ASSESSMENT OF LABORATORY LEACH TEST METHODS FOR EVALUATION OF ENVIRONMENTAL IMPACTS BY COAL AND GOLD MINE WASTE

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DECLARATION

I, Ramasala Rofhiwa Joyce, hereby declare that the dissertation hereby submitted by me to the Institute for Groundwater Studies in the Faculty of Natural and Agricultural Sciences at the University of the Free State, in fulfilment of the degree of Magister Scientiae, is my own independent work. It has not previously been submitted by me to any other institution of higher education. In addition, I declare that all sources cited have been acknowledged by means of a list of references.

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ABSTRACT

Leach tests involves the extraction of the removable component from solids using a solvent. Leach tests are widely used to assess the potential impact of waste material on the environment. A variety of leach test methods exist and the selection of a leaching method depends on the type of leaching solvent and its chemical characteristics. While these methods have been in use for decades, there is limited research to compare the performance of the different leach test methods. Such information is particularly important when selecting method to use on the basis of the time efficiency and costs. This study therefore seeks to evaluate the performance of four conventional standard leach test methods: Toxicity Characteristic Leaching Procedure (TCLP) using acetic acid; Synthetic Precipitation Leaching Procedure (SPLP) using acid rainwater; Diluted Sulphuric Acid Base (DSAB) leach test method using dilutes sulphuric acid to mimic AMD and Water Leach – as for TCLP but replace with reagent water (deionised water). These leach test methods are assessed in a comparative way on solid mine wastes samples from coal and gold mines obtained from South Africa. The assessment of the four static leach test methods was conducted on the field samples, each sample with the same mineralogical composition in order to evaluate their performance. In order to assess the performance of these methods, the study compares the leached concentration results with the leachable concentration threshold from the NEM: WA No.59 of 2008 standard, furthermore it compares leached total dissolved salts (TDS) from the samples with the Water Quality Salinity Classification and Groundwater Quality Classification. The findings reveals that the leach test methods classify waste materials inconsistently. The leachate fromTCLP and DSAB methods falls under different waste Type classes. While leachates from SPLP and Water leach test methods falls in Type 3 class, which is known to be very low hazardous risk. In this way the Water leach test method, becomes more favorable because of less cost involved. The results further show that even though the sample leachate are classified as very low hazardous risk by the NEM: WA No. 59 of 2008, it can also pose salinity risk. In results, this shows that the leach test methods performs in different ways depending on the applied extraction fluids.

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CHAPTER 1

INTRODUCTION

1.1 General Introduction

Leaching of solid waste material from the mining industry is a great environmental concern worldwide due to the generation of waste material in massive quantities (Tiwari *et al.,* 2015). One of the most important environmental concerns at any mining operation is how to manage huge volumes of waste and to minimize their long-term environmental effects while maximizing any long-term benefits. The long-term environmental effects caused by mine waste materials cannot be overlooked since they may pose danger to public health even though mining provides enormous social and economic benefits to nations (Mining Minerals and Sustainable Development (MMSD), 2002; Fashola *et al.,* 2016).

Waste materials from mining operations are discarded as waste rock and fine-grained tailings/dumps produced during ore extraction processes. Depending on the geology of the area, mine waste materials contain different minerals. For example; gold and coal mine waste contains sulphide minerals such as pyrite (FeS_2), arsenopyrite (FeAsS), galena (PbS), chalcopyrite ($CuFeS_2$), and sphalerite ((Fe, Zn)S) (Verplanck, 2008; Hooda, 2010). These minerals contain trace elements such as arsenic (As), lead (Pb), zinc (Zn), nickel (Ni), cadmium (Cd), silver (Ag), cobalt (Co), chromium (Cr) selenium (Se), manganese (Mn), iron (Fe), boron (B), copper (Cu), vanadium (V) molybdenum (Mo), barium (Ba) and other trace elements (Hooda, 2010). Some of these trace elements at elevated concentrations are toxic to the environment and organisms (DWAF, 1998; Hobbs *et al.,* 2008; Lim *et al.,* 2009).

Leaching of the trace elements in the environment depends on chemical, physical and biological factors. When sulphides minerals are exposed to oxygen and water, they react to form acid-mine drainage (AMD) or neutral mine drainage (NMD) depending on the chemical composition of the material. The rate and degree by which AMD forms in the presence of sulphide minerals can be increased by different factors such as oxidation and the presence of certain bacteria (Coil *et al.,* 2014; Kumar, 2013).

Oxidation of sulphide bearing minerals results in leached elements which tend to contaminate the surrounding soil and groundwater making them acidic (Stumm & Morgan 1981, Backes *et al.*, 1986; Lim *et al.*, 2009). In areas where waste materials containing sulphide minerals are chemically unstable, they can serve as a more or less permanent source of pollutants to natural water systems (Van Zyl *et al.,* 2011).

The concentration of trace elements in the leachate governs the amount of impact they will cause on the environment and natural water system (Van Zyl *et al.,* 2011; Fashola *et al.,* 2016). Single extraction Leach test methods are conducted on waste materials in order to determine the concentration and potential impact of trace elements to the environment (Hammarstrom and Smith , 2002).

These tests include all tests in which a specific amount of leaching fluid is placed into contact with a specific amount of waste for the specified period, without renewal of the leaching fluid. The resulting leachate is then removed from the test, either at various times to derive kinetic information (changing concentrations over time) or, more commonly, at the end of the test and then analysed for chemical constituents (Washington State, Department of Ecology, 2003). Leach tests methods reveal the soluble phases of samples and help quantify toxic inputs due to the mobilization of contaminants (Chezom *et al.,* 2013).

Various countries depending on their respective regulations apply different leach test methods. In South Africa, National Environmental Management: Waste Act (NEM: WA) No.59 of 2008 requires leach test methods to be conducted in order to assess the potential impacts of waste materials on the environment.

The regulation states that different waste materials are to be evaluated using the Australian Standard Leaching Procedure (ASLP) and Water Leach method. The ASLP method uses extraction fluid with pH 5.0 or pH 2.9 (0.1M acetic acid) or an extraction fluid consisting of a 0.1M sodium tetraborate decahydrate of pH 9.2±0.1. The Water Leach test method uses reagent water (deionised water) as extraction fluid (NEM: WA Act No.59 of 2008).

Furthermore the NEM: WA Act no.59 of 2008 endorses the application of leach test methods on mine waste materials. The investigation is to also check if there is any difference in the performance of extraction fluids used in leach test methods performed to classify mine waste material. This research was conducted to assess the performance of the toxicity characterizing leaching procedure (TCLP), which is similar to ASLP using acetic acid, Water Leach test method using deionised water.

In addition to the assessed leach test methods is the Synthetic Precipitation Leaching Procedure (SPLP) leach test method which uses sulphuric acid/ nitric acid as extraction fluid to simulate acid rainwater and the developing Diluted Sulfuric Acid Based (DSAB) leach test methods which use diluted sulphuric acid to simulate acid mine drainage. These leach test methods are assessed in order to evaluate and compare their performance on mine waste materials.

1.2 Aims and Objectives

The aim of the study is to assess the performance of laboratory leach test methods for the evaluation of environmental impacts by coal and gold mine waste.

The objective of this study is to:

- Determine if the use of different leach test methods will result in leached elements within the leachable concentrations threshold in the NEM: WA Act No.59 of 2008 (National Norms and Standards for the Assessment of Waste for Landfill Disposal, 2013).
- Determine if the use of different leach test methods will result in different classification of leachate based on the TDS salinity classification.
- Determine if the use of different leach test methods affect the hydrogeochemical characteristics of the leachate and salinity.

1.3 Study Rationale

A variety of single extraction test/batch leach test methods exist depending on the type of leaching solvent and its chemical characteristics. The single extraction test/batch leach test methods have been in use for decades in various countries for different purposes. The main difference among these tests methods is extraction fluids, liquid to solid (L/S) ratio, and duration of agitation. The assumption made when conducting a single extraction test is that a steady-state condition (equilibrium) is achieved by the end of the testing period, though this may not necessarily be the case in practice. Reaching equilibrium in single extraction leach testing is critical to predicting leaching behaviour over long periods of time (EQM, 1998; Washington State, Department of Ecology, 2003; Alexander *et al*., 2015)

The challenge is the limited information on the comparative performance of the different leach test methods on solid mine waste materials. The other challenge observed by other researchers is that some of the extraction fluids are not aggressive enough to represent what is happening in the field after the initial stage of leaching mining waste materials (Deysel, 2015). Another challenge is that most of the leach test methods applied in mining waste material was not designed for the mine waste materials, adequate studies have not yet been undertaken to support the use of leach test specified in this research to be applied in mine waste material.

The other known challenge is the limited information on the comparative performances, particularly with regards to their practical applications on mine waste, their testing time and cost requirements. The assessment of the leach test methods will also provide an opportunity to cross-examine leach test methods concerning their application, cost-effectiveness and time consumption on mine waste material.

Applying these leach tests on mine waste should be a carefully considered study due to the different mine waste materials composition, degree of harmfulness to the environment and the inhabitants compared to other waste materials that these methods have been developed to assess. In this research, the focus is on evaluating different laboratory leach test methods used by the South African Department of Environmental Affairs in order to assess and compare their performance on coal and gold mine waste material.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Leaching is the process by which soluble constituents are dissolved from a solid material (such as rock, soil, or waste) into a fluid by percolation or diffusion. Thus, when fill materials interact with liquid (including percolating rainwater, surface water, groundwater, and liquids present in the fill material); constituents in the solid phase will dissolve into the liquid, forming a leachate (Hesbach *et al.,* 2005; Deysel, 2015).

Leaching is constantly taking place in the environment as waste materials are exposed to weathering, precipitation and other processes. This process leads to major elements, trace elements, acids, bases, organic elements and other constituents from geologic and anthropogenic sources running off into adjacent streams, water bodies, and ecosystem on an on-going basis negatively affecting the environment (Liaghati, 2004). To fully understand this phenomenon, it is important to have a tool that aids the geoscientist to measure both qualitatively and quantitatively the leachability of these materials. Such information would help policy makers with developing appropriate mitigation measures. Laboratory leach test methods studies have been shown to be useful ways to assess the leaching potential of different waste material.

2.1.1 Leaching

As already highlighted in the above section, leaching involves the dissolution of soluble constituents from solid materials. The extent to which the constituents dissolve into the contact liquid will depend upon a site and material-specific conditions (chemical, physical, and biological factors) and the length of the contact time. Some processes depend on the chemical conditions of the solution, which includes its pH, chemical composition, and oxidation-reduction potential (Kalembkiewicz and Sitarz-Palczak, 2015; Department of Environment Regulation State of Western Australia, 2015). The leaching process is influenced by a number of factors, these are discussed below: (In section 2.1.1.1 to 2.1.1.4)

2.1.1.1 Climate and Meteorological Conditions

The amount of net precipitation at a landfill site will influence the amount of water available for infiltration through the site. The higher infiltration is in the landfill the higher the possibilities of waste material leaching in to the environment. Temperatures also have an effect on the area, when the temperature is high evaporation will also be high and this will lead to high solubility of elements that leach in high temperatures. In addition, an increase in temperature increases the rate of chemical reactions, and concentration of elements within the remaining water leading to the leachate being brine (van der Sloot and Kosson, 2010).

2.1.1.2 Landfill Site Design

The depth of the landfill will affect the quality of the leachate. Water entering through the top surface of the landfill material as infiltration will move through interconnected void spaces until it eventually reaches the bottom of the unit as leachate. Dissolution from the solid phase to the water will occur until the reaction reaches equilibrium. The deeper the landfill, the greater the contact time between the percolate and the landfill material and thus there will be a greater opportunity for the leachate to reach saturation limits (Lu *et al.,* 1985; Washington State Department of Ecology, 2003).

Also, the deeper the unit, the longer it will take contaminants to be depleted. In addition, the presence of a cap, pavement, or other low permeability structure will reduce the opportunity for infiltration and leachate generation. Topography affects the direction in which surface water flows, which will affect the site’s runoff pattern and the amount of water entering (via run-on) and leaving (via run-off) the landfill site (Washington State Department of Ecology, 2003).

2.1.1.3 Hydrogeological Condition

Subsurface geologic conditions and depth to groundwater at a landfill site can affect the generation of leachate. For landfill sites placed at or below the water table will be affected by groundwater fluxes, such fluxes would promote groundwater to flow through the material and this can provide a source of additional water to precipitation and run-on (Kalembkiewicz and Sitarz-Palczak, 2015). The pH of the material and the pH of its environment are crucial in determining the release rates of many constituents. This is valid for a variety of materials (monolith, granular, cement, soil, waste, sediment etc.) (Washington State Department of Ecology, 2003).

The dissolution and sorption processes of most minerals are pH dependent. The pH value of the surrounding fluid determines the maximum water phase concentration at that pH value, and each material has its own pH-dependent release curve (van der Sloot and Kosson, 2010). In natural conditions, the influence of atmospheric conditions and the presence of microorganisms in landfills influence the physical, chemical and biological processes. These processes give rise to, primarily, the ageing of the deposited material, weathered and leaching. Ageing generally reduces the solubility and weathering to the creation of partially soluble products. Leachability applies to an easily soluble metal form present in the waste, for example, salt, in which the composition has sulphates, calcium, potassium, sodium and magnesium (Kalembkiewicz and Sitarz-Palczak, 2015).

2.1.1.4 Vegetation

The lack of vegetation in the fill site may result in erosion that cuts gullies through the cover material, which allows precipitation to flow directly through the fill site. Vegetation is known to affect infiltration by intercepting precipitation directly thus improving evaporation from the surface and by taking up soil moisture and transpiring it back to the atmosphere (Kalembkiewicz and Sitarz-Palczak, 2015). Other factors that tend to affect leaching are summarised below in Table 1.

Table 1 summary of the main physical and chemical factors that influence the leaching process.

Chemical processes	Physical factors	External factors
-Dissolution	-Percolation	-Amount of water
-pH	-Diffusion	-Contact time
-Chemical form	-Surface wash off	-pH of environment
-Total composition/ availability	-Granular/ monolithic	-Temperature
-Redox	-Size (particles or monoliths)	-Redox of environment
-Acid-base buffering	-Porosity	-DOC/Adsorption
-DOC	-Permeability	
-A composition of water phase/ionic strength	-Tortuosity	
-Temperature	-Erosion	
-Time		

(van der Sloot and Kosson, 2010; Kalembkiewicz and Sitarz-Palczak, 2015).

2.1.2 Background of Leach test methods

There are varieties of leaching tests developed and tested over the past 52 years, which are available for application to waste materials. The initial work was done during the 1960s and 1970s directed mainly to devising tests for specific purposes and scenarios (Hesbach *et al.*, 2005). In recent years, there are more than one hundred leaching methods developed, but within these methods, there is no agreement on which method is most suitable to estimate the environmental effects caused by solid waste materials (Kim, 2005).

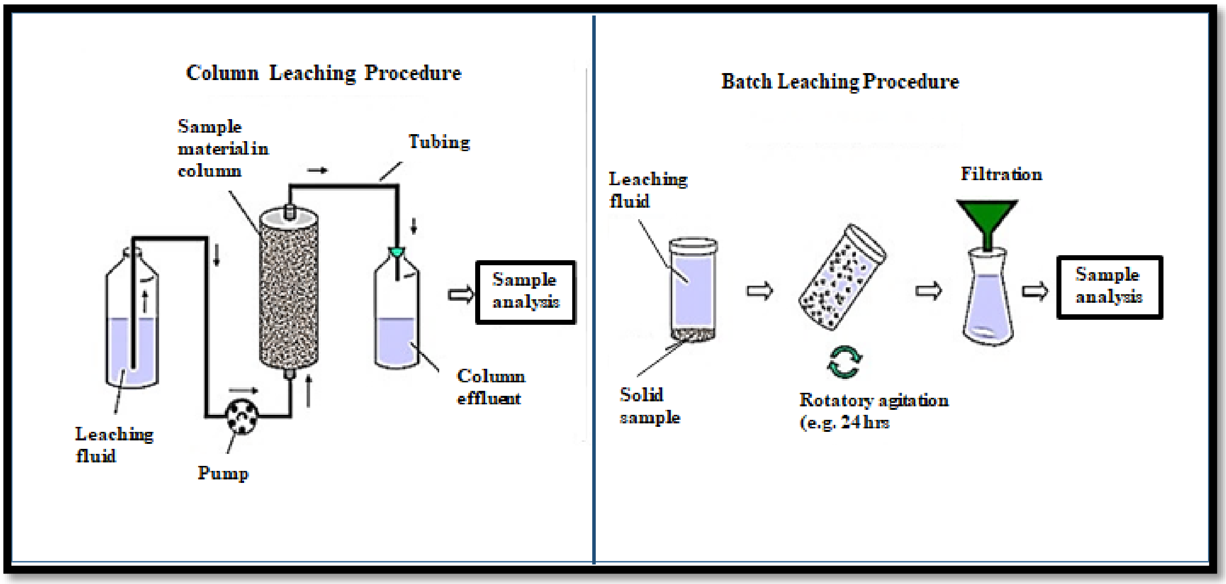
Some methods are regulatory-driven or provide a detailed characterization of a solid phase, but may not be suitable as evaluation tools for initial application, material reuse, or disposal and management scenarios (Hesbach *et al.*, 2005). These leaching tests are used to reveal the soluble phases of samples and help quantify toxic inputs due to the mobilization of contaminants. They also help in determining the proportions of metals present in the residue and the proportions of those that can be removed by leaching and in ascertaining the behaviour of waste material when exposed to external influences (Chezom *et al.*, 2013). Some of the uses of leaching tests include regulatory purposes, environmental impact assessments, scientific studies, and waste management (Sorini, 1997).

Unfortunately, there are many variations of leach test as these are often designed to assess leach parameters under specific conditions wherein some of the researchers have compared various leaching methods and made recommendations on the suitability of such tests in many papers (Riley, 2007). Hesbach *et al.*, (2005) conducted an inter-laboratory comparison of leach test methods which reviews commonly used procedures worldwide. Washington State, Department of Ecology (2003), provides an assessment of different leaching tests as predictors of impacts caused by fill materials on ground and surface. Riley (2007) noted that no single test is completely satisfactory for assessing water quality impacts for all projects in various environmental settings.

Literature reveals that there are two primary types of leaching tests available such as Static tests (batch) and Kinetic/Dynamic (column) tests refer to Figure 1 (Kim, 2005). The Static/Single tests (batch) typically involve mixing a sample of waste or other fill material with a specific amount of extraction fluid without renewal of the extraction fluid (Washington State Department of Ecology, 2003). These tests are a short-term (minutes to days), they are relatively inexpensive, simple and they generate chemical data for mechanistic applications (Kalembkiewicz and Sitarz-Palczak, 2015). These tests include both agitation (shake) and passive (non-shake tests) (Townsend *et al.*, 2003; Tiwari *et al.*, 2015).

Kinetic/Dynamic (column) tests typically involve a specific amount of leaching solution, sample materials are mixed and the leaching solution is periodically or continuously renewed (Washington State Department of Ecology, 2003). These tests are long-term (weeks to years), they are relatively expensive and more operationally complex, but they generate results that reflect real systems subject to fluid flow and solute transport (Kalembkiewicz and Sitarz-Palczak, 2015; Tiwari *et al.*, 2015). At the end of each leaching test period, the liquid is extracted and analysed (Townsend *et al*., 2003).

The analysed results from these methods are generally reported as concentrations, sometimes as the concentration in the extraction fluid (mg/L) or as the leached concentration from the solid (mg/kg). In many methods, the liquid (L) to solid (S) ratio (L/S) is used to quantify the volume of extraction fluid with respect to the amount of solid sample, usually as mL/g or L/kg (Kim, 2005).



(Washington State Department of Ecology, 2003).

Figure 1 Simplified schematics of a batch equilibrium and column leaching procedures.

There are different leaching tests used by various countries worldwide, these methods are used for the evaluation of potential impacts of leachates on the environment. The most commonly used batch leaching methods are the Toxicity Characteristic Leaching

Procedure (TCLP) (Peralta, 1997), the Extraction Procedure Toxicity Test (EPTOX), the Synthetic Precipitation Leaching Procedure (SPLP), the Standard Test Method for Shake Extraction of Solid Waste with Water (ASTM D-3987) and the California Waste Extraction Test (CA WET) (Kim, 2005).

The Leachate Extraction Procedure approved by the Canadian General Standards Board (CGSB) and the Leachate Extraction Procedure (LEP) of Ontario are very similar to EPTOX, Meteoric Water Mobility Procedure (MWMP), Sequential leach extraction, Project-specific leach tests, EN 12457 (European test protocol), MA100-Lix.Com.1.1 (Quebec) and other methods (Tessier *et al.,* 1979; Washington State Department of Ecology, 2003; Deysel, 2015).

Leach test methods use different extraction fluids, for European test methods, the distilled or deionised water is the solvent of choice. The theory is that distilled water is clean of contaminants and therefore acts as an effective solvent for leachable compounds. Some methods, however, prescribe the use of biocides such as sodium nitride to prevent biological activity affecting the leaching properties. In the USA, acetic acid is added as an organic matrix modifier to enhance the solubility of organic constituents (Stone, 2014).

2.1.3 Static/Batch/Single Extraction Leach tests

Static leach test also referred to as Batch or Single extraction leach tests include all tests in which a specific amount of leaching fluid is placed in contact with a specific amount of waste for a specified period, without renewal of the leaching fluid (Bradley *et al.,* 1980; Peralta, 1997; Kosson *et al.,* 2002). The leachate is extracted from the test either at various times to derive kinetic information or at the end of the test and then analysed (Washington State Department of Ecology, 2003; Kalembkiewicz and Sitarz-Palczak, 2015).These tests are single measurements and short-term (minutes to days), which assume that at the end of the period of the process, equilibrium was attained in the laboratory within the specified period (Kalembkiewicz and Sitarz-Palczak, 2015). The single extraction leach methods are more aggressive than the column method in extracting elements of concern probably because of the better interaction of the waste with the extraction fluid during rotary agitation. These leach methods are simple and more reproducible with controlled agitation (Peralta, 1997; Kosson *et al.,* 2002; Washington State Department of Ecology, 2003).

2.1.4 Extraction Fluid

The volume of the extraction fluid in which the mass of waste material is leached in is the ultimate influence of the concentration of elements in the leachate. The liquid to solid ratio (L/S) controls this relationship, a smaller L/S ratio may result in lower concentrations of less soluble species and higher concentrations of more soluble species. A smaller L/S ratio may limit the amount of constituent leached because of the common ion effect (Lowenbach, 1978). A higher L/S ratio may result not only in higher concentrations of some constituents but in a larger total number of constituents leaching (Lowenbach, 1978; van der Sloot *et al.*, 1997).

The leaching behaviour and the solubility of the material are influenced by the ionic strength of the extraction fluid. Ionic strength is the relationship of the concentration of ions in solution and the charges of those ions. Ionic strength affects reaction rates as well as the solubility of ionic species, with solubility generally increasing as ionic strength increases (Lowenbach, 1978; Washington State Department of Ecology, 2003).

2.1.5 Static Leach Test Methods used in Developed Countries

Different countries apply different leach test methods for different purposes to leach different types of waste materials, in this segment only a few different leach test methods are described for selected developed countries as an example.

2.1.5.1 Europe

2.1.5.1.1 BS EN 12457:2002 (Characterisation of waste Leaching Compliance test for leaching of granular waste materials and sludge).

This is a multi-part standard with each of the four parts detailing different leachate methodology; however, they all follow the same general protocol. The granular material is agitated for 24 hours (6 and 18 hours for the two-stage test) in a bottle filled with deionised water. The eluates are the filtered through a 0.45 µm membrane filter and analysed. Results are reported as concentrations or leached volumes as a function of L/S (Saveyn *et al.*, 2014).

These leach test methods are thus broken down into a series of strings of single stage batch test leachates at either the 2:1 or 10:1 L/S ratio, in addition to BS EN 12457-3, which is a collective of two-stage leachate that has been used conventionally for waste classification purposes (Stone, 2014).

- BS EN 12457 Part 1: single-stage batch tests at 1:2 (L/S) liquid to solid ratio with a particle size below 4 mm. Single-step leaching for 24 hours,
- BS EN 12457 Part 2: single-stage batch tests at 1:10 (L/S) liquid to solid ratio with a particle size below 4 mm. Single-step leaching for 24 hours, and
- BS EN 12457 Part 3: two-stage batch tests at 1:2 (L/S) liquid to solid ratio and 1:8 (L/S) liquid to solid ratio for materials with a high solid content and with a particle size below 4 mm (without or with size reduction). Two-step leaching for 18 hours.

The leach test assesses the leachability under mild extraction circumstances for waste disposal or material reuse options. The pH of the extraction fluid is not controlled externally during this test; it is determined by the pH of the waste material itself. The BS EN 12457 series does not detail sample-holding times, analytical preparation methods or chemical testing techniques (Ilyushechkin *et al.,* 2012).

2.1.5.1.2 Availability Test (NEN 7341)

The availability test (Netherlands Normalization Institute 1993a) is an agitation extraction method that was established in the Netherlands. It is established on leaching of finely ground sample under two controlled pH conditions, pH 4 and pH 7. The purpose of this leach test is to specify the magnitude of an element that may be leached from a material under environmentally extreme conditions, for example; in the very long-term, after disintegration of the material, when the material is fully oxidized and with complete loss of acid neutralization capacity (de Groot and Hoede, 1994; Sorini, 1997).

2.1.5.1.3 French Leach Test (Agence Francaise de Normulisution 1987)

The agitation extraction leach test method from the French Ministry of the Environment standard regulatory for determining the soluble fraction of a solid waste in a liquid solution (Environment Canada, 1990). It requires particle size reduction and encompasses mechanical stirring of the sample with water in a 10:1 liquid-to-solid ratio for 16 hours. A second and third extraction is performed and the cumulative extracted soluble fraction for each constituent can be determined (Sorini, 1997).

2.1.5.1.4 German Leach Test (DIN 38414 S4 Shake Test) (Institut fur Normung 1984)

Leach test method that is widely used for regulatory compliance purposes in Germany, Spain (Catalonian regulation) to classify solid waste (Kasselman, 2004). It is an agitation extraction test involving table shaking of the extraction slurry for 24 hours with 10:1 liquid-to-solid ratio. The method is applicable to solids, pastes and sludge (van der Sloot, 1995; Sorini, 2007).

The advantages of this method are its rapidity, extremely good reproducibility and simplicity. However, the method was criticized for the use of 10: 1 liquid-to-solid ratio, which is rarely reached under landfill conditions (Rankers and Hohberg, 1991). Gomes and Pinto, (2006) mentioned that this test will be outdated for regulatory use by the EN 12457 batch leaching tests and other tests recently developed under CEN TC/292.

2.1.5.2 United States

2.1.5.2.1 Environmental Protection Agency (EPA)

- EPA Method 1311 -Toxicity Characterising Leaching Procedure (TCLP)

TCLP is a well-known leaching procedure approved by the Environmental Protection Agency (EPA) for characterizing hazardous waste under the Resource Conservation and Recovery Act (RCRA). The procedure is designed to simulate the worst-case scenario of co-disposal of waste materials in municipal landfills (Hageman *et al.*, 2000; Al-Abed *et al.*, 2006). It requires end-over-end rotation for 18 hours with the extraction fluid used as a function of the alkalinity of solid phase; it uses a ratio of 1:20 solid-to-liquid (Hageman *et al.*, 2015).

