (GAA28GC-36 and 37) in which pyrite was not detected, have high sulphur content in leach B, but these samples still classified as being non-PAG using Price *et al*., (1997) guidelines.

From a total of seven (7) carbonaceous shale samples analysed, five (5) (72%) classified as PAG when considering the NNP values. These samples, however, classified as Non-PAG when considering guidelines as provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997). The sulphide sulphur content of these samples was recorded below 0.3%. In one case (sample 31) an extreme NNP value of -104.41 was recorded. This result is of concern for the future if this over-and interburden material is to be used as backfill.



# **5. Discussion**

#### **5.1 Techniques used in the prediction of acid producing and neutralisation potential**

The most widely used version of the static tests has been the Sobek method which involves the use of the Laboratory Equipment Corporation (LECO) analyser after the samples are subjected to different acid species under defined conditions. The LECO analyser instrument measures sulphur in a sample by combusting the sample in a stream of pure oxygen at  $1370^{\circ}$ C for approximately two minutes. Thirty seconds following the combustion procedure oxygen is blown directly into the combustion crucible. The SO<sup>2</sup> formed is detected and measured in an IR cell after integrating the absorption signal over a period of about 2 minutes. The signal is then extrapolated and printed out as the concentration of the sulphur (Jackson, *et al*., 1984; Rait and Aruscavage, 1823).

The method of determining the total sulphur using the LECO analyser in many studies (Alam, *et al*., 2012) can prove to be non-beneficial since sulphur dioxide is a gas, meaning that the gas is likely to escape into the atmosphere and would therefore not be available for re-analysis or re-evaluation. The method using the LECO analyser is also highly dependent on the amount of oxygen available to react with the sulphur, the greater the amount of oxygen available, the higher the sulphur content that can be reacted to form sulphur dioxide, which is then taken up for measurement. The method highlighted in the current study (using ICP-OES) preserves the residue leached out of the sample. This means that tests can be run more than once. This increases reliability and confidence on the results produced during ICP-OES analysis.

Analysis using the ICP-OES allows for the measurement of the different elements (found in compounds) that may also relate to the acid-producing and acid-neutralising capabilities of the sample. Examples of such elements include iron, sodium, potassium and calcium. These elements and compounds are also important and should be taken into account when considering the AP/NP of a sample since the minerals involved in acid producing/neutralising reactions contain one or more of these minerals as a major constituent.

The LECO analyser only measures sulphur content of the sample (Rait and Aruscavage, 1823), assuming that pyrite  $(FeS_2)$  is the only acid-producing mineral in the sample. Sulphur may be available as sulphide sulphur, sulphate sulphur, native sulphur and organic sulphur in the samples, but it is only the sulphide sulphur that produces the environmentally degrading acidic drainage. The acid-producing capacity of a given species when using the sulphur content is then overestimated since the instrument does not differentiate the sulphur species. Iron is also not considered during this analysis, but ferric iron  $(Fe^{3+})$  can also play a role in acid production, and when minerals that contain iron as  $Fe^{3+}$  are identified during mineral identification, the iron content may have to be taken into consideration when analysing the acid-producing capacity of that given sample.

The current method (using the ICP-OES for analyses of leached solutions) uses hydrochloric acid and nitric acid which yield high recovery rates (about 97%) for the sulphur species (Mketo, *et al*., 2016; Alam, *et al*., 2012). Hydrochloric acid and nitric acid target the sulphate and sulphide sulphur species respectively. This means that the sulphur species being analysed is clearly defined during measurement with the ICP-OES. This allows for a clear definition of the content of the specific sulphur species that is likely to produce acidic drainage. During analysis with the LECO analyser, the different sulphur species are extrapolated by calculation from the total sulphur content measured and using the ICP-OES is advantageous since it considers the different sulphur species uniquely, with each of these sulphur types being measured from the residue after extraction. Since the acid used to leach the sulphur species from the samples targets the different sulphur species individually, this aids in the differentiation of the sulphur species whilst minimising the probability of an overestimation of the acid-production when using the sulphur content of the sample as a source for the characterisation of acid production/neutralisation potential prediction. Analysis of the iron content can also prove to be beneficial, especially the iron content related to acid-producing minerals. Analysis of the K and Na content also improves prediction of the acid neutralisation potential of the samples.