The standard TCLP involves the crushing the sample to pass through a 9.5-mm screen. The method uses extraction fluid of either sodium acetate buffer solution having a pH of 4.93 ± 0.05 or an acetic acid solution having a pH of 2.88 ± 0.05 (Sorini, 1997). Incorrect use of the TCLP can lead to the inaccurate characterization of a sample because test might fail to accurately mimic the leaching process that occurs in the natural environment (Washington State Department of Ecology, 2003; Hageman *et al.*, 2015).

The TCLP approach is somewhat different from European approaches and typically used to establish leaching characteristics for waste material. Most European test methods use distilled or deionised water as the solvent of choice. Some methods, however, prescribe the use of biocides such as sodium nitride to prevent biological activity affecting the leaching properties. In the USA, acetic acid is added as an organic matrix modifier to enhance the solubility of organic constituents (Stone, 2014).

- EPA Method 1312 -Synthetic Precipitation Leaching Procedure (SPLP)

The SPLP (USEPA Method 1312) Method is designed to predict and determine the potential for leaching metals into ground and surface waters from which municipal solid waste is excluded (Alforque, 1996). The procedure is time and resource intensive and 1:20 solid-to-liquid ratio, it provides a rigorous leach of the materials within 18-hours of agitation. The extraction fluid for the SPLP is a slightly acidified extraction fluid (of sulphuric and nitric acids 60/40 w/w) that were designed to simulate acid rain (Hageman *et al.*, 2000).

Extraction fluid 1 (pH of 4.2 ± 0.05) is to be used in studies of sites east of the Mississippi River (USA). Extraction fluid 2 (pH of 5.0 ± 0.05) is designed for use in studies of samples from sites west of the Mississippi River. Consequently, the SPLP is likely to have a higher suitability for use in ARD test work than the TCLP. Both procedures are described in EPA publication SW-846 (Washington State Department of Ecology, 2003; Riley, 2007). The SPLP method was not designed for mining waste but rather the SPLP comes closest to simulating conditions in a waste rock dump (Smith, 1997; Hammarstrom and Smith , 2002).

2.1.5.2.2 American Society for Testing Materials (ASTM)

- American Society for Testing Materials (ASTM) Method D-3987, Standard Test Method for Shake Extraction of Solid Waste with Water

The ASTM extraction procedure is based on extended extraction with distilled or deionised water as extraction fluids. This procedure provides a halfway point between acidic TCLP conditions and in-situ conditions, by permitting leaching in deionised water. The ASTM procedure clearly states that the purpose is not to imitate field conditions, but rather to provide a laboratory standard against which various waste types are evaluated. It is designed for rapid production of a leachate from solid waste and estimates the mobility of inorganic constituents (Ilyushechkin *et al.*, 2012).

ASTM Method D-3987 is an agitation extraction method that uses reagent water as the extraction fluid. The water reagent is adjusted to pH 5.5 by carbonic acid addition immediately prior to use. Diluted water is freshly prepared and the adequate amount is added to give a liquid to solid ratio of 4:1 (solids content of 20% by weight). The technique involves an l8-hour contact time between a solid waste and reagent water with rotary agitation. The method does not require particle reduction, but a representative sample of the waste. The method has been tested to determine its applicability to inorganic constituents, but not for application on organic constituents (Sorini, 1997; Ilyushechkin *et al.*, 2012).

The leach is envisioned to duplicate the soluble portion of waste when the major contributor to the pH regime is the waste itself. The analytical measurements obtained from ASTM extracts are expected to be more revealing for a wider range of field conditions than the more aggressive Extraction Procedure (EP) and TCLP methods. As with other procedures described, this method was not developed for use in the mining industry (ASTM, 1999a).

- American Society for Testing Materials (ASTM) Method D-5233, Standard Test Method for Single Batch Extraction Method for Wastes (ASTM 1995d):

This is an agitation extraction method that is very similar to TCLP. The major difference between the two procedures is that ASTM Method D-5233 does not require particle size reduction. The method states that it is applicable for leaching samples of treated or untreated solid wastes or sludge or solidified waste samples to provide an indication of the leaching potential (ASTM, 1995d).

This method is based on the same disposal scenario as TCLP, a sanitary landfill with co-disposal of 95% municipal waste and 5% industrial waste. According to the method, interpretation and use of the test results are limited by the assumption of a single co-disposal scenario and by difference between the extraction fluid used in the method and the real landfill leachate (ASTM, 1995d).

2.1.5.3 Canada

2.1.5.3.1 Leachate Extraction Procedure (LEP):

The LEP (Ministry of the Environment, 1985) is an agitation extraction test that is used as the regulatory leaching test in the province of Ontario, Canada. In addition, this method is identical to the regulatory leaching procedure used by the Canadian provinces of British, Columbia, Alberta and Manitoba (Environment Canada, 1990). The test is very similar to the EP Toxicity Test. As previously mentioned, the EP involves monitoring the pH of the waste in reagent water and using an acetic acid solution to maintain the pH of the slurry at 5.0 ± 0.2. The EP is based on a single co-disposal scenario of industrial waste in a municipal landfill (U.S. EPA, 1980).

2.1.5.4 Australia

2.1.5.4.1 Australia Standard Leaching Procedure (ASLP) Method (AS 4439–1997) Bottle Leaching Procedure

The ASLP was developed with allowances for variable waste types, including non-putrescible and putrescible waste material. The ASLP has been implemented in Western Australia, South Australia and Victoria. The New South Wales EPA refers to Australian Standards in leachates preparation (AS 4439–1997), but it requires the use of standard solutions with different pH values. If the pH of the waste material were less than pH 5 then the pH of the solution would be 4.93 ± 0.05 and if the pH of the waste sample is greater than 5 the pH of the solution would be pH 2.88 ± 0.05.

From the theory, it is observed that the ASLP method reproduces the TCLP requirements. In some instances, the New South Wales EPA may permit the use of extraction fluid with a pH different from those specified above. Most Australian states use ASLP leaching tests for classification of waste and waste management schemes. (Harck, 2010).

ASLP is Standards Australia’s version of the TCLP. The main differences between the ASLP and the TCLP are:

- maximum sample particle size (2.4 mm for ASLP and 9.5 mm for TCLP),
- in addition to the standard TCLP buffer solutions, AS4439 allows using of three alternative buffers depending on the application,
- reagent water – applicable when a waste is undisturbed and left on site,
- tetraborate pH 9.2 – for acid volatile target analytes and in a situation of co-disposal, and
- Local water – when exposure to local ground, surface or seawater is expected.

The buffer solution options available allow ‘waste type’ and ‘disposal situation’ to be included in the decision process.

2.1.6 Leach Test Methods applied in South Africa

Leaching test methods are used to evaluate the potential leachable concentrations of elements to the environment. Different static test methods are applied to waste materials in South Africa for the assessment of the potential leachable concentration of elements for disposal purposes based on the NEM: WA Act No.59 of 2008. South Africa uses a similar standard as that of Australian Standard Leaching Procedure (ASLP); based on USEPA TCLP.

The ASLP allows alternative leaching scenarios with the leaching solution depending on the waste material, in a case of waste disposed of with non-putrescible material, a basic leachate solution consists of a 0.1M sodium tetraborate decahydrate of pH 9.2±0.1 is used. Waste that is to be left undisturbed on-site or dispersed over land without confinement or non-putrescible material uses leachate solution of reagent water.

The ASLP uses a ratio 20:1 L/S, it uses the TCLP pH 5.0 or 2.9, with the particle size <2.4mm but slightly more conservative than TCLP (NEM: WA Act No.59 of 2008). Other tests that should be included is the Toxicity Characteristic Leaching Procedure and the Acid Rain tests (Department of Water Affairs and Forestry, 1998).

2.1.7 Application of Leach Test Methods Based on the Department of Environmental Affairs NEM: WA Act No.59 of 2008

In South Africa, the Department of Environmental Affairs' Minimum Requirements for the Handling, Classification and Disposal of Hazardous Waste, sets out the waste classification system. The process categorises wastes in classes of General or Hazardous, according to their inherent toxicological properties (Department of Water Affairs and Forestry, 1998). According to the NEM: WA Act No 59 of 2008, mining waste is classified under category A, which is hazardous waste.

Hazardous waste are defined as "any waste that contains organic or inorganic elements or compounds that may, owing to the inherent physical, chemical or toxicological characteristics of that waste, have a detrimental impact on health and the environment (NEM: WA Act No.59 of 2008). Such waste includes hazardous substances, materials or objects within business waste, residue deposits and residue stockpiles" (NEM: WA Act No.59 of 2008).

Hazardous wastes are further subdivided according to the risk that they may pose at their disposal using a hazard rating. In this way, less hazardous waste are distinguished from extremely hazardous waste. The requirements for pre-treatment and disposal are appropriately set in accordance with the waste classification system. In the landfill classification system, a landfill is classified in terms of waste class, size of operation and potential for significant leachate generation, all of which influence the risk it poses to the environment. Graded requirements are then set for all aspects of landfilling including public participation properties (Department of Water Affairs and Forestry, 1998).

Requirements for the assessment of waste materials prior to disposal to landfill in terms of regulation are prescribed in the National Norms and standards for the assessment of waste for landfill disposal No. R635 of the NEM: WA Act No. 59 of 2008. The approach to this is that the chemical substances present in the waste should be identified. Chemical substances that are in the waste material are to be determined by sampling and analysis. Sampling and analysis are conducted by laboratories accredited by the South African National Accreditation System (SANAS) to determine the total concentration and leachable concentrations of elements and chemical substances specified in sections 6 of the Norms and standards (NEM: WA Act No.59 of 2008).

The system used in South Africa is based on the Australian State of Victoria's waste classification system for disposal, which uses the Australian Standard Leaching Procedure (ASLP) (AS 4439.1, 4439.2 and 4439.3) to determine the leachable concentrations (LCs) of pollutants (NEM: WA Act No.59 of 2008). The South African Department of Water Affairs offers the use of the test based on the USEPA TCLP test for organic wastes and a similar test using an acid rain lixiviant for inorganic wastes (Harck, 2010).

This method uses the leaching fluid of 0.1M acetic acid with altered pH 5.0 or 2.9, for non-putrescible waste the leaching fluid can be basic 0.1M sodium tetraborate decahydrate solution of pH 9,2 ± 0,1 as well as an acetic acid solution with pH of 5,0 or 2,9. For non-putrescible inorganic waste to be disposed of without any other wastes (mono-disposal scenario), reagent water (distilled water) is used as a leaching agent.

In addition to the above, the total concentrations (TCs) of the constituents of concern need to be determined and compared to the specified total concentration threshold

(TCT) and leachable concentration threshold (LCT) from NEM: WA Act No.59 of 2008. The number of potentially hazardous substances in the new classification system has been significantly reduced from that listed in the old Minimum Requirements of 1998 and brought in line with the potentially hazardous substances being used in other parts of the world to classify waste for disposal purposes. Once the analytical results are known, the waste is classified in line with the criteria presented in Table 2 below and can be briefly described as follows:

- Wastes with any element or chemical substance concentration above the LCT3 or TCT2 values (LC > LCT3 or TC > TCT2) are Type 0 Wastes. Type 0 wastes are extremely hazardous waste, considered very high-risk waste with a very high potential for contaminant release. It requires a very high level of control and ongoing management to protect the health and the environment;
- Wastes with any element or chemical substance concentration above the LCT2 but below LCT3 values, or above the TCT1 but below TCT2 values (LCT2 < LC ≤ LCT3 or TCT1 < TC ≤ TCT2), are Type 1 Wastes (highly hazardous waste, which may only be disposed of at Class A landfill designed with the most conservative barrier system);

- Wastes with any element or chemical substance concentration above the LCT1 but below the LCT2 values and all concentrations below the TCT1 values (LCT1 < LC ≤ LCT2 and TC ≤ TCT1) are Type 2 Wastes, Considered low-risk waste with some potential for contaminant release. It requires proper control and ongoing management to protect the health and the environment (moderate hazardous waste, which must be disposed of on a Class B containment barrier design (or Class A) landfill);
- Wastes with any element or chemical substance concentration above the LCT0 but below LCT1 values and all concentrations below the TCT1 values (LCT0 < LC ≤ LCT1 and TC ≤ TCT1) are Type 3 Wastes (low hazardous waste, which must be disposed of on a Class C containment barrier design (or Class B or A) landfill);
- Wastes with all elements and chemical substance concentration levels for metal ions and inorganic anions below the LCT0 and TCT0 values (LC ≤ LCT0 and TC ≤ TCT0), as well as below the limits for organics and pesticides are Type 4 Wastes (near inert wastes, which must be disposed of on sites with some base preparation, but no formal barrier system (NEM: WA Act No.59 of 2008).

Table 2 A waste risk profiling, waste type, disposal requirements, contaminant concentration criteria and the description of waste material (NEM: WA Act No.59 of 2008).

Contaminant Concentration Criteria	**Waste Risk Profile**	**Waste Type**	**Description**	**Disposal Requirements**
LC > LCT3	**Level 1: Extreme Risk**	Type 0	Considered very high-risk waste with a very high potential for contaminant release. Requires a very high level of control and ongoing management to protect the health and the environment.	Disposal **not allowed**. The waste must be treated first and then re-tested to determine Waste Risk Profile for disposal.
LCT2 < LC ≤ LCT3	**Level 2: High Risk**	Type 1	Considered high-risk waste with high potential for contaminant release. Requires a high level of control and ongoing management to protect the health and the environment.	Disposal only allowed at a landfill with a **Class A** containment barrier design.
LCT1 < LC ≤ LCT2	**Level 3: Moderate Risk**	Type 2	Considered low-risk waste with some potential for contaminant release. Requires proper control and ongoing management to protect the health and the environment.	Disposal only allowed at a landfill with a **Class B** containment barrier design (or Class A).
LCT 0 < LC ≤ LCT1	**Level 4: Low Risk**	Type 3	Very low-risk waste with low potential for contaminant release. Requires some level of control and ongoing management to protect the health and the environment.	Disposal only allowed at a landfill with a **Class C** containment barrier design (or Class B or A).

(NEM: WA Act No 59 of 2008).

Table 3 shows the Leachable Concentration Threshold (LCT) Limits (mg/L) and Total Concentration Threshold (TCT) limit (mg/kg) (NEM: WA Act No.59 of 2008).

Contaminants	**LCT0 mg/l**	**LCT1 mg/l**	**TCT0 mg/kg**	**LCT2 mg/l**	**TCT1 mg/kg**	**LCT3 mg/l**	**TCT2 mg/kg**
Metal Ion Contaminants							
As Arsenic	0,01	0.5	5.8	1	500	4	2000
B, Boron	0,5	25	150	50	15000	200	60000
Ba, Barium	0.7	35	62.5	70	6250	280	25000
Cd, Cadmium	0.003	0.15	7,5	0.3	260	1.2	1040
Co, Cobalt	0.5	25	50	50	5000	200	20000
$Cr_{Total,}$ Chromium Total	0.1	5.0	46000	10	800000	40	N/A
Cr(VI), Chromium (VI)	0.05	2.5	6.5	5	500	20	2000
Cu, Copper	2.0	100	16	200	19500	800	78000
Hg, Mercury	0,006	0.3	0,93	0.6	160	2,4	640
Mn, Manganese	0.5	25	1000	50	25000	200	100000
Mo, Molybdenum	0.07	3.5	40	7	1000	28	4000
Ni, Nickel	0.07	3.5	91	7	10600	28	42400
Pb, Lead	0.01	0.5	20	1	1900	4	7600
Sb, Antimony	0.02	1.0	10	2	75	8	300
Se, Selenium	0.01	0.5	10	1	50	4	200
V, Vanadium	0.2	10	150	20	2680	80	10720
Zn, Zinc	5.0	250	240	500	160000	2000	640000
Inorganic Anions							
TDS	100	12 500	N/A	25 000	N/A	100 000	N/A
Chloride	300	15 000	N/A	30 000	N/A	120 000	N/A
Sulphate	250	12 000	N/A	25 000	N/A	100 000	N/A
NO_3 as N, Nitrate-N	11	550	N/A	1100	N/A	4400	N/A
F, Fluoride	1.5	75	100	150	10000	600	40000
CN^- (total), Cyanide Total	0.07	3.5	14	7	10500	28	42000

Notes:

TCT1 limits were derived from the land remediation values for commercial/industrial land determined by the Department of Environmental Affairs' "Framework for the Management of Contaminated Land". The TCT2 limits were derived by multiplying TCT1 by a factor of 4, as used by the Environmental Protection Agency, Australian State of Victoria.LCT1 limits have, where possible, been derived from the lowest value of the standard for human health effects listed for drinking water (LCTO) in South Africa (DWAF, SANS) by multiplying with a Dilution Attenuation Factor (DAF) of 50 as proposed by the Australian State of Victoria, "Industrial Waste Resource Guidelines: Solid Industrial Waste Hazard. Categorisation and Management", June 2009 (www.epa.vic.gov.aus).

If no standard was available in South Africa then the limits given by the WHO or other appropriate drinking water standard, such as those published in the California Regulations have been used. LCT2 limits were derived by multiplying the LCT1 value with a factor of 2, and the LCT3 limits have been derived by multiplying the LCT2 value with a factor of 4. The factors applied represents a conservative assessment of the decrease in risk achieved by the increase in environmental protection provided by more comprehensive liner designs in higher classes of landfill and landfill operating requirements.

(NEM: WA Act No.59 of 2008).

CHAPTER 3

METHODS AND MATERIALS

3.1 Introduction

In order to develop an understanding of the processes governing the leachability of solid waste materials in the study area, it is important to understand both laboratory methods and the geology around the study sites. This will help in selecting the appropriate leach test methods for various waste materials. This chapter focuses on the methods and materials used in order to attain the results. The study site where samples were collected is descried in terms of the geology of the study site. A detailed description of leach test methods applied to each sample; analytical methods used to analyse samples and ways in which data is analysed are given.

3.1.1 Study site description

The three study sites are located in South Africa: Waterberg Coalfields, Highveld Coalfield and Free State Goldfield. Described in this section is the regional and local geology of the area, the impacts of gold and coal extraction and acid mine drainage impacts in South Africa. For the purpose of this study, two samples were collected from each site; the following sites are described below:

3.1.1.1 Waterberg Coalfields

The Waterberg coalfield is located in the western part of Limpopo province in South Africa, which is located near the neighbouring borders of Botswana, Mozambique and Zimbabwe Refer to Figure 2. Waterberg is situated approximately 400 km North West of Johannesburg and approximately 25 km west of the town of Lephalale. It stretches up all the way to the Limpopo River forming the border with Botswana to the north. The Waterberg area stretches from the town of Lephalale with the dimension of about 85 km from the east to west and about 40 km from north to south (Deysel, 2015).

The study site is mainly composed of farms and it extends to approximately 2300 km^2 in size (Bester, 2009). The Waterberg coalfield is considered to be the third largest coal reserve in South Africa; it extends towards Botswana where it is named Mmamabula Coalfield, which holds coal that is significant to the economy (Bester, 2009). Although the Waterberg is very small in area compared to other coalfields like the Witbank and Highveld coalfields it has a total seam thickness of about 110 m, which makes the in-situ reserves of the Waterberg large (Chabedi, 2014).

3.1.1.2 Highveld Coalfields

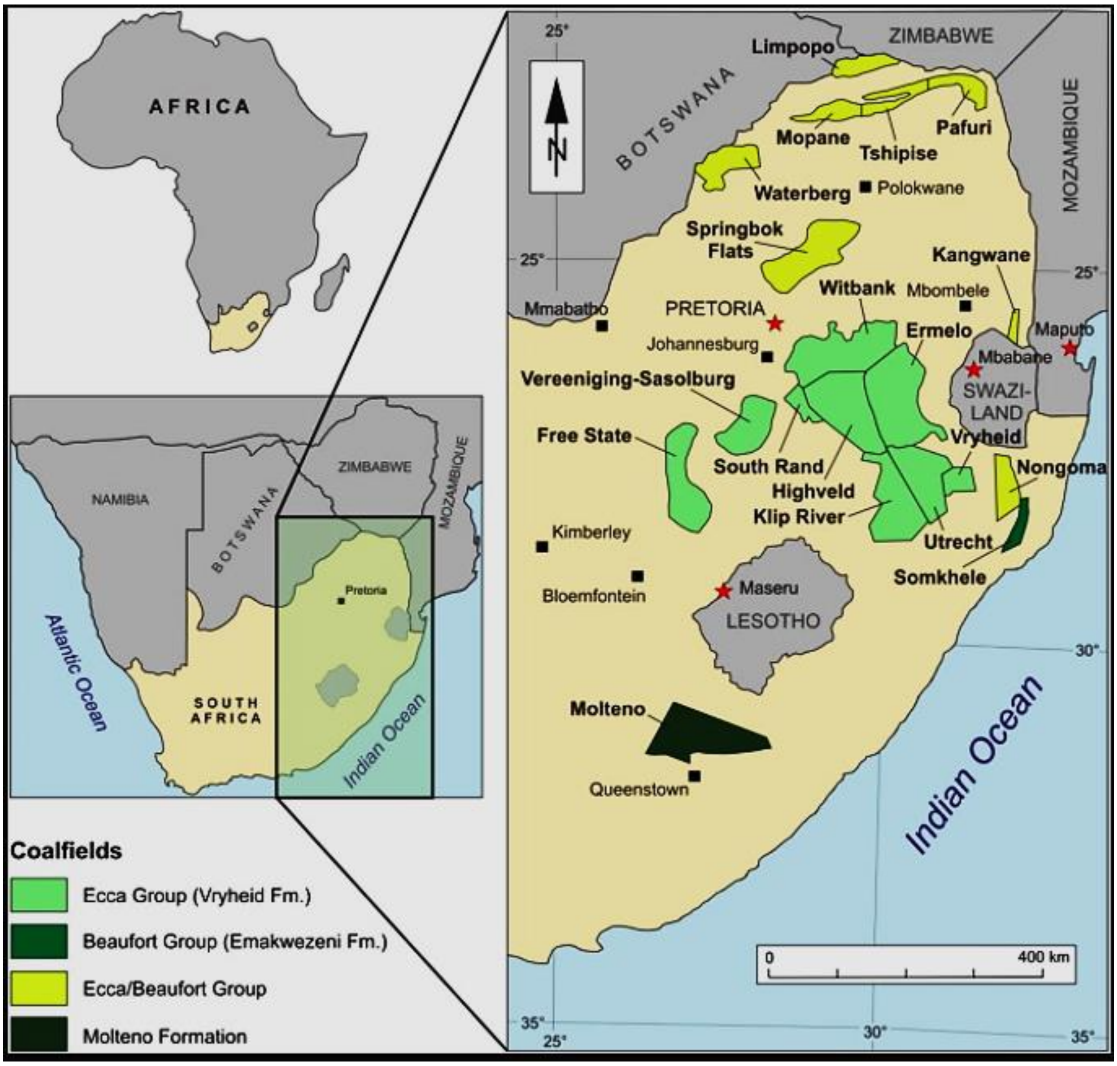
The Highveld Coalfield is located in the province of Mpumalanga; approximately 200 km southeast of Pretoria refer to Figure 2, immediately south of the Witbank Coalfield. It covers an area of approximately 7 000 km^2 (Wagner and Hlatshwayo, 2005), extending over a distance of approximately 95 km from Nigel and Greylingstad in the west, to Davel in the east and about 90 km in a north-south direction. The Highveld coalfield is known to be the next largest producing coalfield after the Witbank coalfields (Emalahleni) in South Africa (XMP Consulting (cc), 2017).

Whilst similar to the Witbank Coalfield in many ways including the overall general stratigraphy, the Highveld Coalfield is considered as a discrete unit and is separated from the Witbank Coalfield by the Smithfield Ridge. The geographic area encompassed by the coalfield is also the home to Eskom's Kriel, Matla and Tutuka power stations. Topographically, the study area is very gentle with an elevation of between 1500 m and 1750 m above sea level (Acocks, 1988; Digby Wells Environmental, 2014).

3.1.1.3 Geological Setting of the Coalfields

The Waterberg and Highveld coalfields are situated within the Karoo Supergroup where Africa's coal reserves are hosted. The Karoo Supergroup underlies approximately 60% of South Africa (Cairncross, 2001). Banks *et al., (*2011) stated that the Karoo Supergroup is a thick sequence of sedimentary rocks deposited between 300 and 180 million years. South Africa host almost 19 known-coalfields (Honcox and Götz, 2014) refer to Figure 2.

The distinction between these coalfields is based on geographic consideration and variation in the mode of sedimentation, origin, formation, distribution and quality of coal (Honcox and Götz, 2014). Wagner *and Hlatshwayo* (2005) made remarks that the largest proven reserves in South Africa occur in the northwest, north and northeast section of the Karoo Basin and that the coal seams are hosted in the division of the Supergroup known as the Ecca Group, which Beukes (1992) states that they were of the Permian age.



(Honcox and Götz, after Synman, (1998), 2014).

Figure 2 Coalfields of South Africa such as Waterberg, Highveld and Witbank Coal modified.

Dougall (2010) states that the Ecca Group consisted of sandstones and mudstones, together with coal seams, which were laid down by large river deltas that entered the ancient Karoo Sea. They also mention that in Southern Africa, the major period of coal formation commenced about 260Ma in the southern and eastern Mpumalanga region and northern**.** The Ecca Group in the Northern sector of the Main Karoo Basin is divided into three formations namely the Pietermaritzburg Shale Formation, the Vryheid formation and the Volksrust formation (Honcox and Götz, 2014). The Vryheid Formation occurs as a sequence of coarse clastic sediments between the overlying Volksrust and underlying Pietermaritzburg shale formations refer to Table 4. The Volksrust is composed mainly of coarse-grained arkose, conglomerate, micaceous siltstone, carbonaceous shale, coal seams and thin layers of limestone (Azzie, 2002).

The Vryheid Formation Coal Seams are composed of predominantly dull coal with minor carbonaceous mudstone intercalations again supplied as thermal coals (Dougall, 2010). Azzie (2002) states that the Vryheid Formation has abundant sedimentary structural features such as large-scale planar and rough cross bedding, indicating the presence of channel bars, ripple marks, scour channels and slump structures.

Some common rock-forming minerals associated with the coal reserves, occur as sedimentary rocks (siltstones, shales and sandstones) and clay minerals (kaolinite and illite) and as mineral grains within the organic matrix of the seam (quartz, carbonates, sulphides, dolomite, siderite and various oxides) (Pinetown and Boer, 2006; Dougall, 2010).

Table 4 shows the age, Group and Formation of the Karoo Supergroup.

SUPERGROUP	AGE (Ma)		GROUP	FORMATION
KAROO SEQUENCE		140	Drakensberg	Drakensberg
	Jurassic	195		Clarens
	Triassic	225		Elliot
	Upper Permian	230	Beaufort	Adelaide Subgroup
	Middle Permian	260	Ecca	Volksrust/Grootegeluk Formation
				Vryheid Formation
				Pietermaritzburg Formation
	Lower Permian	300	Dwyka	

(Golder Association, 2011).