In addition, there is also the use of the fizz test as a means of determining the amount of acid and base to be added to samples as a precursor to NP determining procedures. The fizz test used in the Sobek and Modified Sobek methods to determine the quantity of acid used in the digestion is subjective since it requires a judgement by the test operator (Mills, 1997). With a stronger amount of initial acid, the solution would react at a lower pH and phases that would not normally react at the more realistic pH of the real situation are also involved (Fey, 2003). The subjectivity of the fizz test can therefore, depending on the sample, produce widely differing NP values for a single sample. Using a constant "strong" rating in all the samples would also lead to unusually high NP values that may be misleading (Mills, 1997). The presence of siderite (iron carbonate) can also affect the laboratory determination of NP (Fey, 2003). Due to the subjectivity of the fizz test used in the Sobek method, a single sample can produce widely differing NP values (Mills, 1997).

#### **5.1.1 The development of a new prediction tool**

New methods are developed frequently as a means of rectifying errors and improving efficiency for data analyses and collection. The development process of such a method takes time and errors and continued improvement are a norm in this development process. Even though the current method, as described in Section 3 may contain some defects, it proved to be a useful tool in the determination of the NP/AP potential of the rock samples collected. According to Mketo, *et al*., (2017), one of the most crucial factors when one develops a new method is time. The shorter the duration process, the better the method. The current method is quick, easy to use, and since the leachate is kept during the investigation process, it allows for more than one analysis if discrepancies do arise. The method also looks at other elements/minerals which may be involved in the acid-generation/neutralisation process with the aim of better classifying potential sources for acidity and buffering besides just pyrite and calcite/dolomite, respectively.

# **5.2 Previous studies on acid production/neutralisation in the South African mining context and their relation to the current study**

Mokoena (2012) found that all the coal seams and discards in the eMalahleni coalfield were generally associated with negative NNP values. This means that the acid-producing potential (AP) is greater than the neutralisation potential (NP). Seam 4U and Seam 5 have a higher acid generation potential and lower NNP than Seam 4L, Seam 2 and Seam 1 (Pinetown and Boer, 2006).

A regional ABA study was carried out on the coal seams, interburden and overburden material from the eMalahleni coalfield by Pinetown and Boer (2004). The samples analysed included the No. 1, 2, 3, 4 and 5 coal seams and their interburden and overburden materials. The results found indicated that:

- Soil above the No. 5 seam had little acid-producing potential.
- The No. 5 seam was found to be acid-generating, and this was attributed to the little NP that was available to neutralise the high AP.
- Rock between the No. 5 and 4 seams had the potential to produce acid, but it was negligible because it had a small negative NNP.
- The No. 4U seam was potentially acid generating.
- The No. 4 seam parting indicated little or no acid-generating potential.
- The No. 4L seam was found to be potentially acid generating, however, not significantly.
- Rock occurring between No. 4 and 2 seams (might include No. 3 seam) may have been potentially acid generating, but it was not as strong as the No 4U seam and No 5 seam.
- The No 2 seam was potentially acid generating, but it was not as strong as the No. 4U seam and No. 5 seam.
- Rock between No. 2 and 1 seam had an uncertain acid-generating potential.
- The No. 1 seam was found to potentially acid generating.
- Rock below No. 1 seam had an uncertain acid-generating potential.

In summary, the types of rock were classified in terms of:

- None acid generation layers: soil above No. 5 seam, the No. 4 seam parting, rock between No. 2 and 1 seams and rock below No. 1 seam.
- Fairly low acid generation layers: Rock between No. 5 and 4, No. 4L seam, rock between No. 4 and 2 seams, and rock below No. 1 seam.
- Strong acid generation layers: All the coal seams, specifically No. 5 and 1 seam.