Wagner and Hlatshwayo, (2005) and Honcox and Götz, (2014) described in addition coals contain hydrogen, oxygen, nitrogen and varying amounts of sulphur. Permian coals of the Southern hemisphere generally contain lower sulphides, chlorine and trace elements and have higher ash and inert organic matter than Carboniferous coals of the northern hemisphere. Deysel (2015) states that the sulphur content in coal content may range from low (less than 1%), through a medium (1 to 3%), to high (greater than 3%).

3.1.1.3.1 Geology of Waterberg Coalfield

The Waterberg Coalfield is an extensive deposit of coal in the Ellisras Basin. Coal was found in the Ellisras Basin in 1920, but for many years, little was done to explore the resource since at the time it was considered too remote to justify development (Fourie *et al.,* 2006; Oberholster, 2010). The coal-bearing horizon in the Ecca is the Volksrust formation, which has a thickness of 60m (Jeffrey, 2005) within the Karoo Supergroup. They were deposited from 260 to 190 million years ago and are bounded by the Limpopo Mobile Belt (Fourie *et al.*, 2006). Only after World War II, prospection continued and the Grootegeluk Mine was established in 1980. This mine is still operational today (Deysel, 2015).

The geology of the Waterberg is such that there are two formations being mined, the Upper zone called the Volksrust formation also known as Grootegeluk Formation (Aphane and Vermeulen, 2009). The lower zone is called the Vryheid Formation which contains four coal seams from zone 1 to 4 with the strata having a total thickness of 18m (Roux, 2004) refer to Table 4 and Table 5. The coal-bearing lithology contains 11 zones that are numbered from top to bottom where the coal seams occur in full succession. (Jeffrey, 2005; Aphane and Vermeulen, 2009).

Grootegeluk Coal Mine; have been numbered as coal zones 5–11 (Alberts, 1982; Botha, 1984; De Jager, 1976; Honcox and Götz, 2014). These zones are interlaminated with carbonaceous mudstone, siltstone with minor sandstone layers at the base. As a result, the coal yields from these zones are low (Telfer and Njowa, 2012).

Table 5 The regional geology of Waterberg coalfields and Highveld Coalfields.

Group	**Formation**	**Lithology and thickness**
Stormberg Group	Clarens	Sandstone ±80 m
	Elliot (Red bed)	Siltstone ±90 m
	Molteno	Coarse-medium sandstone ±20 m
Beaufort Group	Beaufort	Mudstone ±90 m
Ecca Group	Grootegeluk(BS1)	Interbedded bright coal and mudstone ±60 m
	Vreyheid	Sandstone, grit, mudstone, thick dull coal seam ±55 m
	Pietermaritzburg	Mudstone ±50 m

(Golder Association, 2011).

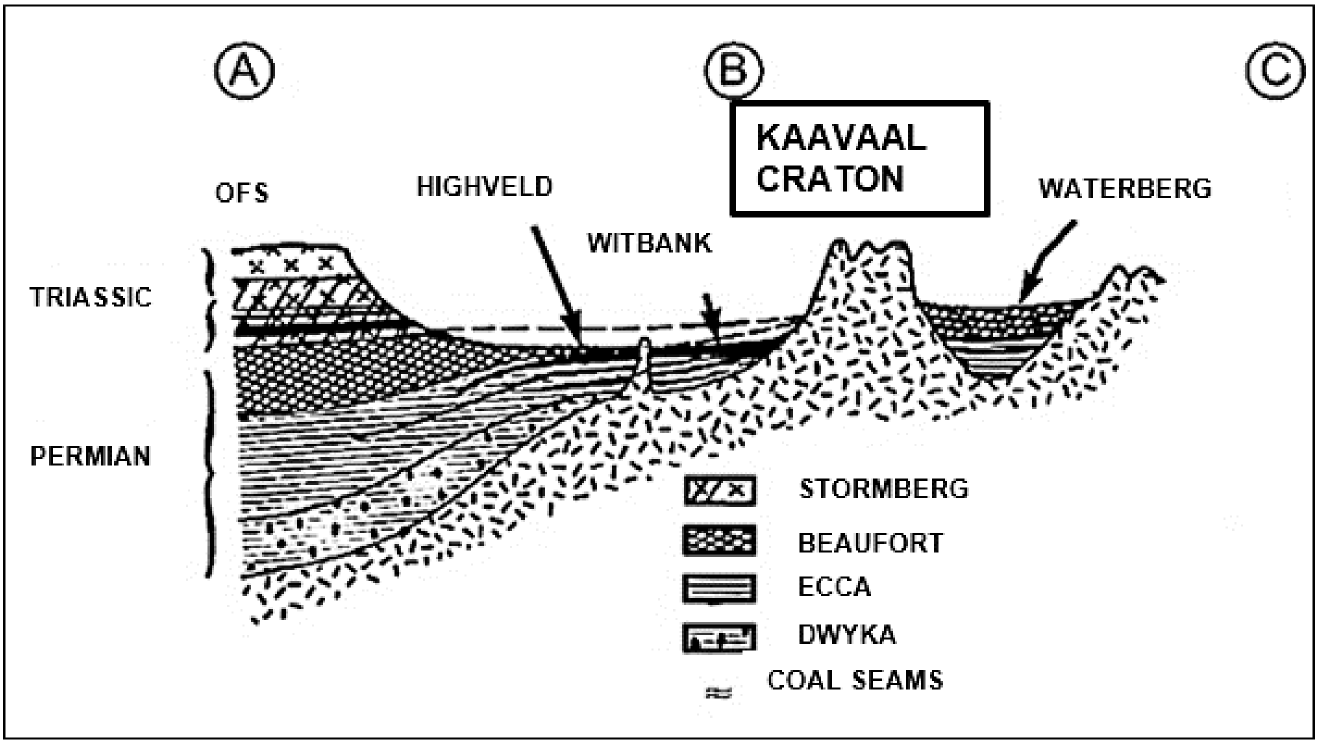
*3.1.1.3.2 **Geology of Highveld Coalfield***

The Highveld coalfields are similar to that of the Witbank coalfields and the Waterberg Coalfield is a counterpart of these two, they are situated in the Karoo Supergroup within the Ecca Group (Figure 3). There are other formations, which have not developed in the Witbank and Highveld coalfields such as the Pietermaritzburg Formation (Honcox and Götz, 2014).

The Vryheid Formation of the mid-Permian Ecca Group of the Karoo Supergroup hosts the sedimentary succession in which the coal deposits of the Highveld coalfield occur. The Coalfield hosts up to five coal seams within the middle Ecca Group sediments. The sediments are ascribed to deposition in glacial to fluvio-glacial and from shallow marine to fluviodeltaic environments (Pinetown and Boer, 2006).

The Highveld coalfield is characterised by numerous post-Karoo age dolerite sills, dykes and rocks of the Vryheid Formation, five separate bituminous coal seams are preserved in the Vryheid Formation, deposited under cool wet climatic conditions. The strata of the Vryheid Formation and Dwyka Group, which form the main part of the Karoo Supergroup in the study area, consisting primarily of sandstone, carbonaceous shale, siltstone and minor conglomerate (Pinetown and Boer, 2006; Honcox and Götz, 2014*)*.

There are five seams in this field, numbered from the No.1 seam at the base to the No. 5 seam on top. The No.4 seam, like its Witbank counterpart, is divided into an Upper and Lower Seam (Barker, 1999), both are widely developed but it is the Lower No. 4 seam, which is the prime target of this field (Snyman, 1998). Lithologically the succession consists of massive diamictite, with lesser matrix supported conglomerates and coarse-grained sandstones, with occasional siltstone and sandstone interbed, pebbly mudstones and varved siltstone. The diamictites are composed of sub-angular to sub-rounded clasts, set in a fine-grained pale brown dirty matrix (Pinetown and Boer, 2006; Honcox and Götz, 2014).



(Wagner and Hlatshwayo after (Falcon, 1986b), 2005).

Figure 3 Sedimentary succession Witbank-Highveld and Waterberg coalfields.

3.1.1.4 Free State Goldfields

The Free State Goldfields is located in the Free State province of South Africa. The discovery of the reef led to the establishment of the city of Welkom and the town of Riebeeckstad whilst towns such as Odendalsrus, Allanridge and Virginia enjoyed unbelievable growth. Welkom known to be the centre of the Free State goldfields is located approximately 256 km west of Johannesburg and 233 km northeast of Kimberley.

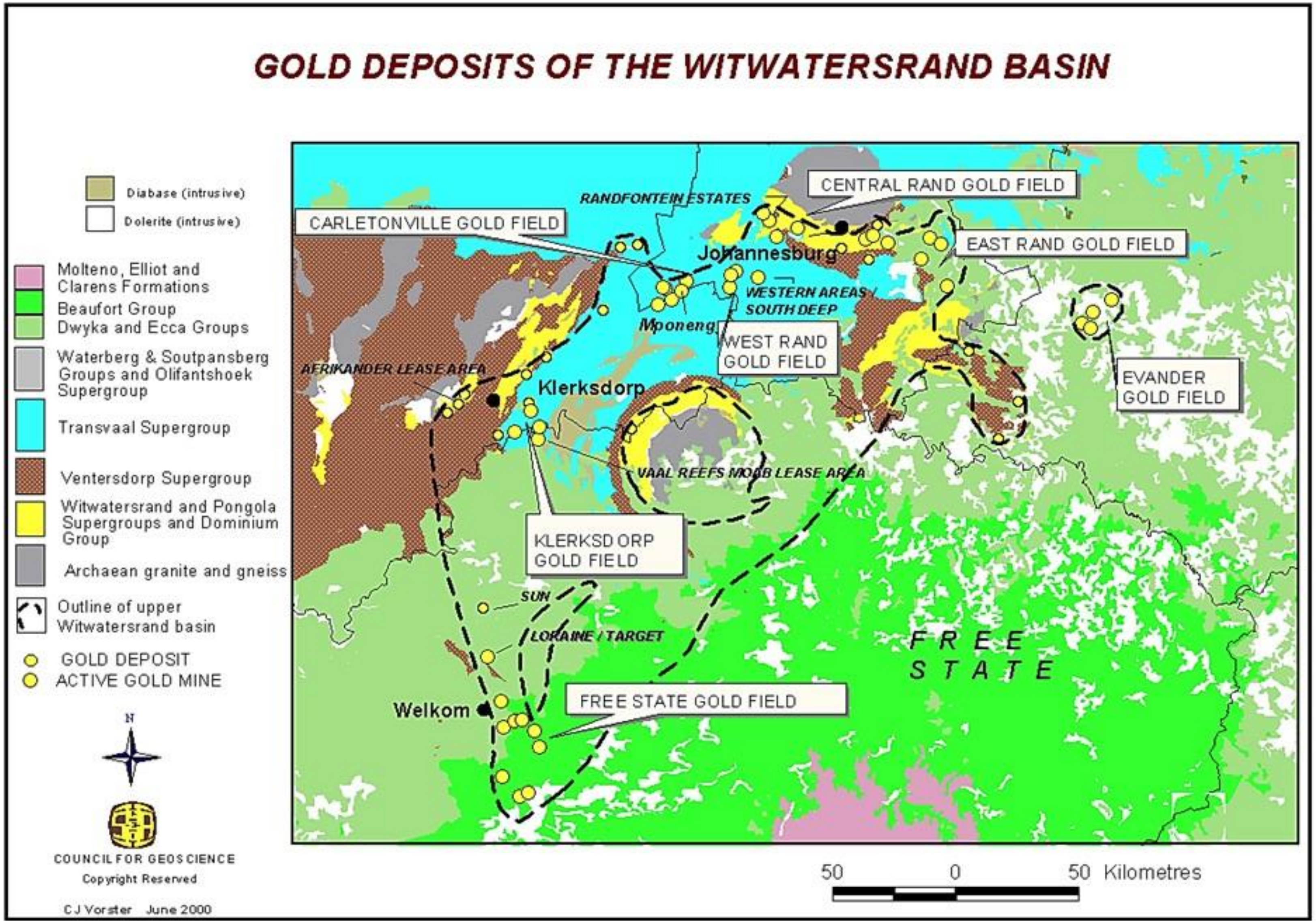
The discovery and development of the Free State Goldfields can be traced back to 1885. After intense exploration, which started in 1936, three gold-bearing conglomerates were identified in 1938. Further drilling led to the identification of the Basal Reef in March 1939, which led to a score of mines being developed in the Free State Goldfields (Honcox and Götz, 2014). The Free State goldfield is divided into two sections, cut by the north-south striking De Bron fault. This major structure has a downward vertical displacement to the west of about 1 500 m in the region of Bambanani, as well as a dextral shift of 4 km.

3.1.1.4.1 Goldfields Geological Setting

The Free State Goldfields is known to be located in the south-western edge of the Witwatersrand Basin (Minxcon (Pty) Ltd, 2010) refer to Figure 4. The Witwatersrand Basin is the largest known gold province in the world and the deposits have now been worked for well over 100 years. The Witwatersrand Supergroup often described as the Witwatersrand Basin is considered to be approximately 2.7 to 2.8 billion years, it is underlain by an Archaean (>3.1 Ga) granite-greenstone basement and the 3.086–3.074 Ma Dominion Group. It is unconformably overlain by rocks of the Ventersdorp (2.7 Ga), Transvaal (2.6 Ga) and Karoo (302-180 Ma) Supergroups (Minxcon (Pty) Ltd, 2010).

The Witwatersrand Basin is comprised of a six-kilometre thick sequence of shales, quartzites and conglomerates which have undergone low-grade regional metamorphism and divided into a lower, argillaceous unit and an upper, more arenaceous unit (Ainslie, 1981). This Basin extends laterally for approximately 300 km north-east/south-west and 100 km north-west/south-east on the Kaapvaal Craton. The upper portion of the sequence contains the laterally extensive, gold-bearing quartz pebble conglomerate horizons (commonly referred to as "reefs"). Further west, south and east of the basin are overlain by up to four kilometres of Archaean, Proterozoic and Mesozoic volcanic and sedimentary rocks (Gray *et al.*, 1998).

Gold is produced from seven goldfields within the basin, mainly from conglomerate horizons of the Witwatersrand, Ventersdorp and Transvaal Supergroups. The main gold producing reefs within the Free State Goldfield is the Basal (Steyn) Reef and the Leader Reef, as well as the Eldorado Reefs. The Leader Reef is located approximately 60 m below ground level (Minxcon (Pty) Ltd, 2010).



(Council for Geoscience, 2017).

Figure 4 Different Goldfield in South Africa.

Although the gold generally occurs in native form and is usually associated with pyrite and carbon, most of it has been subsequently modified and locally remobilised during secondary hydro-thermalism (Gold Fields, 2009). It was discovered that gold grains minerals were difficult to date due to them being composed primarily of gold and other minor amounts of heavy elements such as silver, mercury, bismuth, platinum, selenium group metals and other metals such as rhenium heavy metals including vanadium (Kirk *et al.,* 2003).

3.1.1.5 Impact of Gold and Coal Extraction

The process of extracting minerals between coal and gold differs to gold mines. The gold-mining process involves extracting the gold-bearing conglomerate layer and transporting it to the surface where it is crushed and the gold is extracted. Some conglomerate remains unmined as pillars for underground support. After extraction of the gold, the crushed rock is deposited on waste heaps known as slimes or tailings dumps (Gold Fields, 2009). The conglomerates that contain gold mineral typically contain about 3% pyrite, which ends up on the dumps.

The coal can be extracted by both underground and opencast mining methods. Unlike gold mining, coal is removed from the site and there is very little surface dumping. Both the coal and the host rock contain pyrite, but it is generally more abundant in the coal layers. The opencast overburden materials are removed and used as backfill then covered with soil and the terrain is then rehabilitated and vegetated (McCarthy, 2011).

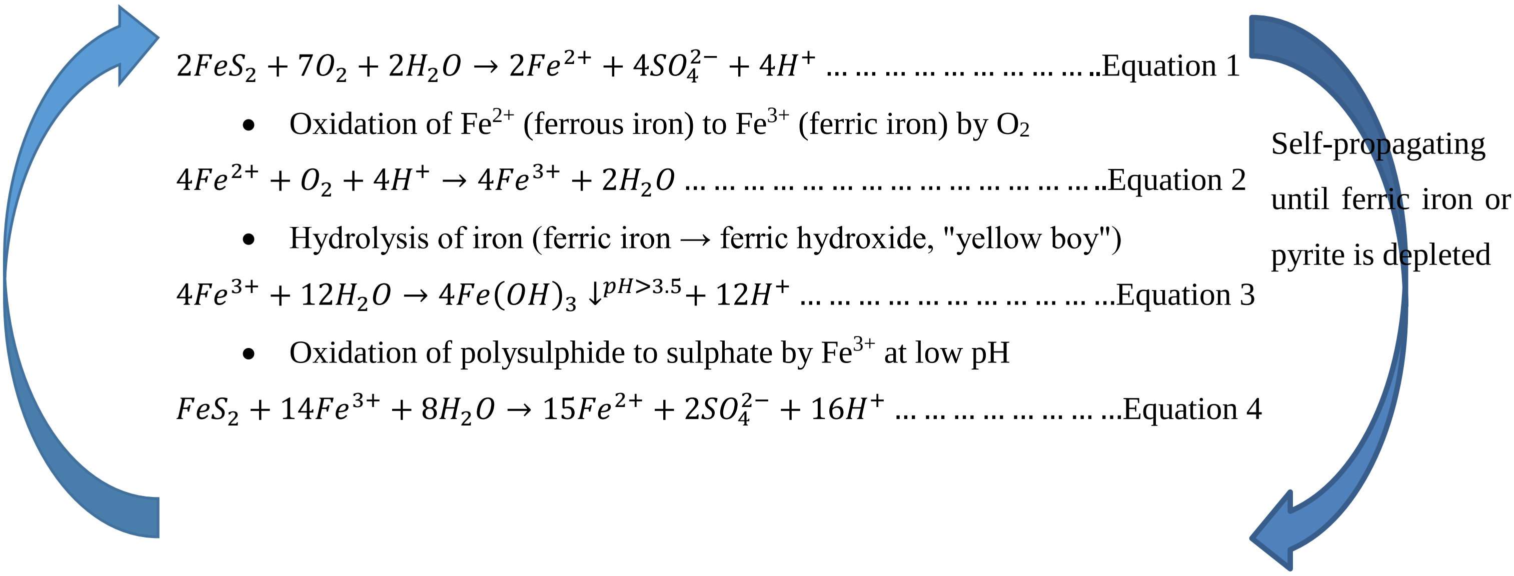
Mining increases the exposed surface area of sulphur-bearing rocks, walls of opencast and underground operations; it disturbs the host rock and hydrological regime around mined areas, allowing for excess acid generation beyond natural buffering capabilities found in host rock and water resources (Jennings *et al.*, 2008; Kuyucak, 2012). The vast volume of material moved and processed at mine sites in combination with reactive minerals means that mine drainage waters develop variable compositions that are distinctly different from natural background waters (Plumlee and Logsdon 1999a).

Epithermal Gold mines may produce mine drainage ranging from neutral mine drainage (NMD) with neutral pH and low dissolved element concentrations to acid mine drainage (AMD) with acidic pH values and elevated concentrations of trace elements. AMD is formed when rock-containing some of sulphide minerals mentioned in Table 6 are exposed to air and water, either because of opencast or underground excavation or from tailings disposal areas, resulting in the production of highly acidic water (Kumar, 2013).

Rainwater penetrating into the backfill dumps and oxidises the pyrite minerals forming sulphuric acid that percolates through the backfills or dumps dissolving heavy metals (Jamal *et al.*, 2013). The solution then emerges from the base of the dump or decants from the mines in the close openings to join the local groundwater or surface water as a pollution plume acidified by pyrite. AMD is characterized by pH values as low as 2-3 (high acidity), high salinity levels, elevated concentrations of sulphate (SO^4), iron (Fe), aluminium (Al) and manganese (Mn), raised levels of toxic trace elements such as cadmium (Cd), cobalt (Co), copper (Cu), molybdenum (Mo), mercury (Hg), arsenic (As), antimony (Sb), zinc (Zn) or others, which are in some cases radioactive (Akcil and Koldas, 2006; Oelofse, 2008).

At low pH, these metals are very soluble in water and are mobilized from mine working to downstream in dissolved form. Some of these metals become less soluble with increasing pH and can precipitate or adsorb to substrates at various pH thresholds. The precipitates are commonly Fe oxyhydroxides or occasionally more complex chemical compounds. The presence of these precipitates is often the most distinguishing characteristic of AMD and the bright yellow-orange colour of streambeds, due to Fe oxyhydroxides, historically led people to call it 'yellow-boy' (Nengovhela *et al.*, 2006). The acid mine generation process is illustrated in Equation 1 to Equation 5.

Oxidation of polysulphide to sulphate by O_2



$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2-} + 4H^+$ … … … … … … … … … ..Equation 1

- Oxidation of Fe^{2+} (ferrous iron) to Fe^{3+} (ferric iron) by O_2

$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$ … … … … … … … … … … … … … … ..Equation 2

- Hydrolysis of iron (ferric iron → ferric hydroxide, "yellow boy")

$4Fe^{3+} + 12H_2O \rightarrow 4Fe(OH)_3 \downarrow^{pH>3.5} + 12H^+$ … … … … … … … … … … …Equation 3

- Oxidation of polysulphide to sulphate by Fe^{3+} at low pH

$FeS_2 + 14Fe^{3+} + 8H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2-} + 16H^+$ … … … … … … … …Equation 4

Self-propagating until ferric iron or pyrite is depleted

……………………………………………………………

$$FeS_2 + \frac{15}{4}O_2 + \frac{7}{2}H_2O \rightarrow 2Fe(OH)_3 + 2SO_4^{2-} + 4H^+ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \text{...Equation 5}$$

(Nengovhela *et al.*, 2006; GARD 2009; Kuyucak, 2012).

The U.S. Environmental Protection Agency (1994) indicates that there are different major factors affecting the generation of AMD such as:

1. pH of the environment; concentration and type of the sulphur in rock.
2. Type and concentration of carbonate mineral present,
3. Mineral surface area available for reaction. Particle size of waste,
4. Extent of mineral liberation in the rock,
5. Available water and oxygen,
6. The presence of bacteria such as *Thiobacillus thiooxidans*, *Ferrobacillus ferrooxidans*, *Thiobacillus ferrooxidans*. These organisms are able to flourish under acidic conditions at PH as low as zero. There are different Stages in which AMD is formed concerning the oxidation of Pyrite minerals (GARD 2009).

Table 6 shows a partial List of Sulphide Minerals with the example of a rock containing this minerals shown in Figure 5.

Minerals	**Composition**
Pyrite	FeS_2
Marcasite	FeS_2
Chalcopyrite	$CuFeS_2$
Chalcocite	Cu_2S
sphalerite	ZnS
Galena	PbS
Millerite	NiS
Pyrrhotite	$Fe_{1-X}S$ (where $0<X<0.2$)
Arsenopyrite	FeAsS
Cinnabar	HgS

(U.S. Environmental Protection Agency. after (Ferguson and Erickson, 1988), 1994)**.**

Figure 5 Example of rock containing different sulphide minerals (Witthüser, 2016).

Figure 6 Example of Acid water from a mine (Witthüser, 2016).

3.1.1.6 AMD Impact in South Africa

South African mining industries so far have generated a huge amount of solid waste materials which throughout the years have been leaching and polluting the environment and affecting the living animals and organisms (Environment news, article and legislation, 2011). Mining has released highly toxic contaminants into the environment from AMD for more than a century. In the process, it has raised apprehensions under several economic, social and cultural rights (Digby Wells *et al.*, 2008).

AMD is an old issue, which has been expediently silenced by the mining houses and South African government for decades. The new government of South Africa has known about it since they came into power and the ex- apartheid government knew about it for decades. AMD is an issue for which there is no quick solution, not to mention the costs involved in the remediation of this problem (Environment news, article and legislation, 2011).

Mining poses a threat on the environment wherein AMD has contaminated water bodies that residents use to irrigate crops, water livestock, wash clothes, and swim, whereas dust and smog from coal and gold mining have blanketed communities. Some homes are built near and sometimes on those toxic and radioactive dumps (Docherty and

International Human Rights Clinic Harvard Law School, 2016). AMD from coal mining is problematic in the Highveld Coalfield in Mpumalanga and has been reflected by media attention on the consequences of severe pollution seen in the Loskop Dam and the Olifants River Catchment. It is likely that new coal mining in the Waterberg Coalfield (Limpopo Province) will lead to similar problems in the future if not well managed (CSIR, 2009).

On the West Rand, toxic water from the goldfields has already destroyed life in the Wonderfontein Spruit, Tweelopie Spruit, Tudor Dam and the Robinson Lake near Randfontein; even some of the borehole water are contaminated. In some areas, AMD has polluted the soil, so people cannot grow vegetables (Environment news, article and legislation, 2011).

South Africa has made significant progress in shifting policy frameworks to address mine closure and mine water management. The mining industry has changed its practices to conform to new legislation and regulations, but vulnerabilities in the current system remain (Oelofse, 2008). For the South African government to meet its corresponding obligations, it should take steps to remedy ongoing harm and prevent additional effects in the near term as well as to develop a more complete solution for the future (Environment news, article and legislation, 2011).

3.1.2 Soil Sample Collection and Preparation

3.1.2.1 Sample Collection

Samples were collected and stored at IGS Acid-Base Accounting (ABA) laboratory, part of the samples were used for other studies while the remaining samples were used for this research. The coalfields soil samples were collected from dump site and the gold samples were collected from the tailings dams. The samples contain minerals that are found in the mining environment where all ore are processed using methods that are currently in use. Samples from each field were mixed together with the aim to make them homogeneous and then the samples were used to create a dump such as a stockpile or tailings, which is almost a representation of un-oxidized tailings/stockpile in the field.

Previous mineralogical studies showed that the mine waste samples are of mixed sulphide mineralogy, containing varying amounts of iron (Fe)-based, pyrrhotite, pyrite, chalcopyrite, sphalerite, galena, arsenopyrite and are potential repositories for acid-generating potential and metal contaminants (Chopard *et al.*,2015). Not all sulphide minerals (for example, galena, Chalcopyrite and sphalerite), these minerals do not produce acid when oxidised by oxygen (Olubambi and Potgieter, 2009) but they are acid-generating and have the capacity to release metals on exposure to acidic water with ferric iron as the oxidant (Dold, 2000; GARD 2009; Jones *et al.*, 2016).

There are six samples in total, two samples weighing 1.6 kg from Waterberg coalfields, two samples weighing 1.5 kg from Highveld coalfields and two samples weighing 1.6 kg from Free State goldfields. The samples were 100% solid containing, they were then crushed and pulverised to a smaller size, passing through a 10 µm sieve.

3.1.2.2 Sample Preparation

Each sample is divided into four subsamples of 250 g for testing. The 250 g samples were further divided into sub-samples for agitation depending on the solid to liquid ratio required by each leach test method refer to Figure 7. After the agitation of the samples and extraction fluid, two leachates samples are extracted and submitted to the IGS laboratory for analysis.