# **5.3 Analysis of lab data**

## **5.3.1 Current case studies**

The results obtained in the current study have shown that the method (described in section 3) has some potential. Even though the development of a method requires time and considerable effort, the current method was shown to be successful when the results obtained were considered for the respective mines taken as case studies. The observations from the results are summarised as follows:

### *5.3.1.1 Inyanda coal mine*

The results obtained from considering samples collected at the Inyanda coal mine are summarised in section 4.2.1. From a A total of 14 samples were analysed from Inyanda coal mine, it was observed that:

- Only two of the samples analysed had pyrite as a mineral phase i.e. INYC01 and INYC02 (coarse discard coal material). These are also the only two samples that had %S> 0.3 in both leachates and AP>NP. Consequently, the samples classified as PAG when considering the NNP values and guidelines as from Price *et al*, 1997 and Soregaroli and Lawrence (1997);
- Composite samples of backfill material were characterised by low sulphide sulphur content. This means that the material is unlikely to produce any acidity into the future;
- The abovementioned findings are different to those reported by Groundwater Square (2014), where all the analysed samples collected form the Inyanda coal mine were reported to have significant potential to generate acidic drainage, and the samples that did not produce any acidity had no potential to neutralise the acidity produced by the other rocks;
- Pyrite was detected in the coarse discard material, and no acid-neutralising minerals were identified to counteract the acid that may be produced.

According to Bowell *et al*., (2000), anorthite, nepheline, and diopside are fast-weathering minerals that also have neutralisation potential. Enstatite, augite and glaucophane have some neutralisation potential as well, with an intermediate weathering rate. Even though albite, montmorillonite, goethite, kaolinite, K-feldspar and muscovite have some neutralisation potential, they have very slow weathering rates. They may prove to be viable neutralising components in the long term. Muscovite, kaolinite and microcline were reported in the backfill material from the Kalbasfontein Pit. The presence of these minerals mitigates acid produced in the long term, meaning the backfill material is unlikely to be acid generating when the mine is no longer operational. The classification coincides with that reported by Golder (2015), conducted on samples collected in the same mine.

Unlike the case of CRM SARM 18, the B leaches of the coarse discard samples yield most of the S and Fe. The S/Fe ratios reflect atomic ratios of 1.59 in both cases, suggesting that either some Fe is leached from siderite, or pyrrhotite might be present in addition to pyrite. Further, in contrast to the CRM SARM 18 test, leaches A did not yield significantly more Ca than leaches B, indicating that using leach B Ca results alone for ABA accounting, as done here, might underestimate the neutralization potential. All Ca concentrations of leaches, and all Fe concentrations except for the leached B of coarse discard samples, would reflect calcite and pyrite contents below the detection limit of XRD. Thus, there is no contradiction between the chemical and XRD analyses. Further, in samples where pyrite and carbonate minerals are absent, the sulphur and calcium content can also be derived from other minerals that would not necessarily influence acid-generating or acid-neutralising potential of the rocks.

The classification of the samples coincides with the classification found from Groundwater Square (2014) and Golder (2015). High sulphide sulphur contents were found in the coarse discard material as reported by Golder (2015). This shows that the method developed in the current study was a reliable analytical method for samples from the Inyanda coal mine. Even though the reported sulphide values may differ sometimes, the outcome from the analysis shows the same observations as noted in the abovementioned publications. **UNIVERSITY** 

### *5.3.1.2 Khutala coal mine*

From a total of thirty-four (34) coal samples from Underground Seam 4 of the Khutala coal mine in the eMalahleni coalfield:

- Three of the coal samples were found to be PAG when classifying using guidelines as provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997).
- Average NPR values for Seam 4 classified the samples as having Low-PAG when using guidelines from Price *et al*., (1997).

A total of fourty two (42) coal samples were analysed from the Underground Seam 2 of Khutala coal mine, and it was found that:

• Nine of the samples were found to be PAG when classifying using the guidelines as provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997) and six (7) of the samples were PAG when classified using the NNP values.

 Average NPR value for the samples classified as having no potential for acid generation when using Price *et al*., (1997) guidelines. In general, samples from Seam 4 were found to have less acid-generating potential than samples from Seam 2.

Calcite and dolomite were found to be abundant in the coal samples from the Khutala coal mine. This means that even though pyrite was also detected by XRD analysis, there is NP from the acid-neutralising minerals found in the coal samples. By comparison, Underground Seam 2 generally has a higher potential for acid generation than Underground Seam 4. It is worth noting, however, that previous studies had reported coal from Seam 2 and Seam 4 as being PAG and also having uncertain acidgenerating potential.