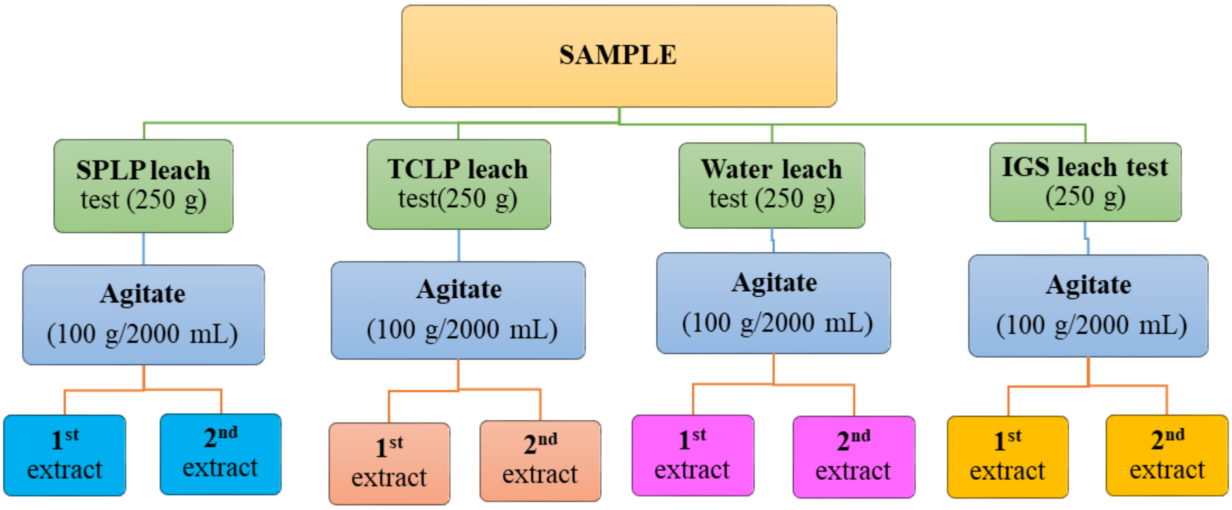


Figure 7 Sample distribution for leaching process divided according to the leach test methods.

3.1.3 Mineralogical Analysis of Samples

Mineralogical analysis is conducted to assess the chemical composition and the mineralogy of the samples before they are leached. X-ray diffraction (XRD) and X-ray fluorescence (XRF) spectrometer are used in order to analyse minerals and chemical compositions of the sample (PANanalytical, 2017). XRD analysis was conducted at the University of Free State’s Geology laboratory using Panalytical Empyrean, Cu tube, 45kV 40mA instrument whereas XRF analysis was conducted using the Panalytical Axios, Rh tube equipment.

XRD is the only laboratory technique that reveals structural information, such as chemical composition, crystal structure, crystallite size, strain, preferred orientation and layer thickness (PANanalytical, 2017). XRD is the mineral analysis that distinguishes minerals from each other based on their atomic or crystal structure rather than their optical properties or chemical composition. XRD is a quantitative method that identifies the minerals present within the samples (Baraka-Lokmane *et al*., 2007).

XRF spectrometer determines the chemical composition of a sample and can analyse several elements from beryllium to uranium. XRF spectrometry is one of the most widely used and versatile instrumental analytical techniques. An XRF spectrometer uses primary radiation from an X-ray tube to excite secondary X-ray emission from a sample. XRF is a semi-quantitative whole rock analysis mainly used to identify the chemical compositions of major and trace elements from selected samples (PANanalytical, 2017).

3.1.4 Leach Test

Leaching tests have an important role in providing information to support the assessment of potential environmental risks associated with the use of waste materials as soil amendment agents. This is because these tests will help determine the concentrations of chemical constituents in a sample that the extraction fluids are in direct contact (Department of Environment Regulation State of Western Australia, 2015). For these laboratory leach test method study, four batch leach tests methods were conducted, including tests that have been used for regulatory purposes. These different methods include Toxicity Characterising Leaching Procedure (TCLP), Synthetic

Precipitation Leaching Procedure (SPLP), Water Leach test method and the Diluted Sulphuric Acid-Base (DSAB) Leach test method. The samples were leached using specific extraction fluid chemistry, leaching ratios and equipment.

To conduct the static leach test, a certain amount of extraction fluid is required by the method to leach samples; the sample is leached with the extraction fluid based on the liquid to solid ratio required for the method. Sample material and the extraction fluid are then agitated together for a specific period, after agitation, leachate samples were extracted from the agitated material. Sample of the leachates were filtered and preserved for analysis at the laboratory and another portion was stored in the laboratory for further studies and as a reference in case the sample is not enough for analysis.

3.1.4.1 EPA Method 1311 -Toxicity Characterising Leaching Procedure (TCLP)

The TCLP leach test method is widely used by state and national agencies, this method is designed to determine the mobility of both organic and inorganic analytes present in the liquid, solid and multi-phase wastes (SERAS for TCLP, 2005). TCLP is a leaching procedure approved by the EPA for characterizing hazardous waste under the RCRA. The procedure is designed to simulate the worst-case scenario of co-disposal in municipal landfills (Al-Abed *et al.,* 2006). This procedure does not apply to volatile organic analytes (SERAS for TCLP, 2005).

The intent of this leachate procedure is to simulate the conditions that may be present in a landfill where water may pass through the landfilled waste and travel into the groundwater carrying the soluble materials with it (SERAS for TCLP, 2005). It was also designed to simulate leaching of heavy metals and organics from industrial wastes to be co-disposed in municipal solid landfills. Over several years, severe limitations of using TCLP in assessing contaminant leaching from industrial wastes such as mine and mineral processing wastes (MPW) have come to light due to its specificity only to landfill conditions and other physicochemical parameters (Al-Abed *et al.,* 2006).

TCLP uses a 1:20 solid-to-liquid ratio; it requires end-over-end rotation for 18 hours with extraction fluid used as a function of the alkalinity of the solid phase (Hageman *et al.,* 2015). The standard TCLP involves the crushing the sample to pass through a 9.5-mm screen. The method uses extraction fluid of either sodium acetate buffer solution having a pH of 4.93 ± 0.05 or an acetic acid solution having a pH of 2.88 ± 0.05 (Sorini, 1996). Incorrect use of the TCLP can lead to the inaccurate characterization of a sample because test might fail to accurately mimic the leaching process that occurs in the natural environment (Washington State Department of Ecology, 2003; Hageman *et al.*, 2015).

- ***Procedure***

For determining which extraction fluid to be used, samples were subjected to a required test of measuring 5 g small sub-sample of waste material into a 500 mL beaker where a 96.5 mL of reagent water was added into the samples and then sealed with parafilm. The samples were stirred for 5 minutes, after the pH was then measured. Samples had high pH, which led to them being subjected to the second step of the experiment test.

The second step requires addition of 3.5 mL of 1 N HCl solution to the samples and covered with parafilm, samples were then stirred at 50 ºC heat for 10 minutes and left to cool down. The pH was measured and found to be lower than 5 for all the samples. Since all the samples had lower pH, the leach test method required the use of extraction fluid #1 to leach all the samples.

- Extraction Fluid #1 - Add 5.7 mL of glacial CH_3CH_2OOH to 500 mL of reagent water. Add 64.3 mL of 1 N NaOH, and dilute to a volume of 1 L. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05.
- Extraction Fluid #2 - Dilute 5.7 mL of glacial CH_3CH_2OOH with reagent water to a volume of 1 L. When correctly prepared, the pH of this fluid will be 2.88 ± 0.05 (SERAS for TCLP, 2005).

To prepare extraction fluid #1 the method required the addition of 5.7 mL of glacial CH3CH2OOH to 500 mL of reagent water. Then add 64.3 mL of 1 N NaOH and dilute to a volume of 1 L. When correctly prepared, the pH of this fluid will be 4.93 ± 0.05. Since this research required a lot of extraction fluid, 142.5 mL of glacial CH_3CH_2OOH was added to a 12.5 L, then 1.61 mL of 1 N NaOH was added and diluted to a volume of 25 L with the pH observed to be 4.86 ± 0.05.

3.1.4.2 EPA Method 1312 -Synthetic Precipitation Leaching Procedure (SPLP)

The U.S. Environmental Protection Agency (US EPA) Method 1312, Synthetic Precipitation Leaching Procedure (SPLP) (US EPA, 2007) has been used in both regulatory and more commonly in non-regulatory leaching studies. This method is designed to predict and determine the potential for leaching metals into ground and surface waters from which municipal solid waste is excluded (Alforque, 1996). The intent of this leachate procedure is to simulate the conditions of an acidic precipitation that may be present in the States where rainwater may pass through the waste and travel into the groundwater carrying the soluble materials with it. This procedure does not apply to volatile organic compounds (US EPA, 2007).

The standard SPLP requires a solid sample to be crushed to pass a 9.5 mm sieve and requires a 20:1 liquid-to-solid ratio (Hageman *et al.,* 2015). This method requires a sample to be subject to end-over-end agitation for 18 hr with the use of slightly acidified extraction fluids that were designed to simulate acid rain using sulphuric and nitric acids 60/40 w/w. Extraction fluid #1 (pH of 4.2 ± 0.05) is to be used in studies of sites east of the Mississippi River (USA). Extraction fluid #2 (pH of 5.0 ± 0.05) is designed for use in studies of samples from sites west of the Mississippi River (Hageman *et al.,* 2000). For this study, all the mine waste samples were leached using the extraction fluid #1 with the pH 4.2 since it is more acidic. A modified version of the SPLP was used in this study and leaching parameters are provided below:

- ***Procedureb***

Leachate extraction fluid was prepared using 25 L of Distilled water acidified using concentrated H_2SO_4/HNO_3 with the ratio 6:4 (g/g) to a pH of 4.2 ± 0.05, this was conducted to simulate the acid rainfall in the mining environment.

3.1.4.3 Water Leach Test Method

This method is similar to that of TCLP, but then the only difference is that instead of using acetic acid or acid rain as extraction fluid, deionised water/reagent water is used. Deionised water with a pH of 6.15 was used to leach the waste materials for this method.

3.1.4.4 Diluted Sulphuric Acid-Base leach test method (DSAB)

The Diluted Sulphuric Acid-Base (DSAB) leach test method also known as IGS extraction leach test method (Deysel, 2015) developed at IGS laboratory. This method is developed to test and predict the leaching behaviour of Coal Combustion By-products (CCBs) and all other samples excavated in the mining process. Samples with a known mass are subjected to the leach test with a diluted sulphuric acid (H_2SO_4) solution of ± 0.1 N that mimics AMD to be tested. The pH of the sample mixture is measured after 24 hours of reaction time. Should the pH of the sample be above 2.50, drops of concentrated sulphuric acid are carefully added to lower the pH to just below 2.50, the medium should not become overly acidic (Deysel, 2015).

The reason for this is to ensure that the medium with the sample is in acidic condition as if exposed to acidic AMD. This is conducted in order to test the environmental leaching possibilities of a sample under acidic conditions. A sample with a base potential may not release any toxic metals in its neutral pH range and this will cause a false range of concentrations of specified constituents that will be below regulatory limits and the hazardous potential of the waste will be overlooked. It is important to test this in samples with a positive NNP (example fly ash/overburden) (Deysel, 2015).

- ***Procedure***

A 0.1 N H_2SO_4 solution was prepared in a 25 L plastic container using a 36 N concentrated H_2SO_4 by measuring 69.4 mL of H_2SO_4 into a 25000 mL to give us 0.1 N H_2SO_4 solution, this is done to mimic AMD. The pH of the extraction fluid was measured to be 2.24 before leaching any waste materials.

The samples are shaken for 1 hour 30 min at a room temperature of 25 ºC and made to rest for 24 hours. After 24 hours the pH is measured. For sample with a pH above 2.50, drops of concentrated sulphuric acid are carefully added to lower the pH to just below 2.50. The sample is stirred for 30 minutes and then left to rest for 18-24 hours after which pH was measured. This process is repeated if pH is still not below 2.50.

Table 7 gives a summary of the leach test methods, criteria and test conditions applied.

Table 7 leach test methods, criteria and test conditions applied.

Leach Test Method	**Liquid/Solid ration**	**Extraction liquid**	**Extraction Time (h)**	**pH Control**	**Temperature (^0C)**
TCLP	20:1	Acetic Acid	18	2.88 or 4.94	19-25
SPLP	20:1	H_2SO_4/HNO_3	18	4.2 or 5.0	19-25
Water	20:1	Distilled Water	18	6.15	19-25
DSAB	10:1	Diluted H_2SO_4	24	2.5	19-25

For each method, six samples of mine waste composite materials were leached according to the leach test method standards; 100 g of the sample was weighed and placed into a 2 L Schott Durban bottle where 2000 mL of extraction fluid was added to give the required solid-to-liquid ratio of 1:20. For Diluted Sulphuric Acid Base leach test method, 200 g of a sample was weighed and placed into the Schott Durban bottle where 2000 mL of extraction fluid was added in order to make a 1:10 liquid to solid ratio.

3.1.5 Analytical Methods

3.1.5.1 Leachate Analysis

After agitation of the samples from different leach test methods, the leachates were filtered and analysed using similar procedures, equipment, methodology and instrumentation. Leachate pH was determined on unfiltered and filtered leachate using a handheld Uetech instrument pH SIO (pH/mV/^{0}C meter) with pH electrode (Adwa VI/17 AD 1230) and on a Schott TW alpha plus titration instrument. Electrical conductivity (EC) was measured on unfiltered aliquots of leachate using YSI 3200 EC Conductivity Meter and a Schott TW alpha plus titration instrument. Samples were then filtered using a GN-6 Metrice® Grid 0, 4 µm single paper filter in a vacuum into a 50mL capped tube. Approximately 50 mL of each filtrate was collected in clean tubes.

The collected leachates were preserved by acidification with a drop of ultra-pure nitric acid (HNO_3) for the analysis of trace elements using inductively coupled plasma optical emission spectrometry (ICP-OES) with maximum hold time for the sample of 180 days. For anion analysis, samples were filtered and analysed using Ion Chromatograph (IC) Dionex DX-120 equipment with the maximum hold time of 28 days.

3.1.5.2 Quality Control

Quality control for all the leach test methods was piloted to ensure that the steps taken in attaining the results assures the generation of precise and accurate analytical data. Blanks and duplication of samples were taken to ensure a proper quality control of all the leach test methods and laboratory quality control.

3.1.5.2.1 Preparation Blank

A preparation blank is a sample of the appropriate volume of extraction fluid that is carried through the entire experimental process including analysis. The preparation blank is used to determine whether any added reagents, equipment, procedures or processes introduce any impurities to the samples. For laboratory studies, at least two-preparation blank of extraction fluid was run for each leach test method for the analytical batch.

3.1.5.2.2 Analytical Batch Duplicates

Analytical batch duplicates consist of two identical splits of a site composite that are carried through the entire experimental process, including analysis in order to determine the precision of the analytical results. For laboratory studies, at least one duplicate was run with each analytical batch. In this research, the samples were submitted to the lab as duplicates, two leachate extracts per sample for each leach test method Refer to Appendix 4 to Appendix 11.

3.1.6 Data Analysis and Interpretation

Extraction fluid of the four leach test methods were analysed for ionic strength and pH to check the leaching strength of the extraction fluid. The initial and final pH of the samples was also measured to compare the performance of the different leach test methods; since the material contain the same mineralogy.

The leachate chemical analysis was compared to the leachable concentration threshold standard from the NEM: WA Act No.59 of 2008 legislation and compared against the groundwater quality classification based on TDS from the World Health Organisation (WHO, 2011) and the water quality salinity classification index (Robinove *et al.*, 1958) for the classification of the waste material and leachate.

3.1.6.1 Comparison of Leached concentrations to Leachable concentrations in the NEM: WA Act No.59 of 2008

Leached concentrations from the applied leach test methods are compared to the leachable concentration threshold from the NEM: WA Act No.59 of 2008 (National Norms and Standards for the Assessment of Waste for Landfill Disposal, 2013) legislation. The comparison is conducted in order to classify the waste material to waste type, level of risk and to identify if the waste material poses low or high hazardous risk to the environment.

The comparison of the leached elements from the sample waste materials to the leachable concentration threshold from the NEM: WA Act No.59 of 2008 legislation is imperative; this is because the leachable concentrations from waste materials require comparison with the standardised values of concentrations from the standard regulation. The comparison with the NEM: WA Act No.59 of 2008 leachable concentration threshold will give indications on the performance of the different assessed leach test methods in regards to categorizing and classifying of the waste material.

The different way of categorizing and classifying waste material are described in Table 2 and Table 3. Total dissolved salts obtained from the leachates are compared against the groundwater quality classification based on TDS from the World Health Organisation (WHO, 2011) and the water quality salinity classification index (Robinove *et al.,* 1958) to check the quality of the generated leachate based on the known standards of salinity. This is to check if there is any relationship between the classifications of waste material leachates based on the NEM: WA No.59 of 2008 regulation and the classification based on the salinity and the quality of the leached water quality.

3.1.6.2 Hydrogeochemical Analysis

3.1.6.2.1 Piper trilinear and Stiff diagrams

The hydrogeochemical analysis is conducted by using Piper trilinear diagrams and stiff diagrams. The piper diagrams are used to study the similarities and differences in the composition of leachate and to classify them into certain hydrogeochemical facies. Piper trilinear diagrams were first attempted by Hill (1940) and refined by Piper (1944).

The stiff diagrams are graphics used to represent chemical analyses of major ions of water samples first developed by H.A. Stiff in 1951. Piper trilinear and stiff diagrams were applied to the different leachate generated from the four different leach test methods in order to check the hydrogeochemical facies for different waste materials.

The use of the hydrogeochemical facies is to identify and explain if the different leach test methods leached the materials differently by observing the hydrogeochemical facies generated from the methods and to address the effects of different extraction fluids applied to the leach test methods. The hydrogeochemical facies are generated using the WISH program developed at IGS.

From the leached concentrations, different major and minor elements were observed which are not considered in the NEM: WA Act No.59 of 2008 legislation. Elements which when leached in high concentrations may affect the quality of groundwater and surface water due to high concentrations of other elements not considered in the NEM: WA Act No.59 of 2008 legislation. Elements such as Fe, Al, Ca, Mg, Na, K and others are of consideration in this study but not include in the NEM: WA act No 59 of 2008.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Introduction

This chapter present and discuss the results on the assessed leach test methods. The discussion also includes the analysis of ionic strength and pH of the extraction fluid; the analysis of initial and final pH of waste materials before and after leaching process. The comparison of leached elements from the samples to the NEM: WA No.59 of 2008 regulation leachable concentration threshold standard for disposable purposes is also presented and discussed. Also presented is the results of TDS from samples leachate which were compared to groundwater quality classification based on TDS from the World Health Organisation (WHO, 2011) and the water quality salinity classification index (Robinove et al., 1958) in order to classify the leachate type.

This chapter also includes the analysis of leachate chemistry using hydrogeochemical analysis standard piper trilinear diagrams in order to check the possible water types that will be generated from the waste materials using the different static leach test methods. These are conducted to explain the differences in leachate chemistry generated by the different leach test methods that are applied to the materials containing the same mineralogy.

4.1.1 XRD and XRF Results

Mineralogical and geochemical analysis from X-ray diffraction (XRD) and X-ray Fluorescence (XRF) Spectrometer provides information on the content of minerals and elements from the sample (Baraka-Lokmane *et al.*, 2007). XRD was used to analyse minerals and XRF was used to analyse oxides and elements. The analysis information is important for the prediction of the leaching product during the leach test process. Furthermore, this information can assist in the prediction of the environmental effects of the leaching products (Roberston *et al*, 2015; Deysel, 2015). The aforementioned methods were applied on sample 1 (S1), Sample 2 (S2), sample 3 (S3), Sample 4 (S4), sample 5 (S5) and sample 6 (S6).

4.1.2 XRD

The XRD detected a total number of fifteen different minerals refer to Figure 8 and Appendix 2. Quartz is by far the most dominant mineral in all the samples with S5 containing the highest of 69% and S6 containing the least of 24%. Kaolinite is the overall second most dominant mineral in the samples although the analysis did not indicate any kaolinite on goldfield samples S1 and S2, the highest kaolinite is on S6 with the content of 36%. In terms of the mica content, S6 has 17% whereas the lowest is on S5 with 11%. Clinochlore has a high percentage on S1, S2 and S3 but not in S4, S5 and S6.

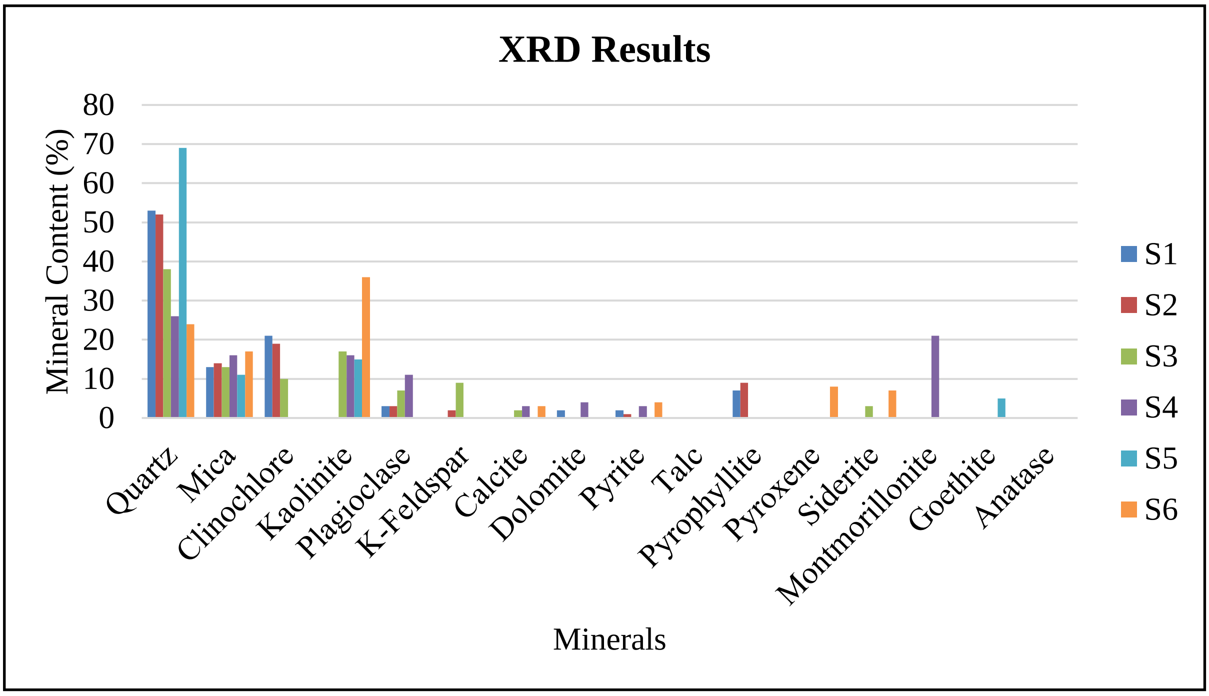


Figure 8 XRD results showing mineral content within the samples.

Sample S1, S2, S4 and S6 samples contain pyrite mineral with the highest content of 4% in S6 and the lowest content of 1% in S2. S3 and S5 do not contain any pyrite mineral. Calcite was detected in sample S3 (2%), S4 (3%) and S6 (3%) but not detected in S1, S2 and S5. Dolomite content of 2% in S1 and 4% was detected in S4 while the rest of the samples have no dolomite mineral detected. The XRD results show a possibility of S1, S2, S4 and S6 generating AMD due to the presence of pyrite mineral, however within these samples, there is a presence of calcite and dolomite minerals, which tend to act as buffers against AMD formation.

4.1.3 XRF

XRF oxide analyses have shown that all samples from the field contain silicon dioxide (SiO_2) with S1 having the highest content of 81.55% and the lowest in S6 with 15.28%. Refer to Figure 9. The second highest observed oxide in all the samples is aluminium oxide (Al_2O_3) with the highest content of 15.44% in S3 and lowest content of 7.11% in S1. XRF analyses confirmed the presence of iron oxide (Fe_2O_3) in the samples with the highest content 5.53% in S5 and the lowest content of 2.39% in S4.

Calcium Oxide (CaO) is also contained within the samples with the highest content of 2.31% in S3 and the lowest content of 0.18% in S5. The analysis results also show the presence of magnesium oxide (MgO) and Potassium oxide (K_2O) with the high content of (1.54 and 2.43%) and the low content of (0.22% and 0.19%) refer to Figure 9. The results observed from the analysis suggest that there is a possibility of acid generation in some of the samples containing Fe_2O_3 if the conditions are favourable and that there can be buffering probability due to the presence of CaO within the samples.

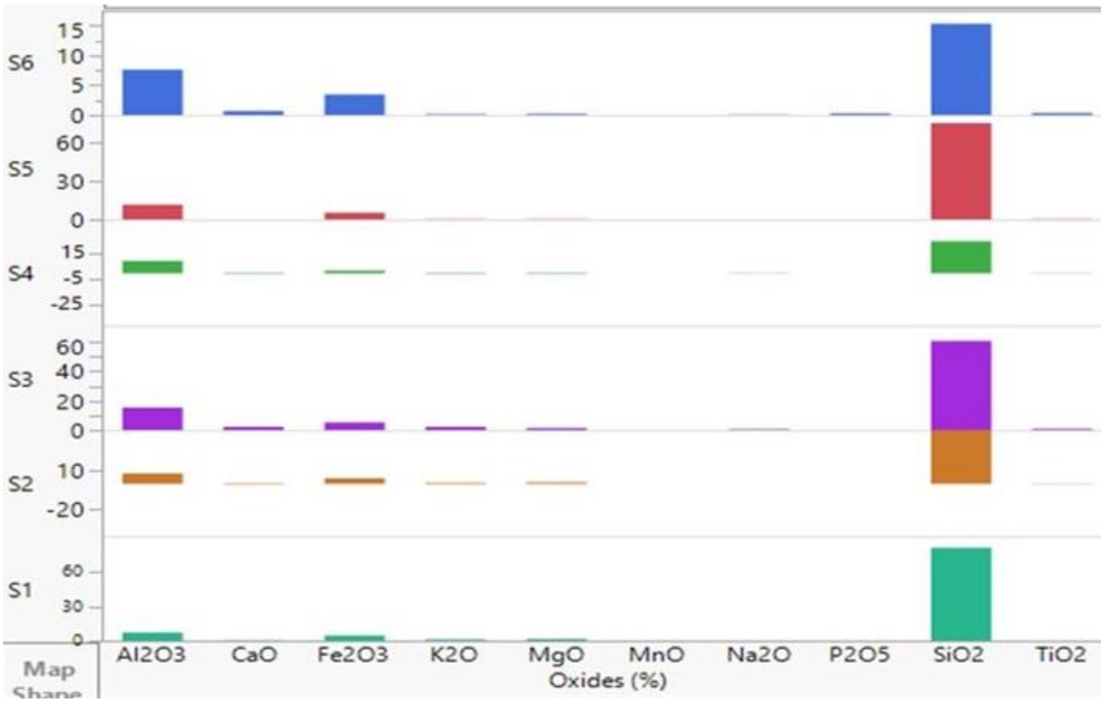


Figure 9 XRF analysis for oxides detected within samples.

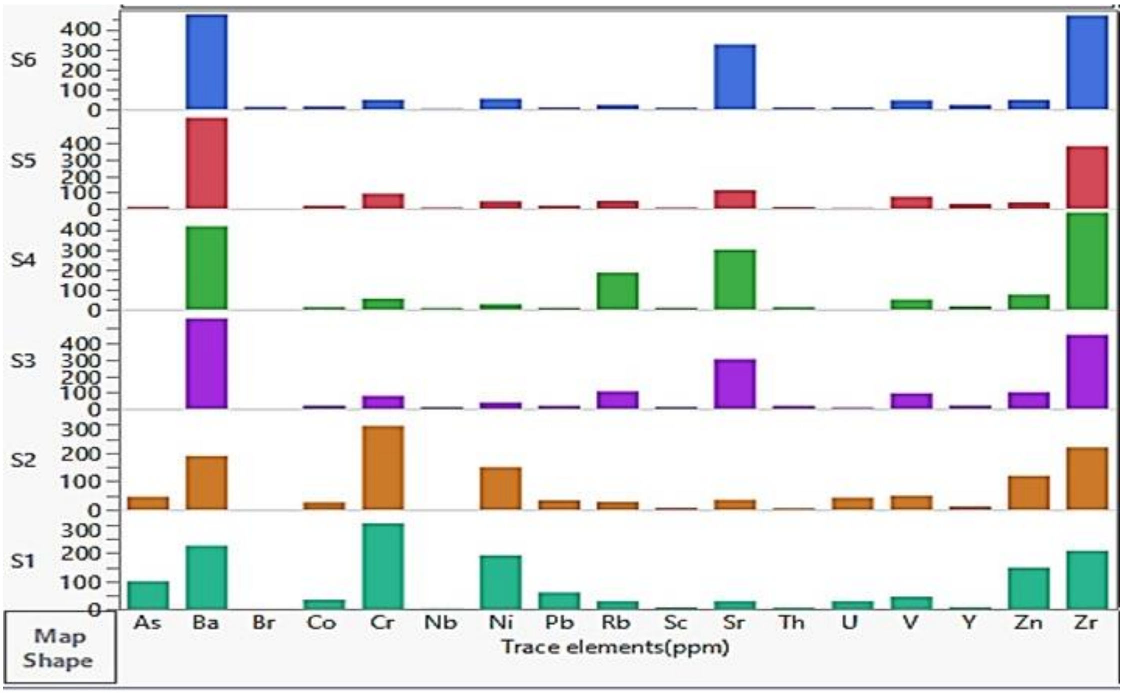


Figure 10 Concentrations of trace elements within the samples obtained from XRF analysis.

The XRF analysis in Figure 10 shows that seventeen trace elements were detected (Appendix 1) with Ba having the highest content of 560 ppm in S5 and the lowest content of 191 ppm in S2 followed by Zirconium (Zr) detected in all the samples with the highest value observed in S4 (490 ppm) and the lowest in S1 (209 ppm). The lowest trace element to be detected in all the samples is Nb, Th, U, Sc, Br, Co and Y. Some of the trace elements are only observed in a certain sample and not in other samples. Refer to Figure 10 for the results.

Minerals that are detected by the XRD in

Figure 8 XRD results showing mineral content within the samples. are known to contain trace elements and oxides while some are detected using XRF in Figure 9 and Figure 10. Some of the samples contain minerals such as pyrite that is known to be the main culprit in the formation of AMD if exposed to favourable conditions such as oxygen and water, while calcite and dolomite minerals are known to contain elements that function as buffers in the acidic conditions.

From the XRF analysis, it is observed that samples contain oxides and trace elements that are mainly found in AMD. Furthermore the XRF results show elevated quantities of Fe_2O_3 and Al_2O_3 oxides. This is because iron is an abundant element on the earth's crust, and it is associated with pyrite mineral or other hard rocks from coal, gold or other hard rock mines. Material from these mines can go through a series of reactions that leads to the formation of AMD resulting in water that has low pH and Fe_2O_3 present in large amounts due to pyrite oxidation, which may be summarized similar to Equation 1 to Equation 5.

The overall result of the reactions is the production of a fluid high in sulphuric acid and carrying large amounts of ferrous iron (Fe^{2+}). The same samples that were examined using XRF and XRD were subjected to leach test methods in order to categorize the total leached elements for the classification of the material and to determine if samples are hazardous or non-hazardous.

4.1.4 pH and Ionic Strength of the extraction fluids

The PHREEQC program (Parkhurst and Appelo, 1999) was used in order to determine the ionic strength of the extraction fluid (Table 8) applied to each leach test methods. Leaching behaviour and the solubility of the material is influenced by the ionic strength and pH of the extraction fluid (Washington state Department of Ecology, 2003). The calculation of ionic strength and measurements of pH values were conducted in order to check which extraction fluid has the most strength to leach the waste materials.

To calculate the ionic strength of the extraction fluid, the chemical analysis of extraction fluid obtained from the laboratory including pH, the temperature was inserted in the PHREEQC program to analyse the ionic strength of each extraction fluid. Ionic strength and pH values help in identifying the difference in the extraction fluids applied to leach the materials; this gives an indication of which method is expected to leach high concentrations of elements within the samples.

Table 8 Ionic strength obtained from PHREEQC and the initial pH of different extraction fluids applied to the leach test methods.

Leach test method	The ionic strength of Extraction fluid (mol/kgw)	Initial pH
SPLP	0.0003484	4.46
DSAB	0.07932	2.24
Water	0.00006005	6.15
TCLP	0.03892	4.86

Table 8 shows that the DSAB test method has an extraction fluid that has high ionic strength followed by TCLP then SPLP and lastly Water leach test method. The extraction fluid also has different pH, were the DSAB test method has the lowest pH followed by SPLP, TCLP and Water leach test methods. The difference in ionic strength and pH values show that the DSAB test method will leach more elements followed by TCLP, SPLP then Water leach test methods. This is because the Ionic strength and pH affects reaction rates as well as the solubility of ionic species, with solubility generally increasing as ionic strength increases and as the pH decreases the more elements becomes soluble.

4.1.4.1 **Initial and Final pH of Samples**

Figure 11 and Appendix 3 shows initial pH of assessed samples before they were subjected to different leach test methods and final pH values after samples were leached, all samples had initial pH higher than 7.00 except S6 which had a pH of 4.20. The different initial pH shows how neutral, alkaline or acidic samples are before subjection to any leaching process. The observation from the different pH shows that S6 is acidic compared to other samples. S1, S2, S3, S4 and S5 are alkaline. According to the logic results, S6 is prone to turn acidic due to the low pH observed before the sample is subjected to leaching.

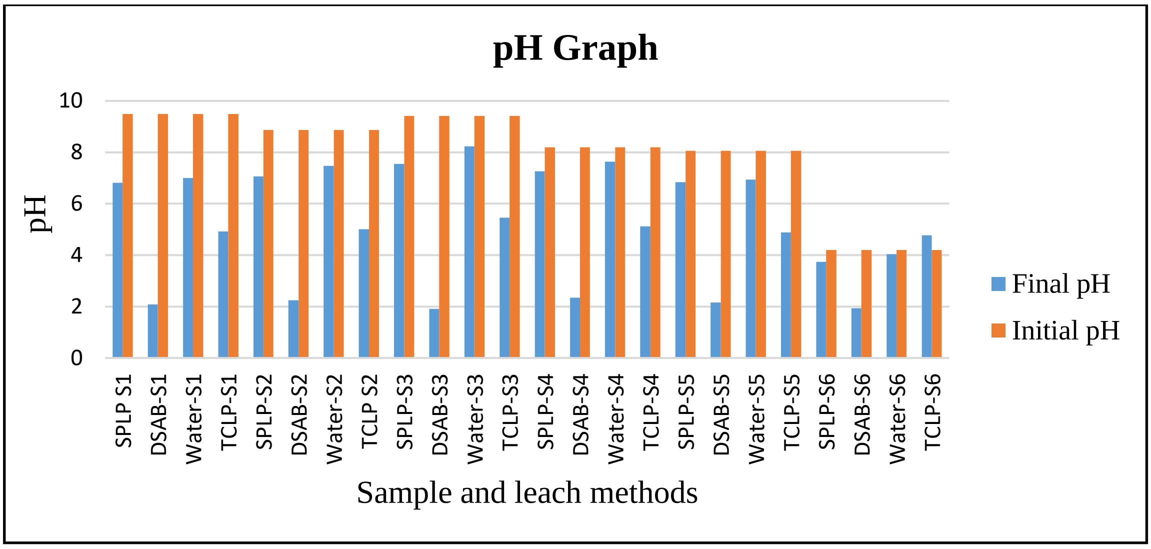


Figure 11 Initial pH of samples before subjection to leach test and final pH of the leachate after applied leach test methods.

The results reveal a gradual decrease in the pH values from the initial pH before any leaching proceeds to the final pH after the leaching process. It is observed that the pH from Water and SPLP leach test methods have slightly dropped but the sample remains neutral compared to the results from TCLP and DSAB leach test method. TCLP leach test method shows a slightly acidic pH value of samples ranging between 5.46 and 4.77 values. The DSAB leach test method shows that samples have acidic pH that is ranging from 2.35 and 1.91 values. The final pH values of the samples after they went through the process of leaching show that the results are influenced by the pH of the extraction fluids.

The results from S6 are different from the other samples; S6 had the acidic pH before undergoing any leaching. It was observed that after leaching the sample remained acidic with decreasing pH except for the TCLP leach test method, which shows a slight increase in the pH value. From the chemical analysis of the extraction fluid, it was observed that the TCLP extraction fluid contains alkalinity which is known to buffer the acid. The buffering of samples by the extraction fluid gives false results of leached elements since the total leachable concentrations will not be reflecting the full potential of leachable elements. To avoid the buffering of the final leachate due to the extraction fluid applied, samples should be leached using the extraction fluid that represent that which is similar to the leachate observed from the field.

4.1.5 Classification of Waste Materials Refer to Table 2 and Table 3.

Samples were subjected to static leach test methods in order to generate the leachates for the analysis of trace elements. The analyzed concentrations from the leachates generated from these different methods help to show the hazardous properties and substances within the material, these are important in order to understand the properties and the risk that the material poses on the environment. In this section, leached element concentrations are compared to the leachable concentrations threshold of elements of the NEM: WA No.59 of 2008 regulation in Table 3, in order to classify the waste for disposal purposes.

The classification of waste material for disposal purposes helps in understanding the severity the material poses to the environment whether the material posed a little risk (termed general waste) or poses a significant risk (a hazardous waste), the waste materials are then classified considering the waste type and waste risk profile refer to Table 2.

4.1.5.1 Comparison of leached elements to leachable concentration threshold

4.1.5.1.1 Sample (S1) and Sample (S2)

The leached concentrations obtained using SPLP, TCLP and Water leach test for the Free State Goldfield samples S1 and S2 show that the leachable concentrations of trace elements are less than LCT0 or equal to LCT0 but below LCT1 standard values (

Table 9 and Table 10). The concentrations are influenced by the ionic strength and pH of the extraction fluids.

The TCLP has leached high concentrations of elements compared to the SPLP and Water leach test methods; even though TCLP has leached high concentrations, the materials can still be classified as Type 3 waste similar to SPLP and Water. Type 3 waste is waste material with very low hazardous risk and must be disposed of on a Class C containment barrier design landfill.

The DSAB leach test method shows elevated concentrations of As, Pb and V in both samples. S1 has As and V concentrations that are above LCT1 but below LCT2 and Pb that is above LCT2 but below LCT3 standard values. S2 has As and Pb above LCT2 but below LCT3 and V that is above LCT1 but below LCT2 standard values refer to

Table 9 and Table 10. The concentration of the highly leached elements was observed from the XRF results where S1 and S2 contain As and Pb elements compared to other samples as earlier shown in Figure 10.

Table 9 Leached concentrations of trace elements for S1 compared to the leachable concentration threshold from the NEM: WA Act No.59 of 2008.

	Leach test methods				**Leachable Concentration threshold (NEM: WA Act No.59 of 2008)**			
Element	**SPLP-S1**	**DSAB-S1**	**Water-S1**	**TCLP-S1**	**LCT0 mg/L**	**LCT1 mg/L**	**LCT2 mg/L**	**LCT3 mg/L**
As	0.03	0.87	0.02	0.00	0.01	0.5	1	4
B	0.00	0.57	0.01	0.02	0.5	25	50	200
Ba	0.00	0.05	0.02	0.11	0.7	35	70	280
Cd	0.00	0.03	0.00	0.00	0.003	0.15	0.3	1.2
Co	0.00	0.99	0.01	0.12	0.5	25	50	200
Cr	0.00	1.09	0.01	0.00	0.1	5.0	10	40
Cu	0.03	1.61	0.03	0.08	2.0	100	200	800
Mn	0.42	15.51	0.33	3.69	0.5	25	50	200
Mo	0.01	0.03	0.02	0.01	0.07	3.5	7	28
Ni	0.02	3.41	0.03	0.37	0.07	3.5	7	28
Pb	0.00	1.13	0.02	0.06	0.01	0.5	1	4
Se	0.00	0.01	0.01	0.00	0.01	0.5	1	4
V	0.20	13.70	0.34	3.53	0.2	10	20	80
Zn	0.02	3.73	0.03	0.33	5.0	250	500	2000
Cl	1.59	0.00	1.40	0.00	300	15 000	30 000	120 000
NO_3 (N)	0.45	0.00	0.09	0.00	11	550	1100	4400
SO_4	307.34	427.83	300.92	291.52	250	12000	25000	100000
TDS	520.65	1417.11	486.42	1159.08	100	12500	25000	100000

Green colour shows that the concentration of the waste material is below LCT0 or equal to LCT0 and above LCT0 but below LCT1 the blue colour shows that the concentration is above LCT1 but below LCT2, oranges show that the concentration is above LCT2 but below LCT3and red colour shows that they are above LCT3.

The results obtained are more influenced by the ionic strength and the pH of the extraction fluid, the lower the pH of extraction fluid, the more the availability and mobility of trace elements increases due to the chemical form in which these trace elements are present in a sample. Due to the elevated concentrations of the mentioned trace elements, these waste materials can be classified as Type 1 waste, considered high-risk waste with high potential for contaminant release. These waste materials require a high level of control and on-going management to protect the health and the environment.

Table 10 Leached concentrations of trace elements for S2 compared to the leachable concentration threshold from the NEM: WA Act No.59 of 2008.

	Leach test methods				**Leachable Concentration threshold (NEM: WA Act No.59 of 2008)**			
Element	**SPLP-S2**	**DSAB-S2**	**Water-S2**	**TCLP-S2**	**LCT0 mg/L**	**LCT1 mg/L**	**LCT2 mg/L**	**LCT3 mg/L**
As	0.01	1.41	0.06	0.00	0.01	0.5	1	4
B	0.00	0.60	0.01	0.01	0.5	25	50	200
Ba	0.02	0.05	0.03	0.15	0.7	35	70	280
Cd	0.00	0.02	0.00	0.00	0.003	0.15	0.3	1.2
Co	0.00	0.57	0.01	0.05	0.5	25	50	200
Cr	0.00	0.87	0.01	0.00	0.1	5.0	10	40
Cu	0.03	1.53	0.03	0.08	2.0	100	200	800
Mn	0.09	25.97	0.05	7.69	0.5	25	50	200
Mo	0.01	0.03	0.03	0.01	0.07	3.5	7	28
Ni	0.01	2.26	0.02	0.20	0.07	3.5	7	28
Pb	0.00	1.32	0.02	0.01	0.01	0.5	1	4
Se	0.00	0.01	0.01	0.00	0.01	0.5	1	4
V	0.08	24.07	0.05	7.72	0.2	10	20	80
Zn	0.02	3.64	0.03	0.39	5.0	250	500	2000
Cl	2.47	0.00	2.26	0.00	300	15000	30000	120000
NO_3 (N)	0.46	0.00	0.08	0.00	11	550	1100	4400
SO_4	203.86	443.08	198.75	201.63	250	12000	25000	100000
TDS	353.83	1551.73	320.56	921.07	100	12500	25000	100000

Green colour shows that the concentration of the waste material is below LCT0 or equal to LCT0 and above LCT0 but below LCT1 the blue colour shows that the concentration is above LCT1 but below LCT2, oranges show that the concentration is above LCT2 but below LCT3and red colour shows that they are above LCT3.

4.1.5.1.2 Sample (S3) and Sample (S4)

SPLP, Water and TCLP leach test methods results show that the leached elements are in very low concentrations while some are below the detection limit (Table 11 and Table 12). The results show that within these two samples the elements are less than LCT0 or equal to LCT0 but below LCT1 standard values

Table 11 leached concentrations of trace elements for S3 compared to the leachable concentration threshold from the NEM: WA Act No.59 of 2008.

	Leach test methods				**Leachable Concentration threshold (NEM: WA Act No.59 of 2008)**			
Element	**SPLP-S3**	**DSAB-S3**	**Water-S3**	**TCLP-S3**	**LCT0 mg/L**	**LCT1 mg/L**	**LCT2 mg/L**	**LCT3 mg/L**
As	0.00	0.04	0.02	0.00	0.01	0.5	1	4
B	0.00	1.75	0.039	0.03	0.5	25	50	200
Ba	0.02	0.05	0.03	1.46	0.7	35	70	280
Cd	0.00	0.04	0.00	0.00	0.003	0.15	0.3	1.2
Co	0.00	1.51	0.01	0.01	0.5	25	50	200
Cr	0.00	0.40	0.01	0.00	0.1	5.0	10	40
Cu	0.01	0.87	0.03	0.02	2.0	100	200	800
Mn	0.01	13.80	0.01	2.06	0.5	25	50	200
Mo	0.03	0.02	0.07	0.01	0.07	3.5	7	28
Ni	0.01	1.01	0.02	0.07	0.07	3.5	7	28
Pb	0.00	0.066	0.02	0.00	0.01	0.5	1	4
Se	0.00	0.01	0.01	0.01	0.01	0.5	1	4
V	0.02	14.10	0.01	1.90	0.2	10	20	80
Zn	0.01	2.48	0.02	0.04	5.0	250	500	2000
Cl	1.56	0.00	1.40	0.00	300	15000	30000	120000
NO_3 (N)	0.45	0.00	0.10	0.00	11	550	1100	4400
SO_4	30.94	2139.58	25.35	25.92	250	12000	25000	100000
TDS	186.82	3998.53	167.71	654.32	100	12500	25000	100000

Green colour shows that the concentration of the waste material is below LCT0 or equal to LCT0 and above LCT0 but below LCT1 the blue colour shows that the concentration is above LCT1 but below LCT2, oranges show that the concentration is above LCT2 but below LCT3and red colour shows that they are above LCT3.

The material can be classified as Type 3 waste material which are considered very low-risk waste with low potential for contaminant release. These waste materials require some level of control and ongoing management to protect the health and the environment. The disposal requirement for this material is only allowed at a landfill with a Class C containment barrier design (or Class B or A).

Table 12 leached concentrations of trace elements for S4 compared to the leachable concentration threshold from the NEM: WA Act No.59 of 2008.

	Leach test methods				**Leachable Concentration threshold (NEM: WA Act No.59 of 2008)**			
Element	**SPLP-S4**	**DSAB-S4**	**Water-S4**	**TCLP-S4**	**LCT0 mg/L**	**LCT1 mg/L**	**LCT2 mg/L**	**LCT3 mg/L**
As	0.00	0.06	0.02	0.00	0.01	0.5	1	4
B	0.16	0.82	0.24	0.17	0.5	25	50	200
Ba	0.03	0.06	0.05	0.83	0.7	35	70	280
Cd	0.00	0.1	0.00	0.00	0.003	0.15	0.3	1.2
Co	0.00	0.13	0.01	0.01	0.5	25	50	200
Cr	0.00	0.05	0.01	0.00	0.1	5.0	10	40
Cu	0.01	0.34	0.04	0.04	2.0	100	200	800
Mn	0.01	3.13	0.02	0.99	0.5	25	50	200
Mo	0.02	0.02	0.06	0.01	0.07	3.5	7	28
Ni	0.01	0.37	0.02	0.08	0.07	3.5	7	28
Pb	0.00	0.03	0.02	0.03	0.01	0.5	1	4
Se	0.00	0.01	0.01	0.00	0.01	0.5	1	4
V	0.01	3.48	0.01	0.89	0.2	10	20	80
Zn	0.01	0.78	0.03	0.04	5.0	250	500	2000
Cl	2.00	0.00	1.24	0.00	300	15000	30000	120000
NO_3 (N)	0.00	0.00	0.00	0.00	11	550	1100	4400
SO_4	65.44	111.74	81.37	70.65	250	12000	25000	100000
TDS	258.68	1016.31	257.60	619.73	100	12500	25000	100000

Green colour shows that the concentration of the waste material is below LCT0 or equal to LCT0 and above LCT0 but below LCT1 the blue colour shows that the concentration is above LCT1 but below LCT2, oranges show that the concentration is above LCT2 but below LCT3and red colour shows that they are above LCT3.

DSAB leach test method show elevated concentration of V in sample S3 that is above LCT1 but below LCT3 (Table 11), this leads to the sample being classified as Type 2 waste. The elevation of elements from this sample is due to the addition of concentrated H_2SO_4 to reduce the pH of the sample to a pH lower of 2.5 since the pH was 3.6 after 24 hrs that the method was conducted.

Sample S4 is classified as Type 3 waste material by all the leach test methods since all the leached concentrations are below LCT0 or equal to LCT0 (Table 12). From these results, it is observed that the low values of chemical elements are caused by the lowering of pH value.

4.1.5.1.3 Sample (S5)

The leached concentrations obtained using SPLP, TCLP and Water leach test for Waterberg Coalfield samples show that the leachable concentrations of trace elements are less than LCT0 or equal to LCT0 but below LCT1 standard values (Table 13). The leached elements from the waste materials are influenced by ionic strength and pH of the extraction fluid.

Table 13 leached concentrations of trace elements for S5 compared to the leachable concentration threshold from the NEM: WA Act No.59 of 2008.

	Leach test methods				**Leachable Concentration threshold (NEM: WA Act No.59 of 2008)**			
Element	**SPLP-S5**	**DSAB-S5**	**Water-S5**	**TCLP-S5**	**LCT0 mg/L**	**LCT1 mg/L**	**LCT2 mg/L**	**LCT3 mg/L**
As	0.00	0.05	0.02	0.00	0.01	0.5	1	4
B	0.00	0.55	0.04	0.01	0.5	25	50	200
Ba	0.10	0.08	0.07	2.98	0.7	35	70	280
Cd	0.00	0.02	0.00	0.00	0.003	0.15	0.3	1.2
Co	0.00	0.58	0.01	0.03	0.5	25	50	200
Cr	0.00	0.17	0.01	0.00	0.1	5.0	10	40
Cu	0.01	0.41	0.03	0.02	2.0	100	200	800
Mn	0.13	44.37	0.03	3.09	0.5	25	50	200
Mo	0.01	0.05	0.03	0.01	0.07	3.5	7	28
Ni	0.02	0.51	0.03	0.06	0.07	3.5	7	28
Pb	0.00	0.04	0.02	0.00	0.01	0.5	1	4
Se	0.00	0.04	0.01	0.00	0.01	0.5	1	4
V	0.08	40.97	0.03	2.79	0.2	10	20	80
Zn	0.01	0.21	0.03	0.02	5.0	250	500	2000
Cl	1.40	0.00	1.15	0.00	300	15000	30000	120000
NO_3 (N)	0.0655	0.00	0.07	0.00	11	550	1100	4400
SO_4	7.64	260.14	5.79	8.60	250	12000	25000	100000
TDS	79.53	1019.26	72.35	776.49	100	12500	25000	100000

Green colour shows that the concentration of the waste material is below LCT0 or equal to LCT0 and above LCT0 but below LCT1 the blue colour shows that the concentration is above LCT1 but below LCT2, oranges show that the concentration is above LCT2 but below LCT3and red colour shows that they are above LCT3.

The TCLP has leached high concentrations of elements compared to the SPLP and water leach test methods due to the difference in the ionic strength of applied extraction fluids. According to the results observed from these leach test methods, waste materials can still be classified as Type 3 waste material. Type 3 waste shows that the waste material is very low hazardous and must be disposed of on a Class C containment barrier design landfill (or Class B or A).

The DSAB test method shows elevated concentrations of V and Mn, in which Mn is above LCT1 but below LCT2 and V is above LCT2 but below LCT3 standard values (Table 13). V element was observed to be contained within the sample with the concentration of 74 ppm from the XRF results; it is not a surprise that V is detected in the sample. Due to the elevated concentrations of the mentioned trace elements, the waste material can be classified as Type 1 waste, which is considered high-risk waste with high potential for contaminant release. These waste material requires a high level of control and ongoing management to protect the health and the environment and should be disposed only at a landfill with a Class A containment barrier design.

4.1.5.1.4 Sample (S6)

All the leach test methods result shows that the leached elements concentration is very small some are below the detection limit. The elements are less than LCT0 or equal to LCT0 but below LCT1 standard values (Table 14). The material can be classified as type 3 waste, which can be considered as very low-risk waste with low potential for contaminant release. This waste material requires some level of control and ongoing management to protect the health and the environment. The disposal requirement for this material is only allowed at a landfill with a Class C containment barrier design (or Class B or A).

For S6, the leach test method that leached more is the DSAB leach test method followed by the SPLP, Water and lastly the TCLP method. This sample was noticed to be more acidic compared to other samples with the pH of 4.2 before undergoing leaching processes. There is a difference in how this sample leached compared to the other samples; all the leach test methods show an increased content of SO_4 elements, which indicates the potential of the sample turning acidic. The results from this sample seem to have not been highly influenced by the ionic strength or pH of the extraction fluid since deionized water has leached high concentrations of some elements compared to the SPLP and TCLP leach test methods.

Table 14 leached concentrations of trace elements for S6 compared to the leachable concentration threshold from the NEM: WA Act No.59 of 2008.

	Leach test methods				**Leachable Concentration threshold (NEM: WA Act No.59 of 2008)**			
Element	**SPLP-S6**	**DSAB-S6**	**Water-S6**	**TCLP-S6**	**LCT0 mg/L**	**LCT1 mg/L**	**LCT2 mg/L**	**LCT3 mg/L**
As	0.00	0.142	0.04	0.00	0.01	0.5	1	4
B	0.01	1.14	0.18	0.06	0.5	25	50	200
Ba	0.07	0.08	0.07	0.09	0.7	35	70	280
Cd	0.00	0.03	0.01	0.00	0.003	0.15	0.3	1.2
Co	0.07	0.16	0.10	0.06	0.5	25	50	200
Cr	0.00	0.00	0.01	0.00	0.1	5.0	10	40
Cu	0.06	0.32	0.05	0.03	2.0	100	200	800
Mn	2.73	5.02	2.20	1.93	0.5	25	50	200
Mo	0.00	0.05	0.02	0.01	0.07	3.5	7	28
Ni	0.36	0.75	0.40	0.30	0.07	3.5	7	28
Pb	0.00	0.04	0.013	0.00	0.01	0.5	1	4
Se	0.00	0.04	0.01	0.00	0.01	0.5	1	4
V	1.41	5.02	2.30	1.71	0.2	10	20	80
Zn	0.20	0.42	0.20	0.11	5.0	250	500	2000
Cl	1.18	0.00	2.31	3.65	300	15000	30000	120000
NO_3 (N)	0.00	0.00	0.00	0.00	11	550	1100	4400
SO_4	555.02	1021.77	706.67	720.93	250	12000	25000	100000
TDS	768.08	2019.46	1013.39	959.89	100	12500	25000	100000

Green colour shows that the concentration of the waste material is below LCT0 or equal to LCT0 and above LCT0 but below LCT1 the blue colour shows that the concentration is above LCT1 but below LCT2, orange shows that the concentration is above LCT2 but below LCT3and red colour shows that they are above LCT3.