# *5.3.1.3 South Rand Heidelberg Project*

From a total of twenty-three (23) samples analysed from the South Rand Heidelberg Project:

- Majority of samples classifying as PAG were the carbonaceous shale material. This is when the NNP values are taken into consideration. This could be of major concern towards the future, especially if the material is to be used for backfilling purposes. The sulphide sulphur content of these samples was, however, noted to be below 0.3%.
- Pyrite was not observed in any of the samples that classified as PAG during analysis with the XRD.
- The coal samples seem to have had enough acid-neutralising minerals to mitigate any acidity that may have been generated by reaction of the pyrite that was detected in the coal samples. These acid-neutralising minerals may be abundant in the coal from the South Rand Heidelberg Project, which could also be the reason why all the coal classified as Non-PAG even though the mineral pyrite was observed in two of the six coal samples from XRD analysis.
- The classification in the current study is different to the data reported by Golder (2015), where it was reported that 93% of the analysed coal samples had classified as PAG when using guidelines as provided by Price *et al*., (1997) and Soregaroli and Lawrence (1997).

The classification of samples in the current study coincides with classification reported in previous studies at the South Rand coalfield, where the majority of the samples reported as having little or no acid-generating potential.

# **6. Conclusions**

The method described in the current study has shown considerable potential, but still needs refinement in certain areas. Refinement still needs to be carried out to ensure: i) better leachate recovery from the analysed samples. A better leachate recovery potential increases analyte recovery, leading to increased confidence in the results obtained. A possible factor resulting in the low recovery rates from CRM analyses is the concentration of the acid. The acid was diluted to ensure suitability for use in the ICP-OES. Using a more concentrated acid combination would ensure better extraction.

It should be noted that 100% of the S was recovered from the CRM coal sample during the analysis. It can therefore be noted that the  $HC/HNO<sub>3</sub>$  combination is successful for the extraction of sulphur from coal samples. However, using a much stronger oxidising agent (hydrogen peroxide) could also result in better extraction quantities. As part of improving the method, hydrogen peroxide could be used as a substitution for the HCl and HNO<sub>3</sub> to ensure efficient sulphur extraction. Mketo *et al.* (2016) describes a method in which the extraction method is coupled with use of microwave for better recovery rates. Adding a catalyst to the current method would assist in the better recovery of the targeted elements during analysis.  $\frac{1}{2}$ 

The method is a static method and should be used in conjunction with other analytical procedures. Conducting kinetic tests on the samples may give a better prediction for the acid-producing/neutralising potential of samples. Using the method with data obtained from XRD analyses had also given a better prediction criterion for each of the samples.

Classification using NPR and NNP was found to be more consistent than using these parameters in conjunction with the sulphur content. In most cases where the samples classified as PAG when using the NPR, the NNP classification would either be similar or have uncertain acid generating potential. The only instances where comparing classification using NPR versus NNP produced extremely opposite results (PAG and Non-PAG) was found in dolerite and carbonaceous shale samples of the SRHP.

Of all the samples, it is the coal material from the eMalahleni coalfield that was classified as having acid-generating potential, in comparison to other lithology. These results coincide with the findings from Pinetown and Boer (2004). It is noteworthy that the backfill material from Inyanda coal mine was classified as non-PAG, meaning that acid is not likely to be generated into the future.

The leached iron and calcium content might be more reliable when it comes to ABA procedures, especially if the iron is mostly related to acid-producing pyrite and the calcium to acid-neutralising carbonates. If other iron and calcium-containing minerals are identified from XRD analysis, these may have to be taken into consideration as well during data analyses, especially if they are considered readily dissolving/weathering minerals. The sulphur content may be unreliable since the sulphur is available as sulphide, sulphate, organic and native sulphur in coal and other rock types. This creates an overestimation of sulphur content during some instances, especially if the reagent for leaching the desired sulphur species is not efficient.



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#### **APPENDICES**

#### **Appendix A: Summary of the fizz ratings from the fizz test conducted by adding a few drops of 6N hydrochloric acid to 2g of sample**







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# **Appendix B: Sample weigh-in masses and amounts of acid added**





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# **Appendix C: List of minerals identified by X-ray Diffraction**



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# **Appendix D: Groundwater Risk Assessment studies for the eMalahleni coalfield**



































# **Appendix E: South Rand Heidelberg Project core logging**