It is noticed that V, As, Pb and Mn has leached more in the extraction fluids used for DSAB and TCLP methods for all the samples. This phenomenon has been noted in some previous studies that shows that V in the +5-oxidation state is not very soluble in water and is usually first dissolved in sodium hydroxide solution (Clark, 1966) TCLP extraction fluid consists of acetic acid and sodium hydroxide; it is therefore possible that V is leaching more in this solution than in the SPLP and Water leach test methods. The reason some of the elements are leached in high concentration for DSAB leach test method is that these elements are highly soluble in acidic conditions. Since DSAB extraction fluid contains diluted H_2SO_4 at a low pH of 2.24 it is apparent that the elements will be highly leachable.

Investigations have found that V in aluminosilicate and mica clay minerals can be leached by sulphuric acid with the addition of hydrofluoric acid (HF), sodium fluorite (NaF), or calcium fluorite (CaF_2) to the leaching processing (Li, *et al.,* 2016). The XRD and XRF results show the presence of the mica and silicate minerals and V element, which could be the reason why V has been leached from the examined samples.

According to the assessment, TCLP, SPLP and Water leach test methods have classified all the tested waste materials under Type 3 waste material, which are very low hazardous risk waste. These waste materials can be considered as low-risk waste with some potential for contaminant release, the material requires proper control and ongoing management to protect health and the environment (NEM: WA No.59 of 2008).

The results from DSAB test method has shown that S1, S2 and S5 waste material can be classified as Type 1 waste material; S3 as Type 2 waste material and S4 and S6 waste can be classified as Type 3 waste materials. Type 1 waste material are considered high-risk waste with high potential for contaminant release, requiring high level of control and ongoing management to protect health, the environment and only allowed to be disposed at a landfill with a Class A containment barrier design.

Type 2 waste materials are considered low-risk waste but moderate hazardous waste with some potential for contaminant release, requiring proper control and ongoing management to protect the health and the environment, these must be disposed of on a Class B containment barrier design or Class A landfill. Type 3 waste material are considered very low hazardous risk waste, which must be disposed of on a Class C containment barrier design or Class B or A landfill (NEM: WA No.59 of 2008).

The DSAB leach test method is more aggressive compared to the other leach test methods. According to Deysel (2015), DSAB leach test method is designed to simulate AMD, which is described to have similar characteristics of the AMD. This method has the extraction fluid that is aggressive enough to leach trace elements similar to the elements leached in acidic conditions observed from the field over time. The challenge is that the method might overestimate the leachable concentrations of the elements due to its low pH and a higher ionic strength.It is observed that the SPLP and Water leach test methods show low values that are below LCT0 or equal to LCT0, due to the low ionic strength of their extraction fluids, they show no aggressiveness when leaching the material, which leads to them leaching elements in low concentrations. These results could show that these methods may underestimate the total leachable concentrations of elements within the samples. These methods seem to give a better representation of the initial stages of leaching of elements and not the leached elements over a long period. TCLP leach test method shows some of the elevated concentration, the only limitation with using these leach test method in leaching mine waste material is because the extraction fluid applied to these method cannot be found in the field, therefore, it does not truly represent what is happening in the field.

4.1.5.2 Salinity Classification of leachate

The salinity of the leachates is compared to the groundwater quality classification based on TDS from the World Health Organisation (WHO, 2011) and the water quality salinity classification index (Robinove *et al.,* 1958) (Appendix 12 and Appendix 13) in order to compare with the classification of waste materials based on the leachates using the NEM: WA No.59 of 2008.

The idea is to understand the classification of leachates based on salinity load (TDS) because it is a general indicator of water quality, assuming that the total salinity load would migrate into the aquifer (Cismowski *et al.*, 2006). This possibly shows that the classification of waste material only based on trace elements might show less risk on the impact of water quality, the salinity of the leachates can be a vast problem if it becomes too high, the final water quality can be unsuitable for use.

Table 15 The classification of TCLP leachate based on the Total Dissolved Salts (TDS) from the different samples.

TCLP				
Samples	**TDS (mg/L)**	**NEM: WA No.59 of 2008 Classification**	**Water quality salinity classification index (Robinove *et al.*, 1958).**	**Groundwater quality classification based on TDS (WHO, 2011).**
S1	1159.08	Type 3 Waste	Slightly saline	Poor
S2	921.07	Type 3 Waste	Fresh	Poor
S3	654.32	Type 3 Waste	Fresh	Fair
S4	619.73	Type 3 Waste	Fresh	Fair
S5	776.49	Type 3 Waste	Fresh	Fair
S6	959.89	Type 3 Waste	Fresh	Poor

The NEM: WA No.59 of 2008 classification is based on the overall classification of elements leachable concentration threshold and not on TDS only.

Table 15 shows the different classification of the leachate from the TCLP leach test method. Based on the leachable concentration threshold from the NEM: WA No.59 of 2008 all assessed waste material by TCLP were classified as Type 3 waste material, which means that the waste materials have a very low-risk hazard to the environment. According to water quality salinity classification index, the leachates from S1 are slightly saline while other samples are fresh and according to the WHO (2011) the leachate would result in water of fair to poor quality.

The results show that even if the leachate is classified as Type 3 waste, the leachate from this has the potential to cause poor water quality. From these results, it can be seen that even when the waste material is classified under very low-risk in Type 3 waste, groundwater or surface water can be impacted negatively due to salinity load of the leachate.

Table 16 The classification of SPLP leachate based on the Total Dissolved Salts (TDS) from the different samples.

SPLP				
Samples	**TDS (mg/L)**	**NEM: WA No.59 of 2008 Classification**	**Water quality salinity classification index (Robinove *et al.*, 1958).**	**Groundwater quality classification based on TDS (WHO, 2011).**
S1	520.65	Type 3 Waste	Fresh	Good
S2	353.83	Type 3 Waste	Fresh	Good
S3	186.82	Type 3 Waste	Fresh	Excellent
S4	258.68	Type 3 Waste	Fresh	Excellent
S5	79.53	Type 3 Waste	Fresh	Excellent
S6	768.08	Type 3 Waste	Fresh	Fair

The NEM: WA No.59 of 2008 classification is based on the overall classification of elements leachable concentration threshold and not on TDS only.

The results from SPLP and Water leach test methods in Table 16 and Table 17 shows that the samples were classified as Type 3 using the NEM: WA No.59 of 2008 based on the leachable concentration threshold. It is also observed that the samples have the same classification based on the water quality salinity classification index, with all the waste materials having been classified as fresh water. These show that there is no impact that will be caused by the waste material on the environment based on the TDS. WHO (2011) classify S1 and S2 as good quality S3, S4 and S5 as excellent water quality which can even be suitable for drinking.

Table 17 The classification of Water leachate based on the Total Dissolved Salts (TDS) from the different samples.

Water				
Samples	**TDS (mg/L)**	**NEM: WA No.59 of 2008 Classification**	**Water quality salinity classification index (Robinove *et al.*, 1958).**	**Groundwater quality classification based on TDS (WHO, 2011).**
S1	486.42	Type 3 Waste	Fresh	Good
S2	320.56	Type 3 Waste	Fresh	Good
S3	167.71	Type 3 Waste	Fresh	Excellent
S4	257.60	Type 3 Waste	Fresh	Excellent
S5	72.35	Type 3 Waste	Fresh	Excellent
S6	1013.39	Type 3 Waste	Slightly saline	Poor

The NEM: WA No.59 of 2008 classification is based on the overall classification of elements leachable concentration threshold and not on TDS only.

For SPLP and Water leach test methods, S6 was classified differently from other samples even though the sample was classified in the same class as other samples in Type 3 using the NEM: WA No.59 of 2008. The leachate from this sample based on the TDS from SPLP method (Table 16) is classified as fair quality by the WHO standard but by the salinity classification, it is classified as fresh water.

For the Water leach test method Table 17 this sample was classified as slightly saline and as poor quality. The results for this sample show the potential to cause poor water quality resulting from the leachate due to the possible slight saline and poor water quality. From the results, it can be seen that the classification of the sample depends on the applied leach test method; this is because each method has leached waste materials differently depending on the ionic strength and pH of the extraction fluid.

DSAB leach test method (Table 18) shows that all the leached samples have leachates that are slightly saline according to water salinity classification index and according (WHO, 2011) the samples is of poor and unacceptable quality. The results of water quality classification suggest that all the samples have the potential of changing the quality water.

Table 18 the classification of DSAB leachate based on the Total Dissolved Salts (TDS) from the different samples.

DSAB				
Samples	**TDS (mg/L)**	**NEM: WA No.59 of 2008 Classification**	**Water quality salinity classification index (Robinove et al., 1958).**	**Groundwater quality classification based on TDS (WHO, 2011).**
S1	1417.11	Type 1 Waste	Slightly saline	Poor
S2	1551.73	Type 1 Waste	Slightly saline	Poor
S3	3998.53	Type 2 Waste	Slightly saline	Unacceptable
S4	1016.31	Type 3 Waste	Slightly saline	Poor
S5	1019.26	Type 1 Waste	Slightly saline	Poor
S6	2019.46	Type 3 Waste	Slightly saline	Unacceptable

The NEM: WA No.59 of 2008 classification is based on the overall classification of elements leachable concentration threshold and not on TDS only.

It is observed that the results of the classification of waste material using the NEM: WA No.59 of 2008 is different from the WHO and the salinity classification, they use different approaches but practically all of them are important because they assess the potential impact on the water quality. The NEM: WA No.59 of 2008 considers elements if they are above leachable concentration thresholds for classification, while the other classifications are more focused on the TDS for classification.

According to the NEM: WA No.59 of 2008, leachate can be classified as highly toxic due to one element that is above the recommended leachable concentration standard. The NEM: WA No.59 of 2008 also includes TDS on the list of considerable elements, if the classification of the material was based on TDS using the NEM: WA No.59 of 2008 the leachates from all the samples and all applied leach test methods would have been Type 3 waste which is considered very low-risk hazard.

4.1.6 Hydrogeochemical characteristics

Hydrochemical facies evaluation is extremely useful in providing a preliminary idea about the complex hydrogeochemical processes in the subsurface. Determination of hydrogeochemical facies has been extensively used in the chemical assessment of groundwater and surface water for several decades. This method is able to provide sufficient information on the chemical quality of leachate, particularly the origin (John, 2016). Hydrogeochemical characterization of leachate presents the condition of leachate with respect to its quality; the aim for using hydrogeochemical characterisation in this study is to distinguish the hydrogeochemical facies generated using different leach test extraction fluids.

4.1.6.1 Piper trilinear and stiff diagrams

Piper trilinear and stiff diagrams were used in order to identify the hydrogeochemical facies of the leachates for different samples. Major ions from the leachates were plotted on the Piper trilinear and stiff diagram to identify the difference between the different leach test methods applied to differentiate the leachate types and designate ionic nature of leachate. This illustration of ionic signature helps in uncovering the principal ions controlling the leachate chemistry. Different classification of leachate type observed from different samples using different leach test methods are displayed from Figure 12 to Figure 24.

This study is focused on mine waste material. The example applied is that the mine drainage samples plot close to the top corner of the diamond shape and towards the SO_4 apex in the anion field while in the cation field. The samples plot almost in the middle along the Ca, Mg axis, indicating that this water type evolved from pyrite or arsenopyrite (Kortatsi *et al.,* 2008).

The analytical results of a leachate generated from DSAB leach test method leachates were not analysed for anions due to the low pH ranging from 2.35 to 1.91 on the samples, which cannot be analysed by the ICP-OES. When the obtained results of cations and trace metals are plotted on the diagrams, they show the elevated concentrations of cations.

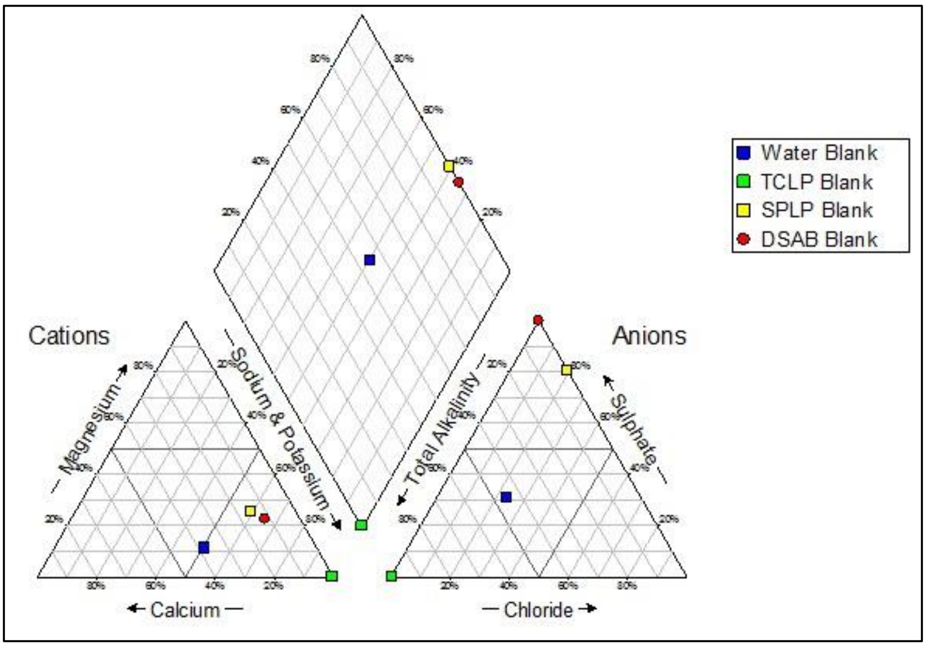


Figure 12 Piper trilinear graph showing the characterization of Blank leachate type for different assessed leach test methods.

Figure 12 shows the results of hydrogeochemical facies of the extraction fluids applied to different leach test methods. The piper trilinear diagram shows that the extraction fluid of DSAB and SPLP leach test method are almost the same containing Ca-SO_4-Cl water. The TCLP leach test method is characterised by Na+K-HCO_3 water. The Water leach test method extraction fluid is characterised by Ca-HCO_3.

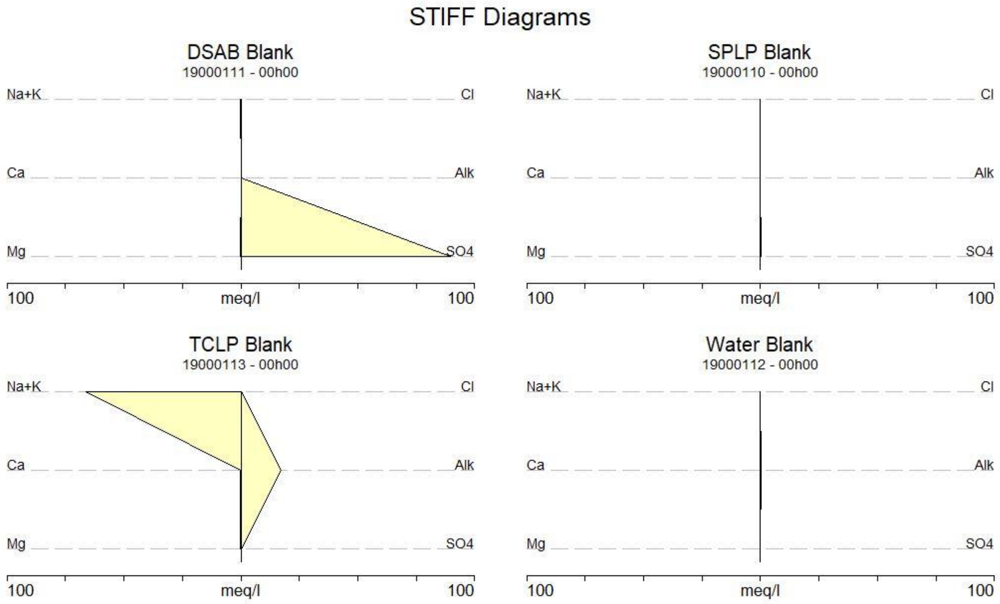


Figure 13 Stiff Diagram showing the water type and the concentration of elements in meq/l for Blank samples.

The results shown from the stiff diagram shows that the blank sample from SPLP and Water leach test methods have very low concentrations of cations and anions in meq/l. The TCLP leach test method blank sample contains high concentration of Na+K and alkalinity. The DSBL leach test method blank sample contains high value of SO_4 concentration than the other methods.

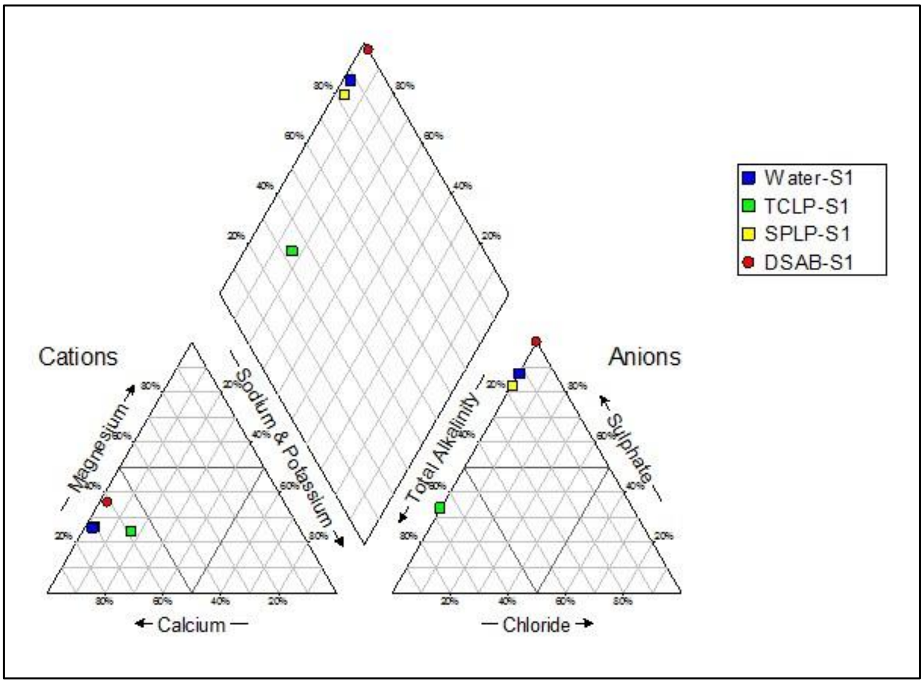


Figure 14 Piper trilinear graph showing the characterization of S1 leachate type for different assessed leach test methods.

The results from Figure 14 show leachate composition of S1. The SPLP and Water leach test method are characterized by Ca-SO_4. TCLP leachate for S1 Ca-HCO_3 this shows that the leachate contains high total alkalinity. Within all the assessed leach test methods, Water and SPLP have similar generated leachate hydrogeochemical facies.

TCLP leachate type is different from leachate type generated using other methods (see Figure 14). This is due to the uniqueness of extraction fluids applied on each method. TCLP method uses different extraction fluid compared to other methods, which contains elements that are not detected in other methods; this influences the composition of the leachate characteristics

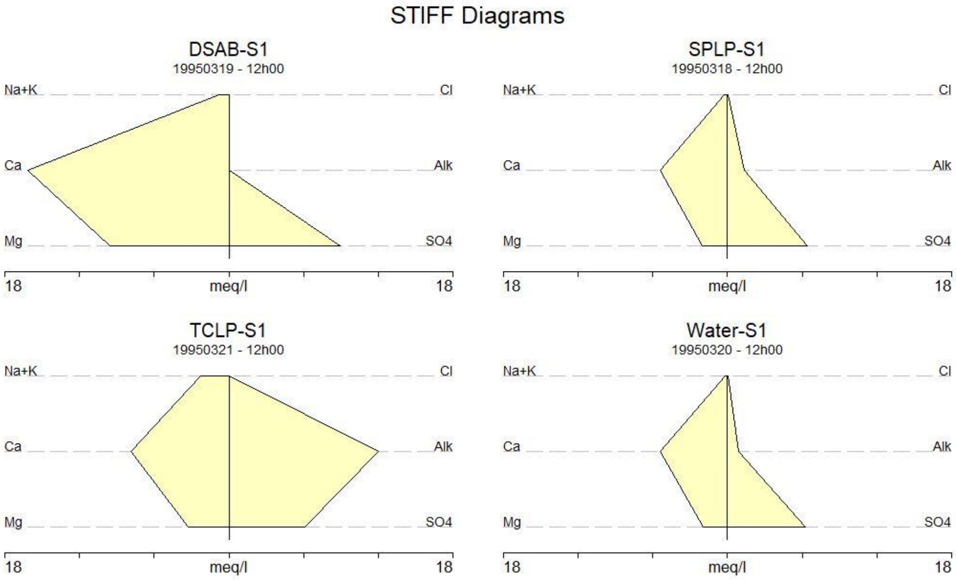


Figure 15 Stiff Diagram showing the water type and the concentration of elements in meq/l for sample S1.

Figure 15 shows the elements contained in S1 in meq/l. The SPLP and Water leach test method shows a similar trend of the type of water chemistry, the water for these two methods contains SO_4 and Ca elements that are higher than the other leached elements. The DSBL leach test method shows high concentration of Ca, Mg and SO_4. The TCLP leach test method shows that the sample contains Ca and high alkalinity.

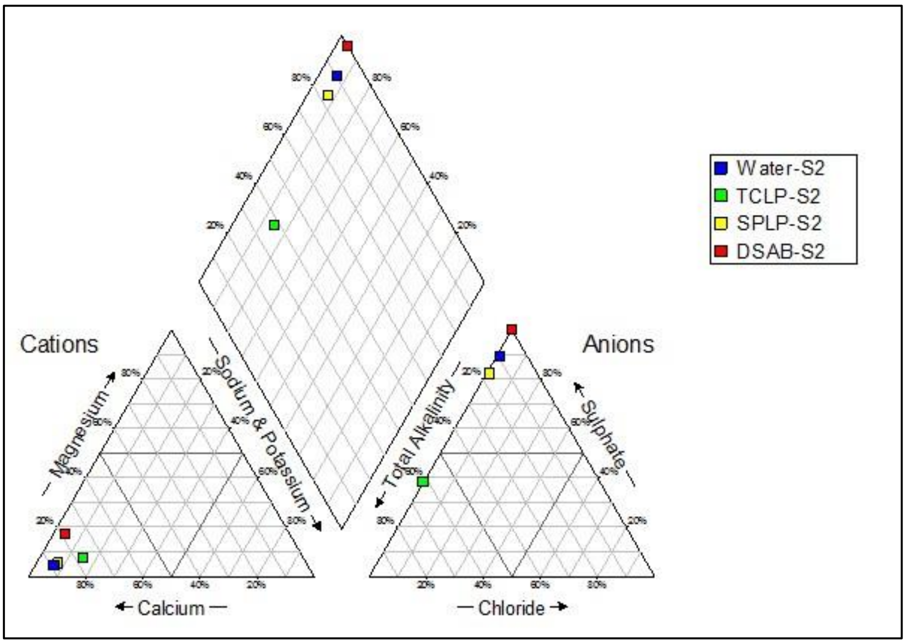


Figure 16 Piper trilinear graph showing the characterization of S2 leachate type for different assessed leach test methods.

Figure 16 show results for S2 leachate, where SPLP and Water leach test leachate is characterized by Ca-SO_4. According to the piper diagram, TCLP leachate is characterized by Ca-HCO_3. Similar with the observation from S1 piper diagram, TCLP leach test methods give a total different leachate type compared to other leach test methods.

The other three-leach test methods show the domination of Ca-SO_4, TCLP shows that the sample containing the same mineralogy contains hydrogeochemical face characterised by Ca- HCO_3. The differences in the hydrogeochemical facies are due to the applied different extraction fluid containing different elements.

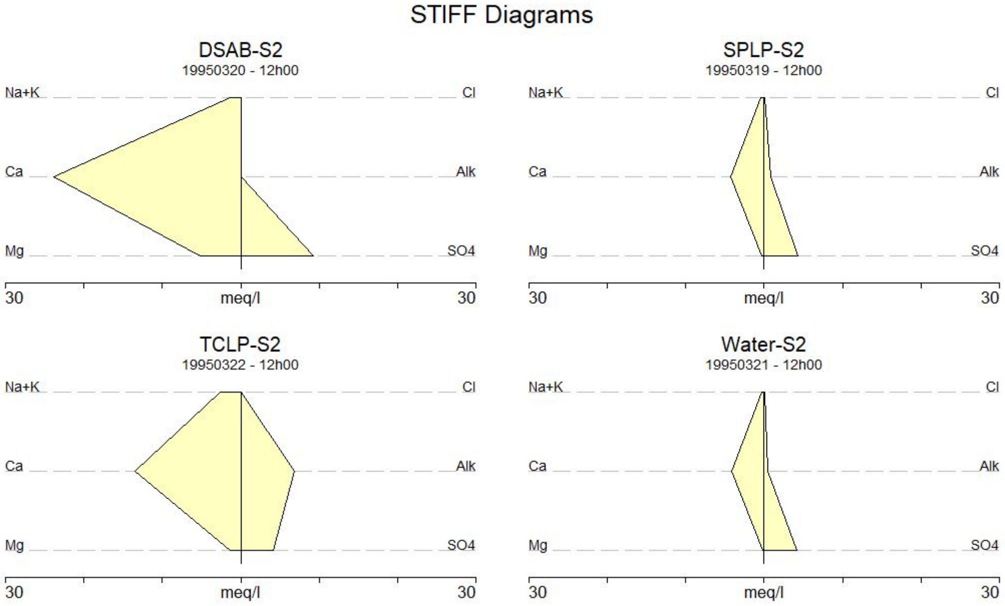


Figure 17 Stiff Diagram showing the water type and the concentration of elements in meq/l for sample S2.

Figure 17 shows that the leach test methods have leached different amount of concentrations for the same sample. The SPLP and Water leach test methods have leached the sample in the same way with the leachate having approximately same concentration (meq/l). The DSBL leach test method leached high concentrations of Ca and SO_4. The TCLP leach test method has leached Ca and HCO_3.

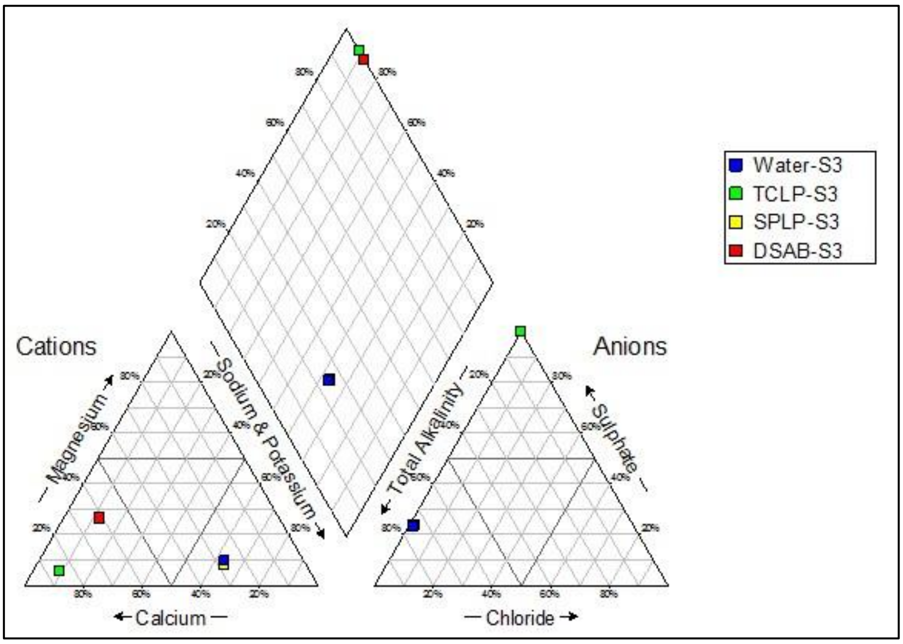


Figure 18 Piper trilinear graph showing the characterization of S3 leachate type for different assessed leach test methods.

The leachate observed on S3 for all the leach test methods seems to differ in relation to what leachate type is generated except that of SPLP and Water leach test methods. The leachate type generated by the TCLP leach test method contains high calcium shown on the left triangle and high sulphide elements shown on the right triangle of Figure 18 these lead to the characterization of the TCLP leachate as Ca-SO_4.

The SPLP and Water leachate contain high sodium and potassium content shown on left triangle and high alkalinity shown on the right triangle, these observations show that the SPLP and Water leachate characterized by $Na + K\text{-} HCO_3$. The uniqueness in the leachate type generated by the different leach test methods is not caused by the samples since these leach test methods were conducted on the waste materials collected from the field containing the same mineralogy. It is observed that the difference in hydrogeochemical facies is due to the uniqueness in the chemical compositions of the extraction fluids.

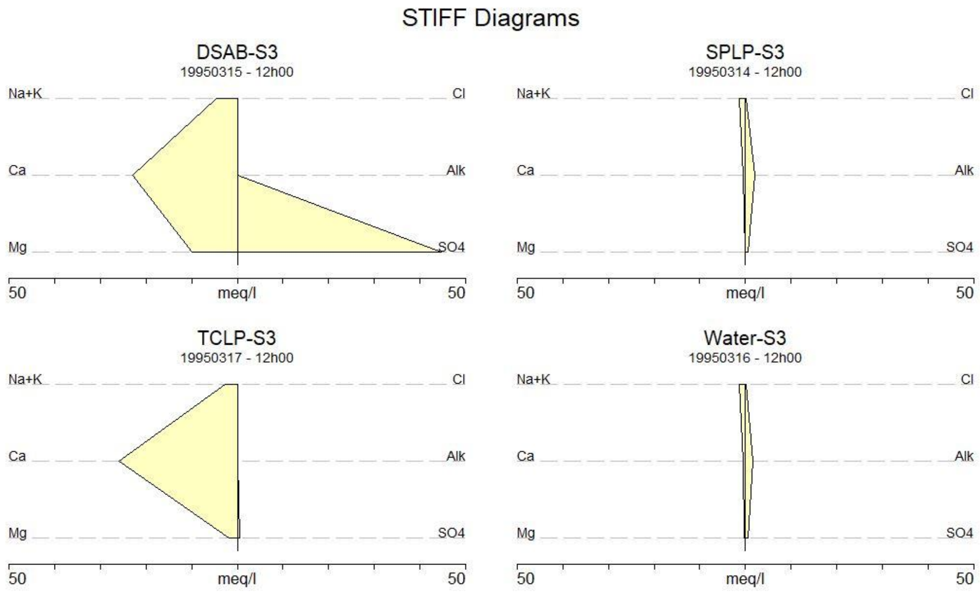


Figure 19 Stiff Diagram showing the water type and the concentration of elements in meq/l for sample S3.

Figure 19 shows that the leachate from the SPLP and Water leach test method have the same leachate type that has very low concentrations of ions. The SBAB leach test method shows high leached concentration of Ca and $SO_{4,}$ the high concentration of SO_4 is due to the addition of SO_4 acid to lower the pH of the sample. The TCLP leach test method shows that the sample contains Ca and that there is very low concentration of anions within the sample.

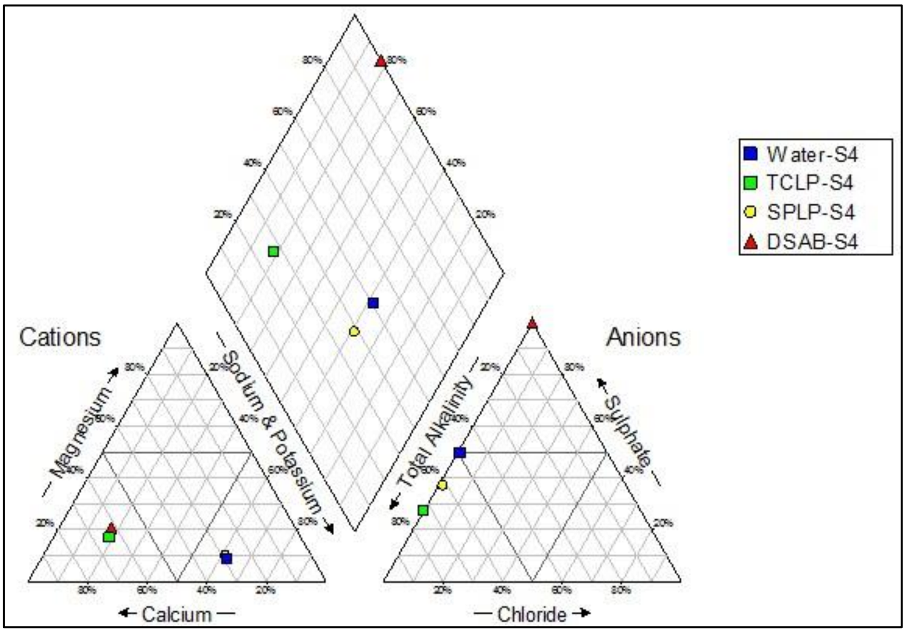


Figure 20 Piper trilinear graph showing the characterization of S4 leachate type for different assessed leach test methods.

The leachate observed on S4 for TCLP leach test method is characterized as Ca-HCO_3; this leachate contains high calcium and alkalinity, which can be observed on the left and right triangle in Figure 20. The uniqueness in the leachate type generated by the different leach test methods is not caused by the samples since these leach test methods were conducted on the waste materials with the same mineralogy. These differences are due to the uniqueness in the chemical compositions of the extraction fluids. The leachate type from SPLP and Water leach test method is characterised as Na + K-HCO_3 due to the elevated concentrations of alkalinity, sodium and potassium as shown in Figure 20.

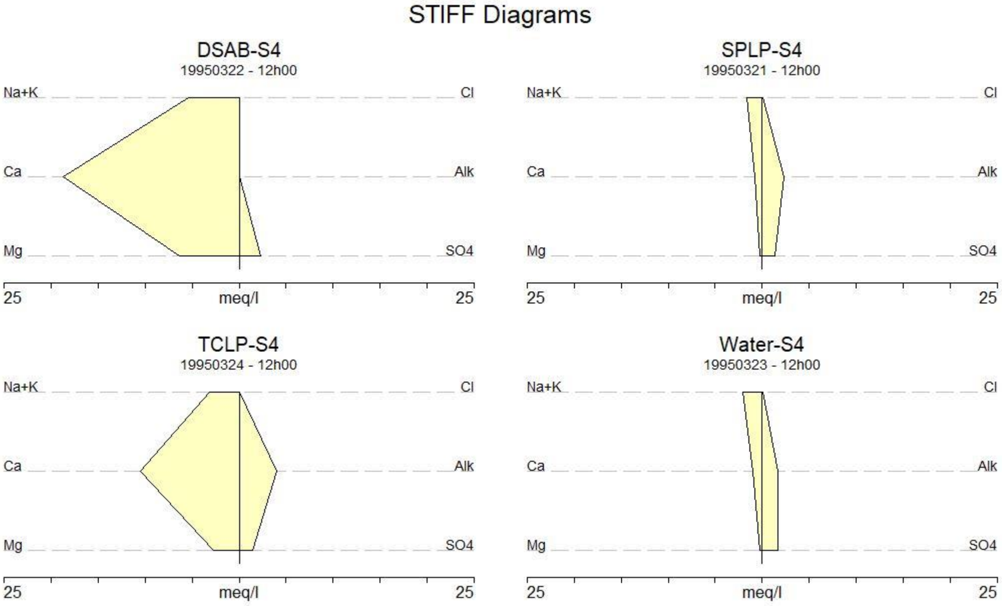


Figure 21 Stiff Diagram showing the water type and the concentration of elements in meq/l for sample S4.

Figure 20 shows that the leachate from the SPLP and Water leach test method have the same leachate type that has very low concentrations of ions. The SBAB leach test method shows high leached concentration of Ca and low concentration of SO_4. The TCLP leach test method shows that the sample contains Ca and alkalinity concentration with in the sample.

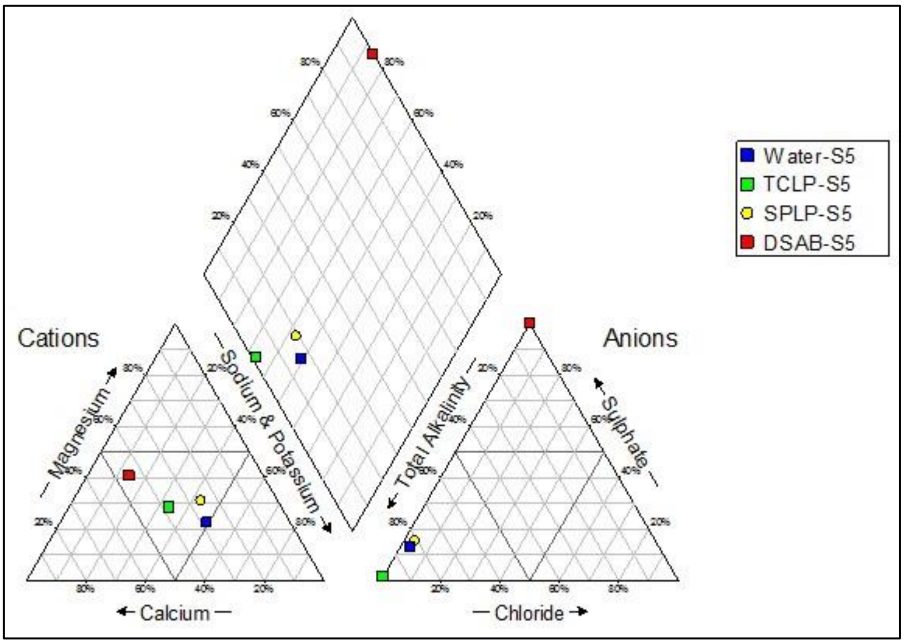


Figure 22 Piper trilinear graph showing the characterization of S5 leachate type for different assessed leach test methods.

S5 leachate type from the SPLP, Water leach and TCLP methods showed that the leachate is characterized as Ca- Mg-HCO_3. The characterisation of the leachate using piper diagrams shows that these samples contain, Ca, Mg, Na+K. and HCO_3 these can be observed from both left and right triangles in Figure 22.

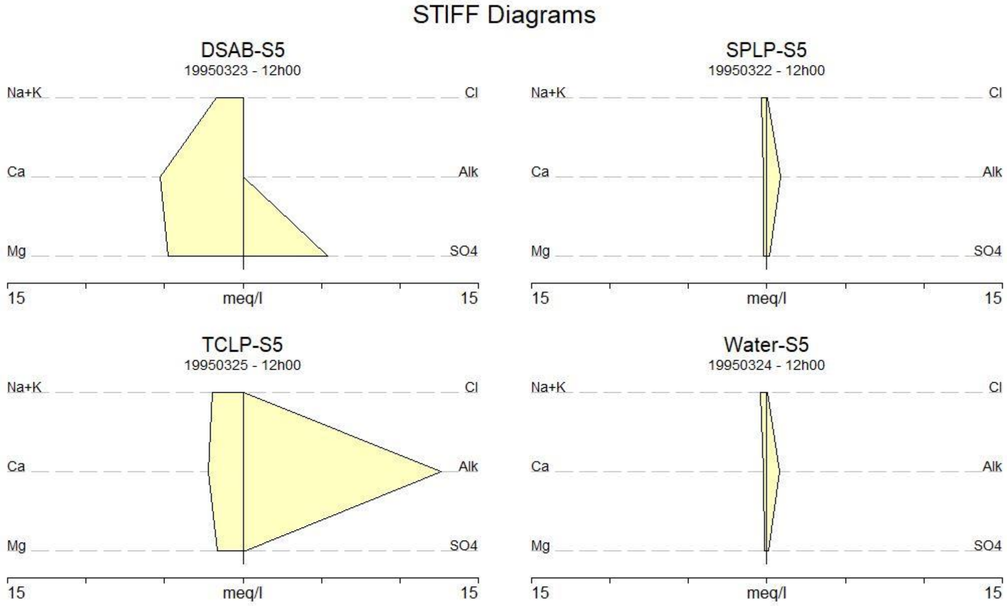


Figure 23 Stiff Diagram showing the water type and the concentration of elements in meq/l for sample S5.

Figure 23 the SPLP and Water leach test methods contain low level concentrations of alkalinity and very low concentrations of cations. The DSAB leach test method contains cations and concentration of SO_4 within the sample. The TCLP leach test method has leached high concentrationof alkalinity within the sample compared to other leach test methods applied.

Figure 24 show that all assessed leach test methods on all samples contain high calcium observed on the left triangle and high sulphate that is observed on the right triangle. For all the leach test methods, S6 leachate type is characterized by Ca-SO_4. The chemistry of the leachate for this sample is contain elevated concentrations of SO_4^{2-} $>Ca^{2+>}Mg^{2+}.>Na^{+}+K^{+}>HCO^{-}_{3}>Cl^{-}>F^{-}>NO^{-}_{3}$.

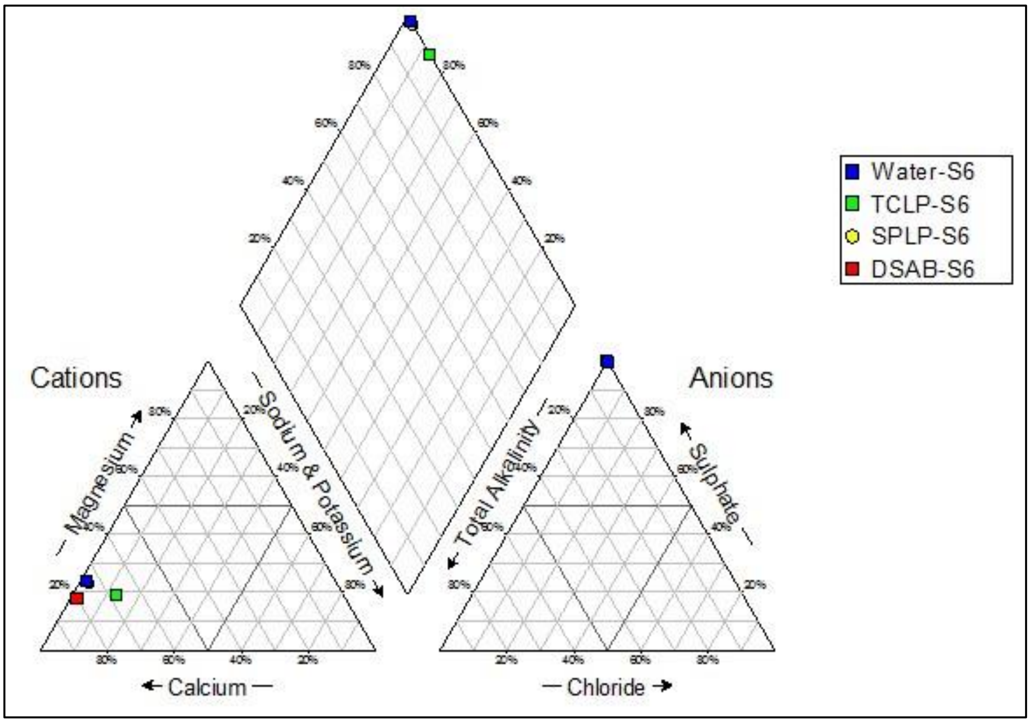


Figure 24 Piper trilinear graph showing the characterization of S6 leachate type for different assessed leach test methods.

This sample shows the same leachate characterization, this is due to the sample being acidic even before being subjected to any leach test methods. The other influence is that the leachates from this sample contain high concentrations of SO_4 (see Table 15). The impact of extraction fluids on this sample are not different, except that the TCLP method shows a slight difference when compared to other leach test methods refer to

Figure 24, which is due to the buffering elements that were observed from the TCLP extraction fluid.

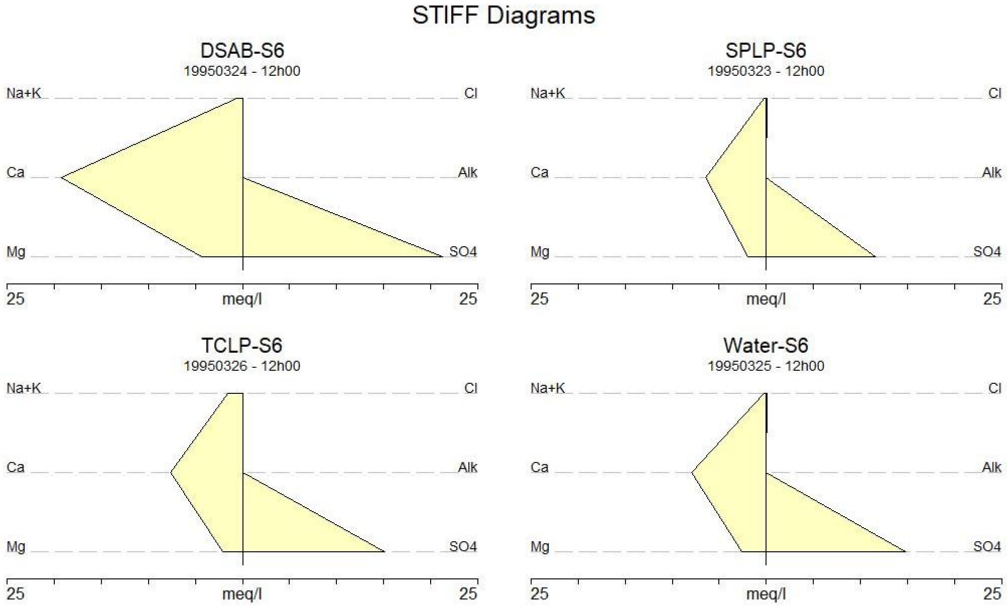


Figure 25 Stiff Diagram showing the water type and the concentration of elements in meq/l for sample S6.

Figure 25 shows the same trend of the leachate chemistry generated using stiff diagrams for the assessed leach test methods. The water type generated for sample S6 contains Ca and SO_4. The DSAB leach test method shows that the leachate contains high concentrations of the elements due to the leaching strength of the extraction fluid.

All six samples show that there is different leachate types generated using the different leach test methods, showing that the chemistry of leachate is very dynamic, largely controlled and modified by its medium of contact in this case also modified by the different extraction fluids applied to the methods.

These leach tests have generated different leachates geochemistry for the same samples, suggesting that the leachate elements are impacted by the ionic strength of the extraction fluid applied which affects the ion chemistry of the samples. Results obtained using piper trilinear diagrams show different leachates characteristics, it was observed that S1, S2 and S6 contain high SO_4 element than other observed elements. S5, S3 and S4 are more alkaline, they have buffering characteristics as shown by the elevated concentrations of Ca, Mg, Na+K and HCO_3.

As much as some of the samples contain large amounts of calcite, which are able to neutralise the acid, unfortunately, it is not always the case for our coal and gold deposits. The natural neutralising processes are sometimes overwhelmed and large quantities of acidic water are released into the environment by mining activities, initially into the groundwater and ultimately into streams and rivers (McCarthy, 2011).

These waste materials from dumpsites are sometimes used to backfill or rehabilitate the old mined out areas. Using the same materials that were extracted from the mines to backfill or rehabilitate the old mined out areas increases the risk of acid generation since the waste materials have the capacity of generating acid mine drainage combined with the remaining unmined rocks which generate acid mine drainage.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1.1 Conclusions

The study was conducted to assess the performance of the Toxicity Characteristic Leaching Procedure, Synthetic Precipitation Leaching Procedure, Water Leach test and Diluted Sulfuric Acid Based leach test methods to evaluate the environmental impact of coal and gold mine waste materials. These methods were applied to assess if they can classify the waste material similarly when compared to NEM: WA Act No.59 of 2008 leachable concentration threshold refer to Table 2 and if they generate similar hydrogeological facies and chemistry when applied to field samples with same mineralogy.

The findings reveal that different assessed leach test methods classify waste materials in different waste type classes and that the waste material has different hazard waste profiling levels. The findings also show that leach test methods applied to waste materials results in leachates with different hydrogeochemical facies, and chemistry. The findings indicate that all samples leached using Toxicity Characteristic Leaching Procedure, Synthetic Precipitation Leaching Procedure and Water leach test methods are classified as the same waste type material (Type 3 waste - which is considered as very low-risk waste with low potential for contaminant release.

The results furthermore reveal that the classification and hydrogeochemical characteristics of the leachates from Synthetic Precipitation Leaching Procedure and Water Leach test methods generate the same water type and same waste classification for all examined samples. This suggests that these two leach test methods operate in an analogous manner compared to the other two-leach test methods. Therefore, one method between Synthetic Precipitation Leaching Procedure and Water Leach test method can be applied to leach waste material when considering the costs, performance and time consumption since they both generate analogous results.

The Diluted Sulfuric Acid Based leach test method classify waste materials differently compared to others methods, where some waste materials are classified as Type 1, Type 2 waste and other materials as Type 3 waste. By principle, Diluted Sulfuric Acid Based leach test method with the pH of 2.24 is acidic and has high ionic strength thus it leaches higher concentrations of elements leading to the classification of samples in different waste type classes. The leached concentration from these methods are less influenced by the sample but highly influenced by the characteristics of the extraction fluid applied to the methods.

The findings show that the Diluted Sulfuric Acid Based leach test method leaches arsenic, lead, vanadium and manganese in high concentrations compared to other elements because these elements are highly soluble in H_2SO_4 acidic conditions. Since the Diluted Sulfuric Acid Based leach test method contains H_2SO_4 in the extraction fluid, the concentrations of these elements are high compared to when they are leached by the other three-leach test methods.

High concentrations values were observed from the gold mine waste materials, coalfield waste material and from one of the sample were drops of H_2SO_4 were added to lower the pH value; from this, it was observed that arsenic, lead, vanadium and manganese are highly soluble in low pH conditions. The leaching of arsenic, lead, vanadium and manganese in high concentration by the Diluted Sulfuric Acid Based leach test method leads to the classification of some waste materials as Type 1 waste. These indicate the possibility of high leached concentrations of arsenic, lead, vanadium and manganese in acidic field conditions.

The results further show that the leachates from the different waste material can classify waste materials as very low hazardous risk but when the results are compared to the groundwater quality classification based on TDS from the World Health Organisation (WHO, 2011) and the water quality salinity classification index (Robinove *et al.,* 1958), the results are different. Some of the leachates when they are classified using the different classifications show that the leachates will have an effect on the water quality due to high total dissolved salt from the methods even if they are classified by the NEM: WA Act No. 59 of 2008 as very low hazardous risk.

The results furthermore show that the leach test methods generated different hydrogeochemical characteristics and different water types from the sample material containing the same minerals. The Toxicity Characteristic Leaching Procedure test method produced inconsistent water type when compared to water types from other leach tests methods in some of the samples. The Toxicity Characteristic Leaching Procedure leached some of the elements in multiple orders of magnitude that were different from the results produced by other leach test methods. The effects of leach test methods on the waste material are observed on the leached concentrations of different elements, Toxicity Characteristic Leaching Procedure leached higher concentrations of elements even though they can still be classified as Type 3 similarly to the other methods.

The Diluted Sulfuric Acid Based leach test method also showed the difference in water type due to leached elements in multiple orders of magnitude compared to other assessed leach test methods. The results show that the water type generated for all samples using this method are calcium-sulphate water type due to the acidic extraction fluid applied. Although this method leaches more elements compared to others, the extraction fluid applied in this method contains similar characteristics of the AMD (Deysel, 2015).

The results further show that all the leach test methods classified the acidic waste material from S6 with the pH of 4.20 as very low hazard risk with low potential of contaminant release in Type 3 waste. All the assessed leach test methods show that the sample can be classified in the same waste class and that the sample generated the same hydrogeochemical characteristics. But when the same sample total dissolved salts is compared to the groundwater quality classification based on TDS from the World Health Organisation (WHO, 2011) and the water quality salinity classification index (Robinove *et al.,* 1958) the results show that the sample has poor and slightly saline water quality which may affect the water quality.

These results are only observed from the acidic sample, though the leached concentration from the Diluted Sulfuric Acid Based leach test method and Toxicity Characteristic Leaching Procedure are higher compared to the other methods, they still classified the waste as Type 3. The performance of the methods on acidic samples has not been clear since there is only one acidic sample examined for this research, which makes it difficult to conclude that the assessed leach test methods operate the same way to all acidic waste material.

5.1.2 Recommendations

Based on the above findings, the following recommendations can be made:

- Water Leach test method is recommended to be of first consideration instead of Synthetic Precipitation Leaching Procedure since they generate analogous results; this is when considering expenses and time consumption. Toxicity Characteristic Leaching Procedure is not to be considered in leaching mine waste material since it was designed to simulate the worst-case scenario of co-disposal in municipal landfills and not applied to volatile organic leachates (Al-Abed *et al.,* 2006) and that the extraction fluid applied to this method is not found in the mining environment.
- Conduct further studies on the classification of mine waste materials considering both the leachable concentration thresholds from the NEM: WA act No 59 of 2008; groundwater quality classification based on TDS from the World Health Organisation (WHO, 2011) and the water quality salinity classification index (Robinove *et al.,* 1958) and the hydrogeochemical facies. This is to ensure that all possible effects that will be caused by the leachates are looked at including the type of leachate that will be generated by the waste materials. These will all also help in the planning for the treatment of the waste materials in advance before disposal.
- It is recommended that further studies need to be conducted on the leach test methods applied to mine waste materials to check the uncertainty associated with leach test methods in classifying the materials. Assessing the uncertainty of each leach test method will improve the classification of waste material since uncertainty is an important aspect of measurement that will affect the quality, costs, decisions, and risks of classifying waste material.
- Conduct further studies on the Diluted Sulfuric Acid Based leach test method with the extraction fluid having different pH values in order to check leachable concentrations of waste materials under the influence of different pH values. This will aid in obtaining knowledge of the capability of waste material to leach total concentrations under the influence of different pH values, there is to be applied to waste material where there is a possibility of acid mine drainage generation.

- Conduct further studies on the application of these leach test methods to waste materials that have positive and negative net neutralizing potential. This will help in explaining the performance of the methods in the material with a different composition for example on ash waste material which is known to have positive net neutralizing potential, this is to be conducted to assess what are the possible outcomes if ash waste material happens to turn acidic when disposed to neutralised AMD.
- Conduct further studies to assess the performance of the four leach test methods on acidic waste materials in order to assess the performance of leach test methods. These is due to the observed results from S6 with low pH of 4.2, were all the assessed methods classified this waste material as very low hazardous risk with no potential of contamination while the sample contain high concentrations of SO_4. This will also be helpful in identifying if the influence is due to the sample or the leach test methods.

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APPENDICES

Appendix 1 Results of oxides and trace elements from the XRF analysis.

XRF Majors (%)						
	Free State Goldfields		**Highveld Coalfields**		**Waterberg Coalfields**	
Oxide	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
SiO_2	81.55	80.66	60.93	25.06	75.22	15.28
TiO_2	0.31	0.34	0.86	0.43	0.54	0.40
Al_2O_3	7.11	8.20	15.44	9.78	11.64	7.66
Fe_2O_3	4.70	4.58	5.42	2.39	5.53	3.44
MgO	1.54	1.51	1.37	0.68	0.36	0.22
MnO	0.05	0.06	0.06	0.01	0.09	0.03
CaO	0.54	0.78	2.31	0.87	0.18	0.69
K_2O	1.06	1.09	2.43	0.76	0.61	0.19
P_2O_5	0.03	0.04	0.15	0.05	0.09	0.29
Na_2O	0.26	0.29	0.61	0.43	0.06	0.08
LOI	3.05	2.82	9.98	58.82	6.02	72.61
Total	100.21	100.36	99.57	99.27	100.35	100.88
XRF Traces (ppm)						
Elements	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Sc	6	8	14	8	5	6
V	44	51	97	50	74	45
Cr	307	296	80	55	93	49
Co	33	26	19	13	17	15
Ni	192	150	42	28	46	53
Br	<2	<2	<2		<2	12
Sr	30	36	305	302	113	327
Y	7	12	23	17	30	22
Nb	2	1	10	7	7	3
Ba	228	191	556	421	560	477
Pb	59	33	18	9	18	11
Th	5	5	17	12	11	11
Zn	148	121	101	76	39	48
As	101	47	<10	<10	13	<10
Rb	29	29	109	187	48	23
Zr	209	220	455	490	383	474
U	30	42	6	<3	4	10

Appendix 2 Results of mineral contents within the samples in percentages obtained from XRD analysis.

Minerals (%)	**S1**	**S2**	**S3**	**S4**	**S5**	**S6**
Quartz	53	52	38	26	69	24
Mica	13	14	13	16	11	17
Clinochlore	21	19	10	0	0	0
Kaolinite	0	0	17	16	15	36
Plagioclase	3	3	7	11	0	0
K-Feldspar	0	2	9	0	0	0
Calcite	0	0	2	3	0	3
Dolomite	2	0	0	4	0	0
Pyrite	2	1	0	3		4
Talc	0	0	0	0	0	0
Pyrophyllite	7	9	0	0	0	0
Pyroxene	0	0	0	0	0	8
Siderite	0	0	3	0	0	7
Montmorillonite	0	0	0	21	0	0
Goethite	0	0	0	0	5	0
Anatase	0	0	0	0	0	0

Appendix 3 A table showing initial pH of samples before subjection to leach test and final pH after leach process.

Leach method &Samples	**Initial pH**	**Final pH**	**Leach method &Samples**	**Initial pH**	**Final pH**	**Leach method &Samples**	**Initial pH**	**Final pH**
SPLP S1	6.81	9.49	SPLP S2	7.07	8.87	SPLP S5	6.84	8.06
DSAB S1	2.08	9.49	DSAB S2	2.24	8.87	DSAB S5	2.16	8.06
Water S1	7.00	9.49	Water S2	7.48	8.87	Water S5	6.94	8.06
TCLP S1	4.92	9.49	TCLP S2	5.01	8.87	TCLP S5	4.88	8.06
Leach method &Samples	**Initial pH**	**Final pH**	**Leach method &Samples**	**Initial pH**	**Final pH**	**Leach method &Samples**	**Initial pH**	**Final pH**
SPLP S3	7.55	9.42	SPLP S4	7.26	8.20	SPLP S6	3.74	4.20
DSAB S3	1.91	9.42	DSAB S4	2.35	8.20	DSAB S6	1.93	4.20
Water S3	8.24	9.42	Water S4	7.64	8.20	Water S6	4.04	4.20
TCLP S3	5.46	9.42	TCLP S4	5.12	8.20	TCLP S6	4.77	4.20

Appendix 4 Laboratory results for SPLP leach test methods, showing chemical analysis of elements on the Blank sample and in S1 and S2 waste materials.

Elements	SPLP-Blank a	SPLP-Blank b	SPLP-S1a	SPLP-S1b	SPLP-S2a	SPLP-S2b
pH	4.22	4.46	7.48	6.81	7.07	7.55
EC	1.13	1.77	58.60	60.00	41.70	42.10
Ca	-0.12	1.15	108.96	108.65	85.23	87.74
Mg	-0.01	1.04	23.69	25.30	4.27	2.23
Na	1.82	1.95	3.42	4.38	6.26	4.92
K	0.74	0.58	4.38	5.22	6.02	5.45
PAlk	0.00	0.00	0.00	0.00	0.00	0.00
MAlk	0.00	0.00	65.80	65.80	43.10	43.10
F	-0.01	-0.01	0.17	0.17	0.07	0.07
Cl	0.78	0.78	1.59	1.59	2.47	2.47
NO_2 (N)	-0.01	-0.01	0.01	0.01	-0.01	-0.01
Br	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04
NO_3 (N)	0.24	0.24	0.45	0.45	0.46	0.46
PO_4	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10
SO_4	3.11	5.72	291.96	322.73	211.06	196.65
Al	0.12	0.01	0.18	0.01	0.03	0.25
As	0.00	0.02	0.02	0.05	-0.02	0.04
B	-0.02	-0.04	-0.02	-0.04	-0.04	-0.02
Ba	0.00	0.00	0.00	0.01	0.02	0.01
Cd	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.00	-0.02	0.00	-0.02	-0.02	0.00
Cr	0.00	-0.02	0.00	-0.02	-0.02	0.01
Cu	0.00	0.01	0.00	0.05	0.05	0.00
Fe	0.00	0.01	0.02	0.02	0.04	0.04
Mn	0.00	0.00	0.43	0.40	0.15	0.04
Mo	0.00	0.01	0.00	0.02	0.01	0.01
Ni	0.00	-0.01	0.02	0.02	0.01	0.00
Pb	0.00	0.00	0.00	-0.03	0.01	0.00
Se	0.00	-0.02	0.00	-0.02	-0.02	0.00
Si	0.17	0.38	1.29	4.07	3.21	1.96
U	0.00	-0.03	0.01	-0.03	-0.03	0.00
V	0.00	0.01	0.00	0.41	0.15	0.00
Zn	0.01	0.01	0.01	0.03	0.03	0.00

Appendix 5 Laboratory results for SPLP leach test methods showing leached chemical elements for sample S3, S4, S5 and S6 waste materials.

Element	**SPLP-S3a**	**SPLP-S3b**	**SPLP-S4a**	**SPLP-S4b**	**SPLP-S5a**	**SPLP-S5b**	**SPLP-S6a**	**SPLP-S6b**
pH	7.55	8.61	7.26	7.63	6.84	7.68	3.74	3.94
EC	21.70	17.05	34.60	31.60	7.02	7.20	93.30	90.20
Ca	12.93	10.97	20.56	10.52	4.68	3.38	137.79	122.26
Mg	3.13	1.10	4.90	1.58	3.50	2.38	25.67	23.08
Na	29.52	24.30	43.32	24.02	4.53	4.41	4.96	4.78
K	8.13	6.52	6.70	8.23	5.47	5.67	3.15	2.81
PAlk	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAlk	101.00	101.00	113.00	113.00	42.10	42.10	0.00	0.00
F	0.40	0.40	1.10	1.10	0.94	0.94	0.60	0.60
Cl	1.56	1.56	2.00	2.00	1.40	1.40	1.18	1.18
NO_2 (N)	-0.01	-0.01	0.01	0.01	0.02	0.02	-0.01	-0.01
Br	-0.04	-0.04	11.87	11.87	-0.04	-0.04	0.01	0.01
NO_3(N)	0.45	0.45	-0.05	-0.05	0.07	0.07	-0.05	-0.05
PO_4	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10
SO_4	34.86	27.03	92.66	38.23	7.65	7.63	580.31	529.73
Al	0.04	0.33	0.01	0.30	0.59	0.30	9.50	4.13
As	-0.02	0.02	-0.02	0.01	-0.02	0.00	-0.02	0.01
B	-0.04	0.03	0.27	0.05	-0.04	-0.01	-0.04	0.05
Ba	0.02	0.02	0.05	0.02	0.08	0.13	0.05	0.09
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	-0.02	-0.01	-0.02	0.00	-0.02	0.00	0.08	0.07
Cr	-0.02	0.01	-0.02	0.01	-0.02	0.00	-0.02	0.00
Cu	0.01	0.00	0.02	0.00	0.01	0.00	0.09	0.04
Fe	0.02	0.09	0.01	0.15	0.28	0.10	1.19	63.24
Mn	0.01	0.01	0.01	0.01	0.15	0.11	3.62	1.85
Mo	0.04	0.02	0.03	0.01	0.01	0.00	0.01	0.00
Ni	0.02	0.00	0.02	0.00	0.04	0.01	0.41	0.34
Pb	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00
Se	-0.02	0.00	-0.02	0.01	-0.02	0.01	-0.02	0.00
Si	4.36	3.58	6.73	3.37	11.57	7.56	8.57	1.83
U	0.04	0.04	-0.03	0.01	-0.03	0.01	0.04	0.03
V	0.01	0.04	0.01	0.01	0.16	0.00	2.83	-0.01
Zn	0.01	0.00	0.02	0.01	0.02	0.00	0.23	0.18

Appendix 6 Laboratory results for DSAB leach test methods, showing chemical analysis of elements on the Blank sample and in S1 and S2 waste materials.

Elements	**DSAB-Blank a**	**DSAB-Blank b**	**DSAB-S1a**	**DSAB-S1b**	**DSAB-S2a**	**DSAB-S2b**
pH	2.24	2.24	2.08	2.08	2.24	2.24
EC	2036.00	2065.00	1168.00	1230.00	1017.00	1045.00
Ca	-0.64	1.11	376.65	269.46	545.85	409.32
Mg	-0.79	0.24	130.12	102.08	68.63	57.96
Na	1.13	1.59	6.06	6.32	11.38	12.58
K	0.26	0.24	19.44	19.99	30.52	31.33
PAlk	0.00	0.00	0.00	0.00	0.00	0.00
MAlk	0.00	0.00	0.00	0.00	0.00	0.00
F	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.00	0.00	0.00	0.00	0.00	0.00
NO_2 (N)	0.00	0.00	0.00	0.00	0.00	0.00
Br	0.00	0.00	0.00	0.00	0.00	0.00
NO_3 (N)	0.00	0.00	0.00	0.00	0.00	0.00
PO_4	0.00	0.00	0.00	0.00	0.00	0.00
SO_4	4268.73	4336.42	461.67	393.99	476.92	409.24
Al	0.08	0.06	122.54	116.50	106.83	108.22
As	0.04	-0.02	0.99	0.74	1.63	1.19
B	0.06	-0.04	0.92	0.23	0.98	0.21
Ba	0.06	0.00	0.06	0.05	0.06	0.05
Cd	0.01	0.00	0.02	0.04	0.01	0.03
Co	0.04	0.00	1.10	0.88	0.65	0.49
Cr	0.04	0.00	1.20	0.98	0.96	0.77
Cu	0.02	0.04	1.69	1.53	1.59	1.46
Fe	0.16	0.04	320.29	264.67	273.80	239.91
Mn	0.04	0.01	17.63	13.40	28.16	23.79
Mo	0.04	0.00	0.04	0.01	0.04	0.01
Ni	0.04	0.00	3.87	2.94	2.61	1.90
Pb	0.03	0.00	1.28	0.98	1.55	1.09
Se	0.04	-0.02	0.04	-0.02	0.04	-0.02
Si	3.48	-0.50	72.57	57.80	101.99	79.85
Sr	0.02	0.00	0.40	0.36	0.95	0.79
U	0.06	0.00	5.68	2.94	9.46	4.97
V	0.02	0.00	15.63	11.77	27.87	20.28
Zn	0.06	0.09	4.56	2.90	4.55	2.74

Appendix 7 Laboratory results for DSAB leach test methods showing leached chemical elements for sample S3, S4, S5 and S6 waste materials.

Elements	**DSAB-S3a**	**DSAB-S3b**	**DSAB-S4a**	**DSAB-S4b**	**DSAB-S5a**	**DSAB-S5b**	**DSAB-S6a**	**DSAB-S6b**
pH	1.91	1.91	2.35	2.35	2.16	2.16	1.93	1.93
EC	953.20	990.00	792.20	786.00	1017.00	1008.00	1449.00	1489.00
Ca	463.64	454.95	322.68	425.40	110.34	100.28	406.05	363.13
Mg	136.05	105.05	63.05	89.97	59.21	56.20	53.18	50.50
Na	61.30	78.62	66.05	123.64	9.24	10.12	7.23	8.17
K	59.78	63.61	49.02	45.82	41.35	56.01	7.47	8.20
PAlk	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAlk	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
F	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Cl	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO_2 (N)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Br	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
NO_3 (N)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_4	2173.42	2105.74	138.09	85.38	226.30	293.98	1055.61	987.93
Al	247.05	292.36	69.85	121.86	181.21	172.06	52.78	68.24
As	0.04	0.04	0.04	0.07	0.04	0.05	0.13	0.15
B	2.97	0.52	1.03	0.61	0.93	0.17	1.85	0.42
Ba	0.06	0.04	0.06	0.06	0.10	0.06	0.10	0.07
Cd	0.02	0.06	0.01	0.01	0.02	0.02	0.02	0.05
Co	2.74	0.28	0.15	0.11	0.62	0.55	0.17	0.15
Cr	0.45	0.35	0.04	0.05	0.10	0.24	-0.39	0.02
Cu	0.89	0.84	0.31	0.36	0.41	0.41	0.33	0.30
Fe	809.88	579.97	95.69	147.35	198.95	193.83	434.79	480.06
Mn	15.36	12.25	2.44	3.82	46.72	42.02	5.03	5.01
Mo	0.04	0.01	0.04	0.00	0.10	0.00	0.10	0.00
Ni	1.29	0.72	0.36	0.39	0.50	0.51	0.83	0.67
Pb	0.07	0.06	0.03	0.02	0.08	0.00	0.08	0.00
Se	0.04	-0.02	0.04	-0.02	0.10	-0.02	0.10	-0.02
Si	162.19	119.97	85.27	82.92	71.83	57.75	18.31	7.83
Sr	9.68	15.01	6.41	12.98	0.55	0.58	4.21	6.10
U	7.64	3.56	1.04	0.96	14.41	9.36	2.05	1.33
V	18.18	10.02	3.71	3.25	44.02	37.91	5.53	4.52
Zn	3.28	1.68	0.86	0.71	0.22	0.21	0.45	0.39

Appendix 8 Laboratory results for Water leach test methods, showing chemical analysis of elements on the Blank sample and in S1 and S2 waste materials

Elements	**Water-Blank a**	**Water-Blank b**	**Water-S1a**	**Water-S1b**	**Water-S2a**	**Water-S2b**
pH	5.16	6.69	7.00	7.41	7.48	7.25
EC	0.21	0.21	60.60	59.14	41.80	39.68
Ca	0.19	0.25	102.90	112.95	79.92	86.44
Mg	0.12	-0.04	22.53	24.74	2.61	2.40
Na	0.63	-0.24	3.02	1.59	5.04	3.23
K	0.04	0.43	4.65	4.81	5.38	5.62
PAlk	0.00	0.00	0.00	0.00	0.00	0.00
MAlk	1.86	1.86	43.80	43.80	22.20	22.20
F	0.01	0.01	0.06	0.06	0.06	0.06
Cl	0.68	0.68	1.40	1.40	2.26	2.26
NO_2 (N)	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01
Br	-0.04	-0.04	-0.04	-0.04	-0.04	-0.04
NO_3 (N)	-0.05	-0.05	0.09	0.09	0.08	0.08
PO_4	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10
SO_4	-0.50	-1.96	302.08	299.76	199.74	197.75
Al	-0.02	0.03	0.01	0.05	0.07	0.06
As	0.00	0.06	-0.02	0.06	0.05	0.06
B	-0.04	0.06	-0.04	0.06	-0.04	0.06
Ba	0.00	0.06	0.01	0.04	0.02	0.04
Cd	0.00	0.01	0.00	0.01	0.00	0.01
Co	-0.02	0.04	-0.02	0.04	-0.02	0.04
Cr	-0.02	0.04	-0.02	0.04	-0.02	0.04
Cu	0.01	0.02	0.02	0.03	0.03	0.03
Fe	-0.02	0.02	0.03	0.05	0.08	0.05
Mn	0.00	0.00	0.33	0.33	0.06	0.03
Mo	0.01	0.04	0.01	0.04	0.01	0.04
Ni	0.00	0.04	0.01	0.04	0.01	0.04
Pb	0.01	0.03	0.01	0.03	0.01	0.03
Se	-0.02	0.04	-0.02	0.04	-0.02	0.04
Si	-0.50	-3.96	0.70	0.70	1.54	1.54
U	0.01	0.06	0.04	0.06	0.00	0.06
V	0.00	0.02	0.33	0.36	0.06	0.04
Zn	0.01	0.04	0.02	0.04	0.02	0.04

Appendix 9 Laboratory results for Water leach test methods showing leached chemical elements for sample S3, S4, S5 and S6 waste materials.

Elements	**Water -S3a**	**Water -S3b**	**Water -S4a**	**Water- S4b**	**Water- S5a**	**Water- S5b**	**Water- S6a**	**Water- S6b**
pH	8.24	7.96	7.64	7.79	6.94	7.25	4.04	3.92
EC	16.90	22.27	34.10	30.24	6.93	8.89	109.00	103.50
Ca	9.23	15.66	20.74	18.29	3.58	5.23	155.21	161.84
Mg	1.09	4.29	2.88	4.07	2.52	1.76	30.31	31.84
Na	29.23	30.02	45.57	43.29	4.07	8.05	4.55	2.35
K	6.61	6.72	6.56	6.18	5.36	4.40	3.11	2.85
PAlk	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAlk	85.80	85.80	84.00	84.00	39.00	39.00	0.00	0.00
F	0.81	0.81	1.13	1.13	0.75	0.75	0.29	0.29
Cl	1.40	1.40	1.24	1.24	1.15	1.15	2.31	2.31
NO_2 (N)	-0.01	-0.01	-0.01	-0.01	-0.01	-0.01	-0.10	-0.10
Br	-0.04	-0.04	12.34	12.34	-0.04	-0.04	-0.40	-0.40
NO_3 (N)	0.10	0.10	-0.05	-0.05	0.07	0.07	-0.50	-0.50
PO_4	-0.10	-0.10	-0.10	-0.10	-0.10	-0.10	-1.00	-1.00
SO_4	23.68	27.02	76.82	85.92	5.69	5.89	738.71	674.63
Al	0.23	0.42	0.09	0.08	0.10	0.59	5.21	4.46
As	-0.02	0.06	-0.02	0.06	-0.02	0.06	0.03	0.06
B	-0.04	0.12	0.20	0.28	-0.04	0.13	-0.04	0.41
Ba	0.02	0.05	0.04	0.05	0.09	0.05	0.07	0.07
Cd	0.00	0.01	0.00	0.01	0.00	0.01	0.01	0.01
Co	-0.02	0.04	-0.02	0.04	-0.02	0.04	0.09	0.10
Cr	-0.02	0.04	-0.02	0.04	-0.02	0.04	-0.02	0.04
Cu	0.01	0.05	0.03	0.04	0.01	0.04	0.05	0.05
Fe	0.16	0.39	0.07	0.06	0.06	0.34	100.46	94.73
Mn	0.01	0.02	0.02	0.01	0.02	0.03	2.16	2.24
Mo	0.02	0.12	0.02	0.09	0.01	0.06	0.01	0.04
Ni	0.01	0.04	0.01	0.04	0.01	0.04	0.38	0.42
Pb	0.01	0.04	0.01	0.03	0.01	0.03	0.00	0.02
Se	-0.02	0.04	-0.02	0.04	-0.02	0.04	-0.02	0.04
Si	3.09	0.92	4.81	1.56	8.64	6.01	1.79	1.79
U	0.04	0.06	0.00	0.06	0.01	0.06	0.45	0.06
V	0.01	0.01	0.02	0.02	0.02	0.05	2.20	2.40
Zn	0.00	0.04	0.02	0.04	0.01	0.04	0.20	0.21

Appendix 10 Laboratory results for TCLP leach test methods, showing chemical analysis of elements on the Blank sample and in S1 and S2 waste materials

Elements	**TCLP-Blank a**	**TCLP-Blank b**	**TCLP-S1a**	**TCLP-S1b**	**TCLP-S2a**	**TCLP-S2b**
pH	4.82	4.85	4.92	4.91	5.01	4.97
EC	454.00	450.00	517.00	492.00	534.00	503.00
Ca	2.49	5.75	144.25	170.76	254.76	284.14
Mg	1.21	1.06	33.61	45.75	13.07	18.39
Na	1460.59	1573.37	35.33	49.02	29.76	69.43
K	1.71	11.11	9.38	23.46	13.65	26.86
PAlk	1460.59	1460.59	0.00	0.00	0.00	0.00
MAlk	868.00	868.00	598.00	598.00	340.00	340.00
F	0.22	0.22	0.10	0.10	-0.32	-0.32
Cl	-2.00	-2.00	0.00	0.00	0.00	0.00
NO_2 (N)	-0.10	-0.10	0.00	0.00	0.00	0.00
Br	-0.40	-0.40	0.00	0.00	0.00	0.00
NO_3 (N)	1.29	1.29	-0.24	-0.24	-0.16	-0.16
PO_4	-1.00	-1.00	0.00	0.00	0.00	0.00
SO_4	-5.00	4.94	293.25	289.79	200.78	202.48
Al	0.03	0.01	1.73	0.82	1.53	0.75
As	-0.02	-0.01	0.00	0.00	0.00	0.01
B	-0.04	0.07	0.00	0.04	0.00	0.02
Ba	-0.02	0.02	0.11	0.11	0.14	0.17
Cd	0.00	0.00	0.00	0.00	0.00	0.00
Co	-0.02	0.00	0.09	0.14	0.05	0.06
Cr	-0.02	-0.03	0.00	-0.01	0.00	-0.01
Cu	0.05	0.01	0.09	0.07	0.09	0.07
Fe	0.01	0.01	0.03	1.07	0.02	0.55
Mn	0.01	0.01	2.98	4.40	6.38	8.99
Mo	-0.02	0.01	0.00	0.01	0.00	0.01
Ni	-0.02	0.00	0.33	0.41	0.19	0.19
Pb	-0.02	0.00	0.07	0.04	0.00	0.02
Se	0.03	0.02	-0.05	0.00	-0.05	0.00
Si	0.64	-0.74	4.02	3.45	7.27	6.83
Sr	0.01	0.02	0.15	0.17	0.38	0.38
U	0.01	0.01	0.06	0.09	0.13	0.17
V	0.01	0.01	2.92	4.14	6.02	9.42
Zn	0.04	0.03	0.27	0.40	0.32	0.46

Appendix 11 Laboratory results for TCLP leach test methods showing leached chemical elements for sample S3, S4, S5 and S6 waste materials.

Element	**TCLP -S3a**	**TCLP -S3b**	**TCLP-S4a**	**TCLP-S4b**	**TCLP-S5a**	**TCLP-S5b**	**TCLP-S6a**	**TCLP-S6b**
pH	5.46	5.47	5.12	5.09	4.88	4.86	4.77	4.81
EC	599.00	565.00	535.00	496.00	472.00	420.00	523.00	495.00
Ca	506.99	529.33	194.79	224.65	38.12	49.84	143.71	160.07
Mg	18.30	23.94	28.22	38.11	17.06	23.01	22.32	28.56
Na	35.58	57.95	32.52	85.35	22.59	42.97	27.27	33.20
K	17.36	36.28	16.13	25.72	16.69	25.01	5.24	9.84
PAlk	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
MAlk	0.00	0.00	198.00	198.00	632.00	632.00	0.00	0.00
F	-0.07	-0.07	-0.32	-0.32	-0.04	-0.04	-0.16	-0.16
Cl	0.00	0.00	0.00	0.00	0.00	0.00	3.65	3.65
NO_2 (N)	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Br	0.00	0.00	11.86	11.86	0.00	0.00	0.00	0.00
NO_3 (N)	-1.79	-1.79	-1.79	-1.79	-1.79	-1.79	-1.79	-1.79
PO_4	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
SO_4	25.50	26.35	74.24	67.06	7.73	9.47	734.20	707.67
Al	0.17	0.10	1.82	0.38	1.63	0.58	0.17	0.42
As	0.00	-0.01	0.00	0.00	0.00	-0.01	0.00	-0.01
B	0.00	0.07	0.00	0.34	0.00	0.02	0.00	0.13
Ba	1.37	1.54	0.70	0.95	2.74	3.22	0.08	0.10
Cd	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Co	0.00	0.01	0.00	0.01	0.00	0.05	0.05	0.06
Cr	0.00	-0.03	0.00	-0.03	0.00	-0.03	0.00	-0.03
Cu	0.02	0.02	0.06	0.03	0.02	0.02	0.04	0.02
Fe	0.03	0.21	0.52	0.08	0.06	0.16	0.02	33.24
Mn	1.69	2.43	0.81	1.17	2.58	3.61	1.62	2.25
Mo	0.00	0.01	0.00	0.01	0.00	0.01	0.00	0.01
Ni	0.10	0.05	0.11	0.05	0.09	0.04	0.30	0.30
Pb	0.00	0.00	0.06	0.00	0.00	0.00	0.00	0.00
Se	0.01	0.00	-0.05	0.00	-0.05	-0.01	-0.05	-0.01
Si	11.81	11.23	14.58	13.68	10.54	9.15	1.44	0.48
Sr	8.82	8.42	5.10	4.89	0.31	0.37	1.67	1.59
U	0.02	0.03	0.01	0.02	0.04	0.07	0.03	0.05
V	1.68	2.12	0.82	0.95	2.55	3.03	1.62	1.80
Zn	0.02	0.06	0.02	0.07	-0.01	0.04	0.06	0.15

Appendix 12 Water quality salinity classification index (Robinove et al., 1958).

Class	**TDS range (mg/l)**
Fresh	0–1000
Slightly saline	1000–3000
Moderately saline	3000–10.000
Very saline	10.000–35.000
Briny	>35.000

Appendix 13 Groundwater quality classification based on TDS (WHO. 2011).

Quality description	**TDS [mg/L]**
Excellent	<300
Good	300-600
Fair	600-900
Poor	900-1200
Unacceptable	>1200